Nanoparticle Catalysis

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"Homeopathic" Catalytic Activity and Atom-Leaching Mechanism in Miyaura–Suzuki Reactions under Ambient Conditions with Precise Dendrimer-Stabilized Pd Nanoparticles**

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Low catalyst loading is essential for the development of "green" palladium-catalyzed C–C bond-forming processes,[1] such as Heck and Suzuki reactions.[2] In this regard, transition-metal nanoparticles (NPs) have attracted much attention as a major alternative to molecular homogeneous catalysts.[3–5] We now report that dendrimer-stabilized Pd nanoparticles synthesized by click chemistry catalyze the Suzuki reaction under ambient conditions with as little as 1 ppm of the PdNP catalyst: Our studies indicate that an atom-leaching mechanism is operating. We also show that the extraction of these PdNPs with thiols provides catalytically active PdNPs of complementary mechanistic interest.

Polymer-stabilized[4] and dendrimer-stabilized NPs[5] have proved to be efficient catalysts for a variety of reactions. The advantage of dendrimers, besides their loose binding of the NP surface, is that a precise and predictable number of Pd atoms exist in the PdNP catalyst or precatalyst. Thus, it is possible to study the influence of NP size on the catalytic parameters (efficiency and stability) and mechanism. The use of dendrimers to form dendrimer-encapsulated NPs (DENs)[6] and dendrimer-stabilized NPs (DSNs),[7] in which dendrimers surround the NPs, was pioneered with PAMAM dendrimers. DENs have been studied largely in catalytic olefin-hydrogenation reactions[6a,c,8] and in several cases in C–C coupling reactions, including the Suzuki reaction.[9]

A leaching mechanism upon Pd catalysis has been proposed by de Vries and co-workers for the high-temperature (130–160 °C) Heck reaction with simple molecular Pd^{II} catalysts,[10] and these catalysts indeed decompose to give PdNPs at high temperature. They propose that Pd atoms are removed from the PdNP surface subsequent to oxidative addition of the aryl halide, and that efficient Pd catalysis proceeds thereafter in solution before these catalytically active Pd atoms are trapped by a PdNP.[10] The mechanism of the Suzuki reaction, however, is controversial. One research group proposed a mechanism that operates only at the NP surface,[11] whereas another research group proposed that under microwave irradiation Pd-atom leaching occurs subsequent to oxidative addition of the aryl halide, as in the Heck reaction.[12] All of these studies were carried out at high temperature, under which conditions Oswald ripening, including atom loss from PdNPs, occurs. We wondered how the reaction would proceed under mild, ambient conditions with a PdNP catalyst. Herein, we show that the use of precise DSNs and DENs of various sizes for comparative styrene-hydrogenation and Suzuki reactions at 25 °C provides a unique means to reach decisive conclusions concerning the leaching mechanism of the Suzuki reaction under ambient conditions.

We recently described dendrimers synthesized by click chemistry[13] with 9, 27, and 81 ferrocenyl termini and 1,2,3-triazole ligands on the dendritic tethers: G_0 with nine terminal ferrocenyltriazole units, G_1 with 36 triazole units (9 interior and 27 terminal), and G_2 with 117 triazole units (9 + 27 interior and 81 terminal; Scheme 1).[13c] PdNPs that can be stabilized by these new dendrimers have been shown to catalyze selective olefin hydrogenation. Molecular engineering to introduce triazole ligands into the dendrimers has enabled the precise delineation of the number of Pd atoms in the PdNPs. Indeed, the ferrocenyl groups located at the termini of the G_0, G_1, and G_2 ferrocenyltriazolyl dendrimers make it possible to monitor the complexation of the triazolyl ligands by $Pd(OAc)_2$ by using cyclic voltammetry (CV). Electrochemical titration on the basis of this CV wave showed one-to-one complexation of the triazole group by $Pd(OAc)_2$. In this way, the number of Pd atoms in the designed PdNP could be predetermined and checked.

The reduction of Pd^{II} in the dendrimers to give PdNPs was most successful with methanol. G_0 is too small to form DENs, as confirmed by TEM data, which show the formation of DSNs. G_1 and G_2 form DENs whose sizes determined by TEM match those expected by theory. Catalytic efficiency in olefin hydrogenation was shown to depend on the size of the PdNPs, which is related to the type of dendrimer stabilization that occurs (DEN or DSN) and the dendritic generation, G_n (G_1 forms smaller and more efficient DENs than G_2). These mechanistic investigations confirmed that all catalytic steps in the hydrogenation mechanism occur on the PdNP surface as expected.

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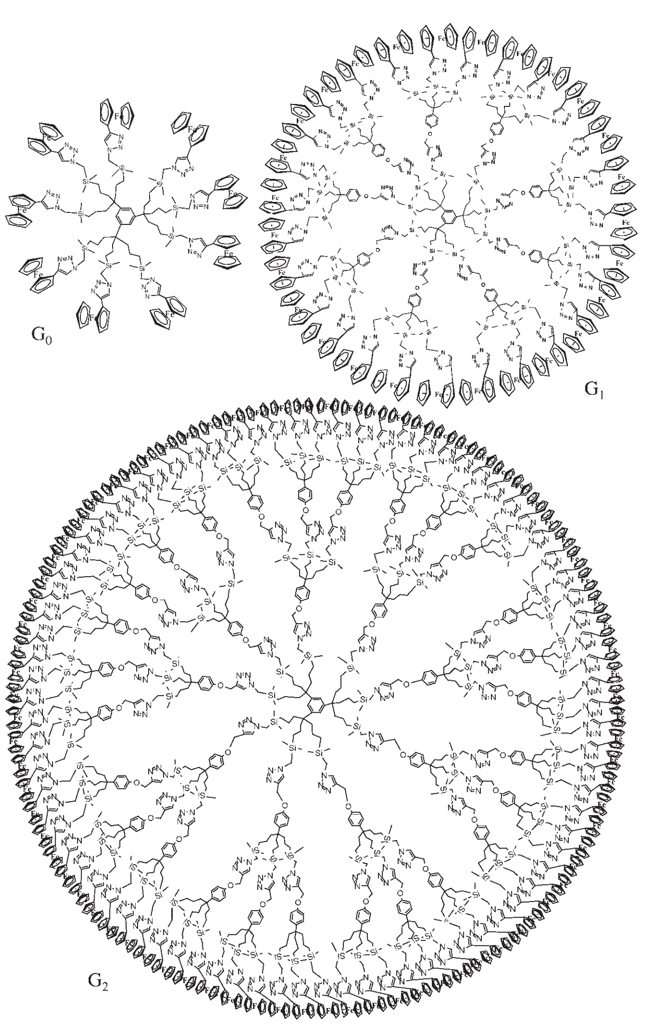
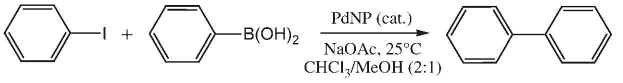


Scheme 1. Structures of the poly-1,2,3-triazolylferrocenyl dendrimers containing triazole ligands.

Now able to differentiate clearly the catalytic hydrogenation efficiency of DSNs and DENs, and that of DENs of two successive generations, we investigated the PdNP-catalyzed Suzuki reaction between aryl halides and phenylboronic acid at 25 °C in the presence of NaOAc as a base. The PdNPs were prepared in the same way as for the hydrogenation study by using methanol as the reductant. The Suzuki reaction between PhI and $PhB(OH)_2$ [Eq. (1)] was never quantitative, whichever DSN or DEN was used, and peaked at 70 % yield with 1 mol % of Pd atoms from the DEN-G$_1$ catalyst (Table 1).



(1)

On the other hand, with the G$_0$ catalyst, the TON increased constantly as the amount of PdNP was decreased to 1 ppm (54 % yield, TON = 540000; Table 2).[14] Remarkably, dilution of the reaction mixture also resulted in an increase in the yield, TOF, and TON with both PhI and PhBr. For example, the yield, TOF, and TON for diphenyl formation from PhI and $PhB(OH)_2$ in the presence of DSN-G$_0$ increased from 31 %, 10, and 31, respectively, to 68 %, 17, and 68 when the reaction medium was diluted by a factor of five with the solvent ($CHCl_3$/MeOH (2:1); the concentration of the catalyst decreased from 4.4×10^{-4} to 8.8×10^{-5} (mol Pd) L^{-1}; 25 °C, 24 h). A similar trend was found with PhBr (Table 3).

Table 1: Comparison of catalytic efficiency (TOF values) and stability (TON values) for the three generations of dendrimer-stabilized and dendrimer-encapsulated nanoparticles at a Pd concentration of 1, 0.1, and 0.01 % mol at 25 °C in $CHCl_3$/MeOH (2:1).

Catalyst [mol %]	PdNP	Diameter [nm][a]	*t* [h]	Yield [%]	TOF[b]	TON[c]
1	DSN-G$_0$	2.8 ± 0.3	24	68	17	68
	DEN-G$_1$	1.3 ± 0.2	24	70	18	70
	DEN-G$_2$	1.6 ± 0.3	24	55	13	55
0.1	DSN-G$_0$	2.8 ± 0.3	24	66	130	660
	DEN-G$_1$	1.3 ± 0.2	24	69	140	690
	DEN-G$_2$	1.6 ± 0.3	24	51	80	510
0.01	DSN-G$_0$	2.8 ± 0.3	48	51	375	5100
	DEN-G$_1$	1.3 ± 0.2	48	52	363	5200
	DEN-G$_2$	1.6 ± 0.3	72	44	225	4400

[a] The diameter of the nanoparticles was determined by TEM. [b] The catalytic activity (turnover frequency: TOF values in (mol PhI) (mol Pd)$^{-1}$ h^{-1}) of the PdNPs was determined on the basis of the yield of diphenyl. [c] TON: turnover number.

Table 2: Influence of the amount of Pd from the DSN-G$_0$ catalyst on the parameters of the Suzuki reaction [Eq. (1)] at 25 °C in $CHCl_3$/MeOH (2:1).

Catalyst [mol %]	*t* [h]	Yield [%]	TOF[a]	TON
0.1	8	66	129	660
0.01	48	51	375	5100
0.001	48	30	6000	30000
0.0001	1 month	54	1042	540000

[a] See footnote [b] of Table 1.

Table 3: Influence of dilution on the catalytic parameters of the Suzuki reaction between PhBr and $PhB(OH)_2$ with DSN-G$_0$ (0.1 mol % Pd) with identical reagent and catalyst content.[a]

Concentration [(mol Pd) L^{-1}]	Yield [%]	TOF	TON
8.8×10^{-5}	12.5	3	125
4.4×10^{-5}	16	7	160
1.8×10^{-5}	26.5	15	265

[a] The reactions were carried out in $CHCl_3$/MeOH (2:1) at 25 °C for 48 h.

The other striking feature of these catalytic processes is that DSN-G$_0$ and DEN-G$_1$ were found to have the same catalytic efficiency, with only a slight decrease observed for DEN-G$_2$. The similarity of the catalytic activities of the three dendrimers indicates that the dendrimer is not involved in the catalysis (except for the existence of a weak "filter" effect in the case of G$_2$). Our inability to obtain the product in quantitative yield shows that the actual catalyst is deactivated in some way, as confirmed by the loss of catalytic activity after a certain period of time, which was found to depend on the amount of catalyst used and the degree of dilution. On the other hand, catalytic deactivation decreases when the amount of catalyst used is decreased. Thus, at 1 ppm, the very long catalyst lifetime and exceptionally high TON show that deactivation is almost nonexistent. These features are consistent with Pd-atom leaching from the PdNP surface subsequent to the oxidative-addition step. Quenching of the catalytically active Pd atoms in solution becomes more efficient as the Pd-atom concentration and PdNP concentration increase.

We attempted to extract the DSNs and DENs with alkanethiols (Scheme 2).[15,16] With undodecanethiol, only DSN-G_0 could be extracted. This distinction in the behavior of DSN-G_0 and the DENs is in accord with the different types of PdNP stabilization: As the nanoparticles are not encapsulated in the case of DSN-G_0, extraction is favored even with a bulky thiol. With less bulky hexanethiol, however, the extraction of DEN-G_1 was also possible. The TEM data for the well-defined thiolate-stabilized PdNPs thus obtained showed that no significant change in the core size of the PdNPs had occurred upon their extraction. The extent of the extraction of G_2 with hexanethiol was negligible, probably because the dendritic filter strongly inhibits intradendritic PdNP approach by the thiol. The catalytic efficiency of these thiolate PdNPs was probed for the Suzuki reaction of PhI with $PhB(OH)_2$ in the presence of NaOH in a mixture of THF and H_2O. The product was formed in quantitative or nearly quantitative yield at 25 °C within 1 day, although the reaction rate was lower than with PdDENs and PdDSNs. Again, the reaction kinetics were found to be independent of the size of the NPs (Figure 1). The extract from DEN-G_2 by hexanethiol showed very weak catalytic activity in accordance with the very low PdNP content and inefficiency of the extraction.

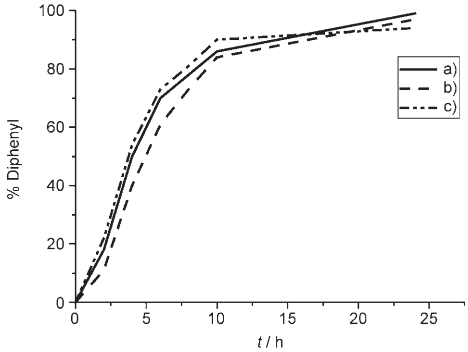
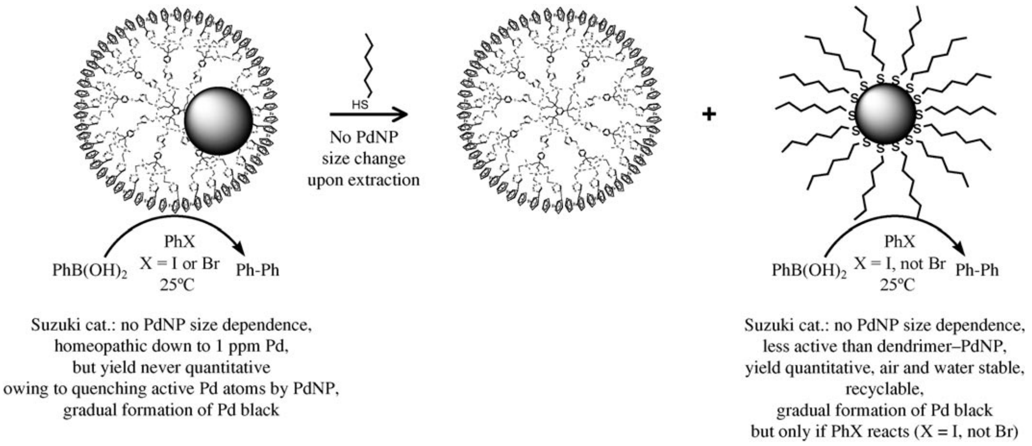


Figure 1. Kinetics of the Suzuki reaction between phenylboronic acid and iodobenzene catalyzed by thiolate PdNPs extracted from DSNs and DENs (1 mol% Pd at 25 °C): a) hexanethiolate PdNPs extracted from DSN-G_0; b) hexanethiolate PdNPs extracted from DEN-G_1; c) undodecanethiolate PdNPs extracted from DSN-G_0.



Scheme 2. Extraction of PdNPs from DSNs or DENs with hexanethiol without any change in the size of the PdNPs to produce air- and water-stable, catalytically active hexanethiolate PdNPs.

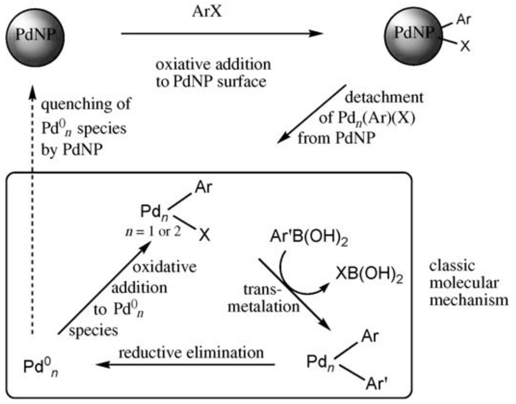
These alkyl thiolate PdNP catalysts are air and water stable (as opposed to the DSNs and DENs, which are air sensitive) and could be recycled twice with little decrease in catalytic efficiency. The catalytic activity of the thiolate PdNPs is accompanied by the formation of Pd black on the wall of the Schlenk flask within a few hours, as also observed with Pd DSNs and Pd DENs. In the absence of PhI, the thiolate PdNPs are stable in solution for months without any formation of Pd black. Whereas the attempted Suzuki reaction between PhBr and $PhB(OH)_2$ with DSN-G_0 led to the expected product of C–C coupling in 12% yield after 8 h and 23% yield after 1 day, the thiolate PdNPs obtained upon the extraction of DSN-G_0 did not promote the C–C coupling reaction: The product was not detected even after several days. We also observed that no Pd black formed in these attempted Suzuki coupling reactions with bromobenzene. The formation of Pd black results from the agglomeration of Pd atoms to form Pd metal and indicates a lack of stabilization at the PdNP level. The observation that Pd black does not form in the absence of a reactive substrate for the Suzuki reaction is in accord with Pd-atom escape from the PdNPs when a reactive substrate is present. Hence, the reason for Pd escape in the presence of the aryl iodide must be oxidative addition of PhI to the PdNP surface, followed by the escape of $Ph(Pd_x)I$ ($x = 1$ or 2), as postulated for the high-temperature Heck reaction.[10]

The striking contrast between the reactivity of PhBr in the Suzuki reaction catalyzed by DSN-G_0 and the complete absence of catalysis with hexanethiolate PdNPs reflects the contrast between the reactive Pd^0 surface in DSN-G_0 and the less reactive Pd surface of thiolate PdNPs. The latter surface is positively charged to a certain extent as a result of the partly oxidized Pd atoms bonded to the thiolate ligands. Even if PhX undergoes oxidative addition to one or two surface Pd atoms that are not bonded to thiolate ligands, electronic delocalization on the PdNP surface lowers electron density on the surface significantly and disfavors oxidative addition. This trend is confirmed by the faster kinetics observed for the Suzuki reactions of PhI on DSNs and DENs than with thiolate PdNPs, although the thiolate PdNPs after extraction are the same size as the DENs and DSNs.

The kinetics of the reactions with alkyl thiolate PdNPs are the same irrespective of NP size and the generation of the precursor dendrimer, as for the DSNs and DENs, and they do not depend on the length of the thiolate ligand. Thus, the mechanism of the Suzuki reaction must also involve oxidative addition of PhI with the escape of $PhPd_xI$ from the NP surface to the solution, followed by catalysis in solution. A significant mechanistic difference, however, between DEN (or DSN) catalysis and catalysis by alkyl thiolate PdNPs is the fate of the catalytically very active Pd atoms in solution. In the case of DSNs (or DENs), these atoms can either be quenched by a DSN (or DEN) or collapse to Pd black as a result of insufficient stabilization. However, the nearly quantitative yields observed with all alkyl thiolate PdNPs indicate the absence of an efficient quenching mechanism: The formation of Pd black is much slower and less efficient with highly protected alkyl thiolate PdNPs than with Pd atoms quenched by weakly stabilized DSNs or DENs.

In summary, the similarity of the TOFs observed with DSNs to those found with DENs for Suzuki reactions of PhI with $PhB(OH)_2$ at 25 °C is in sharp contrast with the finding that the TOF for hydrogenation reactions depends on the type (DSN or DEN), size, and generation of the NPs (and hence that the hydrogenation steps proceed at the NP surface). The TONs increase with decreasing concentration of the DSN or DEN catalyst for the coupling of PhX ($X = I$ or Br) with $PhB(OH)_2$, but the yields are never quantitative: With 1 ppm of the NP catalyst with respect to the Pd-atom concentration, the product of the coupling of PhI with $PhB(OH)_2$ was formed in 54% yield, and the observed TON was 540000. Only the DSNs could be extracted with undodecanethiol; hexanethiol could be used to extract PdNPs from both DSN-G_0 and DEN-G_1, but was inefficient in the extraction of PdNPs from DEN-G_2. TEM data show that such extractions with alkyl thiolates do not modify the size of the PdNPs. The kinetics of the Suzuki reaction of PhI were found to be slower with thiolate PdNPs than with DSNs or DENs, but the yields observed were nearly quantitative, in contrast to those observed with DSNs and DENs. Bromobenzene was found to be unreactive in the presence of alkyl thiolate PdNPs but underwent C–C coupling under the catalysis of DSNs and DENs. Finally, the formation of Pd black was observed only in reactions in which PhX showed catalytic reactivity.

These observations, together with TEM data, confirm the distinction between DSN and DEN formation by the three dendrimer generations. They show that, as already proposed by de Vries and co-workers for the Heck reaction at high temperatures, the catalytic mechanism of the Suzuki reaction at 25 °C starts, in the case of both DSNs (or DENs) and alkyl thiolate PdNPs, by oxidative addition to the PdNP surface followed by the escape of $PhPd_xX$ ($x = 1$ or 2) into the solution, where this species is catalytically extremely reactive (at the 1-ppm level). However, the catalytic species is quenched quite efficiently by DSNs or DENs, and therefore the product yields are limited (Scheme 3). As this quenching is not efficient with alkyl thiolate PdNPs, quantitative yields are observed, and recycling of the catalyst is possible. Another quenching mechanism for the catalytically active Pd atoms in solution in the reactions with DSNs, DENs, and alkyl thiolate PdNPs is the formation of Pd black. The formation of Pd black is much slower than the other quenching mechanism described and therefore does not limit the yields of the reactions catalyzed by alkyl thiolate PdNPs.



Scheme 3. Proposed leaching mechanism for the Suzuki reaction catalyzed by PdNPs at room temperature.

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