

Palladium–dodecanethiolate nanoparticles as stable and recyclable catalysts for the Suzuki–Miyaura reaction of aryl halides under ambient conditions

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Abstract—Palladium–dodecanethiolate nanoparticles (PdTNs) catalyze the quantitative Suzuki–Miyaura coupling of halogenoarenes under biphasic conditions in THF/water at room temperature and can be recovered by precipitation using ethanol and re-used. © 2004 Elsevier Ltd. All rights reserved.

Palladium-catalyzed cross-coupling reactions of aryl halides with aryl boronic acids, referred to as the Suzuki–Miyaura reactions, are useful methods for the synthesis of unsymmetrical biaryls. This reaction is applied in the synthesis of natural products and it is widely used in industry (equation 1).¹

Whereas homogeneous catalysts exhibit a good reactivity and selectivity, heterogeneous catalysts avoid the use of phosphines and are also advantageous for catalyst removal from reaction mixtures and recycling. Nanoparticles (NP),² in particular Pd NPs whose general activity in catalysis is well known,³ offer a compromise that has been recently exploited and also avoid phosphines. On the other hand, alkyl thiols and thiolate are well known as poisons that inhibit the catalysis of reactions by nanoparticles.⁴ It is thus necessary to gain insight into the mode of reactivity of NPs even with thiolate ligands. We report herein a surprising good reactivity of well-defined dodecanethiolate Pd nanoparticles for the Suzuki–Miyaura C–C coupling reaction, actually under ambient conditions for the first time with such simple nanoparticles. The formation of Pd NPs involves various stabilizers that not only protect the metal core, but also sterically inhibits its access. Pd NPs that are used in catalysis are generally stabilized by incorporation into a polymer, since the lack of ligands in polymer-embedded Pd NPs favors the access of the

molecular components onto the Pd NP surface.^{2,3} More recently Crooks' group has investigated the catalytic properties of Pd NPs embedded in PAMAM dendrimers and reported remarkable efficiencies and selectivities.⁵ Au-thiolate NPs are well known⁶ and Ullman and co-workers have reported alkanethiol Pt NPs.⁷ Some thiolate Pd NPs (PdTNPs) and their catalytic activity in the hydrogenation of allylamine was published by Kaifer's group.⁸ These authors⁹ and Newman's group¹⁰ have reported the catalytic activity in the Suzuki–Miyaura reactions of PdTNPs modified, respectively, with β -cyclodextrin and polyoxometallates. Recently, Fox and coworkers reported the catalytic behavior, including for the Suzuki–Miyaura reaction, of Pd NP-cored dendrimers.¹¹ In all these reports of the Pd NP-catalyzed Suzuki–Miyaura reactions,^{8–10} catalysis was run at relatively high temperatures (typically in refluxing water, ethanol or a mixture of these solvents). Indeed, thiols and thiolates are believed to be poisonous compounds that should be avoided in catalysis by NPs.^{4,7,8}

Given the recent report that the Suzuki–Miyaura reaction can be quantitatively achieved at 150 °C in water in the absence of catalyst,¹² we have investigated the synthesis and catalytic properties (including recyclability) of *simple dodecanethiolate Pd NPs (PdTNPs)* for the Suzuki–Miyaura reaction *at room temperature*; we now report preliminary data showing a remarkable efficiency and recyclability.

The PdTNPs tested in this study were prepared using a procedure inspired by Nishihara's report¹³ using the reduction of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ by LiBEt_3H in THF in

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the presence of tetra-octylammonium bromide, followed after 0.5 h by the addition of 1-dodecanethiol in THF to the black Pd NP suspension and precipitation using ethanol; purification was achieved by reprecipitation by acetone of a toluene solution and washing with acetone. The PdTNPs are relatively monodisperse, with a mean diameter of 2.3 ± 0.5 nm as indicated by the TEM picture and histogram shown in Figure 1.

We find that good results for the catalysis of the Suzuki–Miyaura reaction between iodo- or bromobenzene and phenylboronic acid were obtained by using PdTNPs (1 mol% Pd vs halogenoarene) in a 2:1 biphasic mixture of THF–water with NaOH as a base¹⁴ under ambient conditions (Table 1). For instance, on the mmol scale, 2.5 mg of PdTNPs was used leading to quantitative heterocoupling of either iodo- or bromobenzene at 20 °C after one day (1). Alternatively, the reaction could also reach completion when the mixture was heated for 1 h at 63 °C, a temperature at which the PdTNPs are stable. The results are gathered in Table 1. Chlorobenzene, for which bulky, electron-rich phosphines are most often required also give some coupling at 20 °C using homogeneous conditions (see Table 1) with PdTNPs, although the yield is lower and the reaction times longer than with the other halogenoarenes.

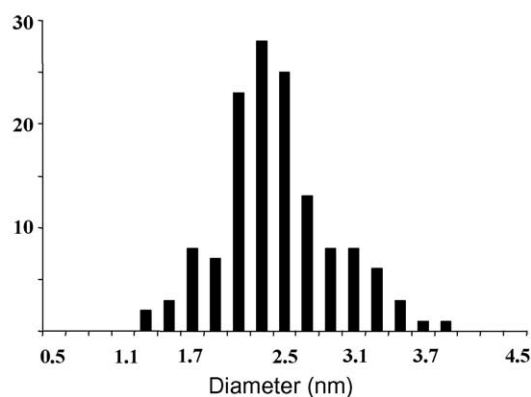
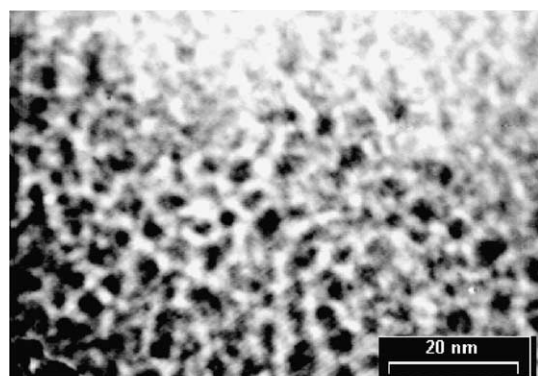
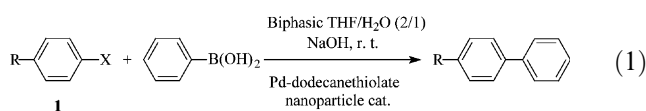


Figure 1. TEM picture and histogram of the PdTNPs with diameter of 2.3 ± 0.3 nm.

Table 1. Suzuki–Miyaura cross-coupling reaction with **1** (Eq. 1)^a

Entry	R in 1	X in 1	Temperature (°C)	Time	Yield ^c (%)
1	H	I	20	1 d	100
			63	1 h	100
2	CH ₃	I	20	1 d	100
3	CH ₃ O	I	20	17 h	100
4 ^b	I	I	20	15 h	87
5 ^b	I	Br	20	15 h	70
6	H	Br	20	1 d	100
7 ^d	H	Cl	63	2.5 h	100
			20	5 d	52
8 ^e	CH ₃	Cl	20	3 d	27

^aReaction conditions: 2 mmol of substrate, 3 mmol phenylboronic acid, 5 mg PdTN catalyst, 6 mmol NaOH, THF/H₂O (16 mL/8 mL).

^b0.5 mmol aryl halide, 1.5 mmol PhB(OH)₂, 2.5 mg PdTN catalyst, 3 mmol NaOH, THF/H₂O (8 mL/4 mL), the product is terphenyl.

^cIsolated yield.

^d1 mmol aryl halide, 1.2 mmol PhB(OH)₂, 6 mL THF, 3 mmol KF, 12 mg PdTN catalyst.

^e1 mmol aryl halide, 1.2 mmol PhB(OH)₂, 6 mL THF, 3 mmol KF, 2.5 mg PdTN catalyst.

We checked the recyclability and re-use of the PdTNP catalyst in the case of the Suzuki–Miyaura reaction with iodobenzene. The PdTNPs could be precipitated after the reaction by addition of ethanol, filtered, and re-used at least six times using this recycling procedure for identical reactions. The reaction yield remained quantitative or almost so upon these six recycling reactions (resp. 100%, 100%, 98%, 94%, 92%, and 87%).

In conclusion, we have shown that easily accessible, well-defined PdTNPs can serve as efficient, recyclable catalysts for the Suzuki–Miyaura C–C coupling reaction of aromatic iodides and bromides under ambient conditions for the first time. The PdTNPs are not as active as the recently designed molecular palladium catalysts for the Suzuki–Miyaura coupling of arylchlorides,¹⁵ but they are phosphine-free and recyclable. The modest yields obtained so far under ambient conditions with the aryl chlorides open the route to more sophistications of the PdTNP structure in order to improve these preliminary results. The efficiency and usefulness of these PdTNPs are already remarkable, however, and research is in progress in our laboratory to improve their engineering. This work also shows that, contrary to common belief, extensive use of simple thiolate ligands is not counter-productive in catalysis. It is especially noteworthy that Pd NP covered with ligands are so active, which may imply that the edges and vertices of the polyhedral nanoparticle cores play an important role for the reactivity in nanoparticle catalysis as recently pointed out by El-Sayed.²

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References and notes

1. Miyaura, N.; Yanagi, T.; Suzuki, A. *Syn. Commun.* **1981**, *11*, 513; Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457; Suzuki, A. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, 2002; pp 53–106.
2. Reetz, M. T.; Breinbauer, R.; Wanninger, K. *Tetrahedron Lett.* **1996**, *37*, 4499; Kabalka, G.-W.; Pagni, R. M.; Hair, C. M. *Org. Lett.* **1999**, *1*, 1423; Li, Y.; Hong, X. M.; Collard, D. M.; El-Sayed, M. A. *Org. Lett.* **2000**, *2*, 2385; Li, Y.; El-Sayed, M. A. *J. Phys. Chem. B* **2001**, *105*, 8938; Kim, M.; Kim, S. W.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc.* **2002**, *124*, 7642; Li, Y.; Boone, E.; El-Sayed, M. A. *Langmuir* **2002**, *18*, 4921; Rocardy, C.; Gladysz, J. A. *Org. Lett.* **2002**, *4*, 1993; Roucoux, A.; Schultz, J.; Patin, H. *Chem. Rev.* **2002**, *102*, 3757; Pittelkow, M.; Moth-Poulsen, K.; Boas, U.; Christensen, J. B. *Langmuir* **2003**, *19*, 7682; Liu, Y.; Khemtong, C.; Hu, J. *Chem. Commun.* **2004**, 398; Narayanan, R.; El-Sayed, M. A. *J. Phys. Chem. B* **2004**, *108*, 8572; Gopidas, K. R.; Whitesell, K. W.; Fox, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 14168.
3. Schmid, G. *Chem. Rev.* **1992**, *92*, 1709; Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693; Bradley, J. S. In *Clusters and Colloids: From Theory to Applications*; Schmid, G., Ed.; VCH: New York, 1994; pp 459–536; Finke, R. G. In *Metal Nanoparticles Synthesis Characterization and Applications*; Feldheim, D. L., Foss, C. A., Jr., Eds.; Marcel Dekker: New York, 2002; Chapter 2; pp 17–54, *Nanoparticles*; Schmid, G., Eds.; Wiley-VCH: Weinheim, 2004; For a recent specific review, see: Widgren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317.
4. Chauhan, B. P. S.; Rathore, J. S.; Bando, T. *J. Am. Chem. Soc.* **2004**, *126*, 8493; *Catalysis from A to Z. A Concise Encyclopedia*; Cornils, B., Herrmann, W. A., Schlögl, R., Wong, C.-H., Eds.; Wiley-VCH: Weinheim, 2000.
5. Niu, Y.; Yeung, L. K.; Crooks, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 6840; Yeung, L.; Lee, C. T., Jr.; Johnston, K. P.; Crooks, R. M. *Chem. Commun.* **2001**, 2290; Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. *Acc. Chem. Res.* **2001**, *34*, 181; Scott, R. W. J.; Datye, A. K.; Crooks, R. M. *J. Am. Chem. Soc.* **2003**, *125*, 3708.
6. Giersig, M.; Mulvaney, P. *Langmuir* **1993**, *9*, 3408; Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. J. Chem. Soc., Chem. Commun.* **1994**, 801; Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293.
7. Yee, C.; Scotti, M.; Ullman, A.; White, H.; Rafailovitch, R.; Sokolov, J. *Langmuir* **1999**, *15*, 4314.
8. Alvarez, J.; Liu, J.; Roman, E.; Kaifer, A. E. *Chem. Commun.* **2000**, 1151.
9. Strimbu, L.; Liu, J.; Kaifer, A. E. *Langmuir* **2003**, *19*, 483.
10. Moreno-Manas, M.; Pleixats, R.; Villarroya, S. *Organometallics* **2001**, *20*, 4524; Kogan, V.; Aizenshtat, Z.; Popovitz-Biro, R.; Neumann, R. *Org. Lett.* **2002**, *4*, 3529.
11. Gopidas, K. R.; Whitesell, J. K.; Fox, M. A. *Nano Lett.* **2003**, *3*, 1757.
12. Li, C.-J. *Angew. Chem., Int. Ed.* **2003**, *42*, 4856.
13. Quiros, I.; Yamada, M.; Kubo, K.; Mizutani, J.; Kurihara, M.; Nishihara, H. *Langmuir* **2002**, *18*, 1413.
14. Soderquist, J. A.; Santiago, B. *Tetrahedron Lett.* **1990**, *31*, 5541; Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.
15. Fu, G. C.; Littke, A. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176 (review); Old, D. W.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722; Wolfe, J. P.; Singer, R. A.; Yang, S. L.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550; Fu, G. C.; Littke, A. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 3387; Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359; Bedford, R. B. *Chem. Commun.* **2003**, 1787; Fürstner, A.; Leitner, A. *Synlett* **2001**, 290; Hu, Q.-S.; Lu, Y.; Tang, Z.-Y.; Yu, H.-B. *J. Am. Chem. Soc.* **2003**, *125*, 2856; Gstottmayer, C.; Bohm, V.; Herdwerck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1363; Roca, F. X.; Richards, C. J. *Chem. Commun.* **2003**, 3002; Miura, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2201.