Catalytically efficient palladium nanoparticles stabilized by "click" ferrocenyl dendrimers†‡

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1,2,3-Ferrocenyl triazole ligands generated by click reactions in dendrimers bind $Pd(OAc)_2$ with a systematic one-to-one stoichiometry as monitored by titration using the ferrocenyl redox sensor attached to the triazole ring, and the dendritic Pd^{II} complexes formed are best reduced by methanol to form palladium nanoparticles of designed types and sizes that show excellent efficiency and selectivity in olefin hydrogenation.

The relatively recent discovery by Sharpless and his group[1] that the Huisgen dipolar addition between terminal alkynes and azides could be catalyzed by Cu^I and made easy, mild and selective has largely enriched synthetic strategies in organic chemistry.[2] Along this line, we recently published "click" ferrocenyl dendrimers (Chart 1) based on this reaction.[3] We now wish to report that 1,2,3-triazole heterocycles formed in these dendrimers serve as templating ligands to bind palladium acetate according to a one-to-one stoichiometry making it possible to pre-determine the number of Pd^{II} complexes encapsulated in this way in the dendrimers, and that reduction of these Pd^{II} species using methanol is the best method to generate catalytically active Pd nanoparticles (NPs) of precise type and size stabilized by these "click" dendrimers. We find that these click-dendrimer-stabilized PdNPs are very stable and more efficient for olefin hydrogenation than previously reported dendrimer-stabilized NPs. Another crucial new finding is that methanol is a much more useful Pd^{II} reductant than $NaBH_4$, currently used so far, in terms of the efficiency of these PdNP catalysts.

Dendrimers[4] have been largely used as supramolecular templates[4,5] or nanomolecular boxes[6] for the encapsulation of various substrates of specific interest. An example is that of transition-metal NPs,[7] a property that has been developed in catalysis[8–10] using polyamidoamine (PAMAM)[4a] and polypropyleneimine (PPI) dendrimers.[6] *Given the variety of properties of ligands in catalysis, the use of "click" dendrimers offers a unique alternative to stabilize NPs in view of catalytic uses*. By carefully organizing the number of transition-metal atoms in NPs, we have here a unique means to investigate the influence of the NP size in order to improve catalytic efficiency and eventually investigate mechanisms.

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‡ This article is dedicated to our distinguished friend Prof. Neil Bartlett (University of California at Berkeley) on the occasion of his 75th birthday.

It has already been shown that ferrocenyl branch termini directly attached to the triazole rings make it possible to monitor the binding of *dicationic* transition metal species by cyclic voltammetry. This redox sensing is now extended to the *neutral* complex $[Pd(OAc)_2]$. The complexation of $Pd(OAc)_2$ to the triazole groups of the poly-1,2,3-triazolylferrocenyl dendrimers is monitored by cyclic voltammetry (CV), UV–vis spectroscopy and ^1H NMR. In the CV studies, the ferrocenyl group, directly attached to the triazole fragment, is used as a redox monitor. The poly-1,2,3-triazolylferrocenyl dendrimers show a single, fully reversible CV wave for all the ferrocenyl groups.[3] 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. Titrations of $Pd(OAc)_2$ with poly-1,2,3-triazolylferrocenyl dendrimers show that each triazole unit binds one $Pd(OAc)_2$ (see Table 1 and Fig. 1–6 of ESI† for CV data).

For complexation of the triazole unit to $Pd(OAc)_2$, the presence of methanol is required, since no interaction was observed in CH_2Cl_2 or $CHCl_3$ (see Fig. 22 of ESI†). It is known that methanol (as well as water) readily breaks the trimeric species $[Pd(OAc)_2]_3$

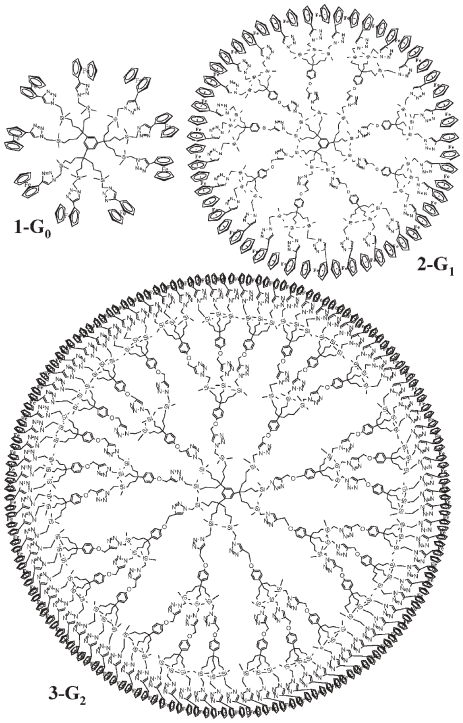

Chart 1 Structures of the poly-1,2,3-triazolylferrocenyl dendrimers containing triazole ligands.

Table 1 Size of the PdNPs stabilized by the triazolyl dendrimers obtained by TEM

PdNP	Number of Pd atoms *per* dendrimer	Calculated diameter[a] (nm)	Diameter method 1[b](nm)	Diameter method 2[c](nm)
DSN-G_0	9	—	1.2 ± 0.2	2.8 ± 0.3
DEN-G_1	36	1.0	1.1 ± 0.2	1.3 ± 0.2
DEN-G_2	117	1.5	1.6 ± 0.3	1.6 ± 0.3
DEN-G_2-36	36	1.0	1.1 ± 0.2	1.3 ± 0.3
DEN-PAMAM	40	1.0	1.1 ± 0.2	—

[a] Calculated using the equation $n = 4\pi r^3/3V_g$, where n is the number of Pd atoms, r is the radius of the Pd nanoparticle and V_g is the volume of one Pd atom (15 Å^3).[12] [b] Method 1: reduction of Pd by $NaBH_4$. [c] Method 2: reduction of Pd by methanol.

upon dechelating one or more acetate ligands.[11] 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, Fig. 20–24 of ESI†). 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 (see Fig. 7 of ESI†). 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 observed upon PdNP reduction using $NaBH_4$ (see Fig. 8 of ESI†). The ^{1}H NMR data also indicate the rapid reduction of Pd^{II} to Pd^0 in the presence of methanol and triazole: after 10 min of reaction, a decrease of the intensity of the dendrimer NMR signals is observed, with only small broad peaks (see Fig. 24 of ESI†). The spectroscopic data confirm the formation of the nanoparticles using either $NaBH_4$ (method 1) or methanol (method 2) as reducing agent.

Due to its small size and open structure, G_0 cannot encapsulate a PdNP. Thus, G_0 forms *inter*dendrimer-stabilized PdNPs (DSNs, Chart 2) in which the NP surface is stabilized by several dendrimers. TEM data show that, in this case, the PdNPs obtained by reduction using methanol are larger with G_0 than with G_1. Also, the nature of the reductant has a crucial influence on the size of the NPs formed. Upon reduction with methanol, 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 G_0-DSN with a diameter of 1.2 ± 0.2 nm (60 Pd atoms stabilised by 7 dendrimers).[12] This size difference can be accounted for, as in polymer chemistry, by the reducing power which is stronger with $NaBH_4$ than with methanol, because no encapsulation of the DSNs drives the size control for G_0. On the other hand, as expected, G_1 and G_2 form very small *intra*dendrimer-encapsulated PdNPs, DENs (Chart 2). Their sizes observed by TEM correspond to the calculated sizes[12] for the number of Pd atoms in the dendrimer which is the same as that of triazole ligands for G_1 (36) and G_2 (117) (Table 1). In contrast to DSN-G_0, we find that for DEN-G_1 and DEN-G_2, the size of the PdNPs is about the same using $NaBH_4$ or methanol (Table 1). This result is easily accounted for by the fact that, in DENs, the size of the PdNPs is governed by the number of Pd atoms inserted in the dendrimers before

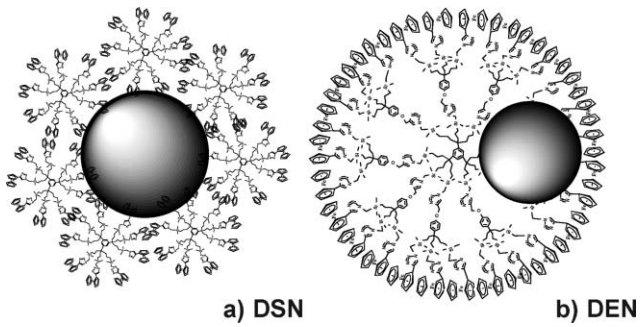

Chart 2 a) DSN formed from G_0; b) DEN formed from G_1.

reduction, not by the reducing power of the reductant. For comparison, we are using a known hydrophobic PAMAM-modified dendrimer (PAMAM-NH_2-G_4 modified with 1,2-epoxydodecane)[13] to form Pd-DENs. The DEN-Pd-PAMAM was mixed with 40 equiv. of $Pd(OAc)_2$ *per* dendrimer in $CHCl_3$–MeOH (2 : 1), and $NaBH_4$ was added (see Table 1).

The dramatic influence of the nature of the reductant on the size of DSN-G_0 also confirms the different type of stabilization, DSN *vs.* DENs, when comparing G_0 with G_1 and G_2. In order to compare DENs formed from G_1 and G_2 with the same number of Pd atoms in the PdNPs (*i.e.* 36), another DEN is synthesized, setting only 36 Pd equivalents in the dendrimer G_2 that contains 117 triazole units (DEN-G_2-36). According to the TEM data, these DENs have a size that is similar to that of DEN-G_1 (1.1 ± 0.2 nm), confirming that these NPs contain about 36 Pd atoms.

The DSNs and DENs formed with the new poly-1,2,3-triazolyl-ferrocenyl dendrimers are efficient catalysts for hydrogenation of styrene at 0.1% mol Pd.[8,9] The 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).[10] On the other hand, the new "click" DENs are very stable under catalytic conditions: they can be re-used in 10 catalytic cycles (TON ≅ 10 000) for DEN-G_1 and 20 catalytic cycles for DEN-G_2 (TON ≅ 20 000). The largest TONs are obtained with the G_0-DSNs (TON ≅ 30 000), although the TOF is lower than that found with DEN-G_1 (Table 2). The catalytic activity of the DSNs and DENs synthesized using methanol as reducing agent is much higher than that of DENs synthesized using $NaBH_4$, with TOF values of 1620 mol H_2(mol Pd)$^{-1}$ h^{-1}

Table 2 Catalytic efficiency (TOF values) and stability (TON values) obtained for all new catalysts for styrene hydrogenation at 0.1% mol Pd

	TOF[a](mol H_2(mol Pd)$^{-1}$ h^{-1})		TON	
PdNP	Method 1[b]	Method 2[c]	Method 1	Method 2
DSN-G_0	200	1200	30 000	31 500
DEN-G_1	310	1620	10 000	9300
DEN-G_2	200	1280	20 000	16 650
DEN-G_2-36	280	1380	7400	10 000
DEN-PAMAM	56	—	7500	—

[a] The catalytic activity of the DENs 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. [b] Method 1: reduction of Pd by $NaBH_4$. [c] Method 2: reduction of Pd by methanol.

(DEN-G_1, Table 2), whereas the opposite was known with polymers.[11]

The large increase of catalytic activity found with these "click" DENs compared to DENs prepared from the commercial dendrimers PAMAM (Table 2) and PPI[10] is shown to be due to both the type of dendrimer and nature of the reductant, and we can also assign the contribution of each of these two parameters influencing the increase of catalytic activity. On the 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 2.

All the previous literature data for DENs had been recorded using $NaBH_4$, possibly because $NaBH_4$ had provided better catalytic results than methanol in the cases of studies with polymer-stabilized NPs.[14] The better results obtained with $NaBH_4$ compared 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. On the contrary, we find that, with the "click" DENs, the size of the PdNPs obtained from TEM data is about the same using $NaBH_4$ or methanol (Table 2). This result is easily accounted for by the fact that the size of the PdNPs is governed only by the number of Pd atoms in the DENs that is the same as that of triazole ligands for G_1 and G_2. Methanol does not leave inhibiting residues on the PdNPs surface subsequent to reduction, whereas $NaBH_4$ does ($B(OCH_3)_3$ and Na^+).[15] The catalytic efficiencies of DEN-G_1 and DEN-G_2 confirm the trend according to which the catalytic activity is a function of the size of the PdNPs, *i.e.* the catalytic reactions are faster for the smaller NPs than for the larger ones. We also examine the influence of the dendrimer size on the catalytic activity of "click" DENs. Comparison of the catalytic activity of DEN-G_2-36 with those of DEN-G_1-36 and DEN-G_2-117 shows that DEN-G_2-36 is more efficient than DEN-G_2-117, but less efficient than DEN-G_1-36. This makes it possible 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 slowing the catalysis kinetics due to steric effects of the large dendrimer framework.[7] Thus, G_1 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.

The size selectivity of DEN-G_1 was investigated by comparing its catalytic activity in the hydrogenation of cyclohexadiene and ergosterol, a steroid that contains a cyclohexadiene ring in its structure (see Fig. 25 of ESI†). It was found that DEN-G_1 catalyzed the partial hydrogenation of cyclohexadiene to cyclohexene with a TOF value of 1150 mol H_2(mol Pd)$^{-1}$ h^{-1}, but no hydrogenation was observed in the case of ergosterol. Moreover, only cyclohexadiene was semi-hydrogenated upon reaction of a mixture of cyclohexadiene and ergosterol. This clearly shows the size selectivity performed by the G_1-DEN catalyst; ergosterol is not able to enter the dendrimer structure to locate its double bonds onto the NP surface. Hydrogenation of various other mono-, di-, and tri-ene substrates is detailed in Table 2 of ESI.†

In conclusion, "click"-dendrimer-NPs open avenues in selective catalysis of potential industrial relevance, bring key information for PAMAM-NPs,[7–10] and should be very useful for mechanistic studies of various catalytic C–C bond formation reactions.

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