



## Organostannoxane-supported Pd(0) nanoparticles as efficient catalysts for Heck-coupling reactions

Vadapalli Chandrasekhar\*, Ramakirushnan Suriya Narayanan

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208 016, India

### ARTICLE INFO

#### Article history:

Received 1 April 2011

Revised 1 May 2011

Accepted 3 May 2011

Available online 8 May 2011

#### Keywords:

Organostannoxane

Cage

Nanoparticles

Palladium

Catalysis

### ABSTRACT

A new functional organostannoxane cage, **SnP**, that contains phosphine ligands in its periphery has been structurally utilized as support palladium(0) nanoparticles **SnPPd**. The latter was shown to catalyze the Heck coupling reactions of wide variety of functionalities efficiently.

© 2011 Elsevier Ltd. All rights reserved.

Palladium nanoparticles (**PdNPs**) are increasingly being used as catalysts in various organic transformations and their advantages stem from the fact they can be dispersed in an organic solvent and can be reused.<sup>1</sup> In general, prevention of agglomeration of **PdNPs** is achieved by the use of stabilizers that include micelles,<sup>2</sup> microemulsions,<sup>3</sup> surfactants,<sup>4</sup> polymers,<sup>5</sup> dendrimers,<sup>6</sup> solid supports (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, zeolites, etc.),<sup>7</sup> polyoxo-metallates<sup>8</sup>, and ionic liquids.<sup>9</sup> Surprisingly, there has been less attention to the stabilization of **PdNPs** by phosphine ligands, particularly since the latter are very effective in molecular catalysis involving Pd(0).<sup>10</sup> Although Hyeon and co-workers have reported the stabilization of nearly monodisperse **PdNPs** using various phosphine ligands these have not been tested for their effectiveness as catalysts.<sup>11</sup> On the other hand, recently, the research groups of Chaudret<sup>12</sup> and Fujihara<sup>13</sup> have reported the asymmetric catalytic applications of chiral phosphorous ligand-stabilized **PdNPs**. More recently, Fan and co-workers have reported the preparation and use of **PdNPs** that were stabilized by a phosphine-containing dendron.<sup>14</sup> In a search for alternative stabilizers for **NPs** we were intrigued by the possibility of using inorganic rings and were encouraged by some preliminary reports in the literature.<sup>15</sup>

Our experience in organostannoxane chemistry suggested to us that we can utilize inorganic-cored star-type ligands for effective

encapsulation of **PdNPs** and recently we had successfully demonstrated this strategy.<sup>16</sup> Considering the importance of the Heck reaction in organic synthesis<sup>17</sup> we were interested in testing the effectiveness of **SnPPd**, the Pd(0) nanoparticles stabilized by **SnP**. These aspects are discussed herein.

As reported recently the reaction of  $[n\text{-BuSn}(\text{O})\text{OH}]_n$  with 4-PPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-COOH afforded  $[n\text{-BuSn}(\text{O})\text{OC}(\text{O})\text{-C}_6\text{H}_4\text{-}p\text{-PPh}_2]_6$  (**SnP**) (Supplementary data). The phosphine unit in **SnP** undergoes a slow oxidation in solution (chlorinated solvents) to the phosphine oxide as confirmed by the presence of two signals at -4.6 (-PPh<sub>2</sub>) and 29.5 (-P(O)Ph<sub>2</sub>) ppm. However, the shelf life of **SnP**, in the solid-state, in air, is quite high. A fresh solution of an aged sample does not reveal oxidation. Also, oxidation does not seem to occur rapidly in solvents such as toluene. **PdNPs** prepared using **SnPPd** possess an average size of 3 nm as revealed by HRTEM experiments.<sup>16</sup> The palladium content was estimated to be 19.9 wt %.<sup>18</sup> The unique advantage of the **SnP** ligand is that it not only is a spherical bulky ligand but also possesses additional phosphine appendages; these two factors are responsible to stabilize **PdNPs**.

**PdNPs** stabilized by **SnP**, **SnPPd**, were used in the Heck reaction. The reaction of iodobenzene with styrene was optimized (100 °C, K<sub>2</sub>CO<sub>3</sub>, 4 h, 1,4-dioxane, Tables S1 and S2, Supplementary data). A variety of substrates could be used in the Heck coupling reaction with good yields and high TON and TOF were observed (Table 1 and Figure S1). Substrates such as vinyl pyridines (entries 2 and 3, Table 1) could be readily used. A variety of acrylates could

\* Corresponding author. Tel.: +91 512 259 7259; fax: +91 512 259 0007/7436.  
E-mail address: [vc@iitk.ac.in](mailto:vc@iitk.ac.in) (V. Chandrasekhar).

**Table 1**  
Heck-coupling reaction of different alkenes with iodobenzene under optimized conditions

Entry	R-CH=CH <sub>2</sub>	R-CH=CH-Ph	Time (h)	Yield (%)	TON 10 <sup>4</sup> mol <sup>-1</sup>	TOF 10 <sup>4</sup> mol <sup>-1</sup> h <sup>-1</sup>
1			4	99	10.06	2.65
2			7	74	7.91	1.13
3			7	89	9.52	1.36
4			6	99	10.6	1.76
5			5	99	10.6	2.12
6			4	99	10.6	2.65
7			7	88	9.41	1.34
8 <sup>a</sup>			8	55 (69)	0.74	0.74
9 <sup>b</sup>			6	30 (70)	0.54	0.54

Reactions and Conditions: (a) PhI (1 equiv), alkene (1.25 equiv), K<sub>2</sub>CO<sub>3</sub> (2 equiv), PdNPs (9.6 × 10<sup>-4</sup> mol %) and solvent (5 mL) at 100 °C. (b) Yields reported are the isolated yields and progress of the reaction was monitored by TLC. (c) The values in brackets of the column of yields of entries 8 and 9 are the overall yield of the reaction

<sup>a</sup> E:Z is 79:21

<sup>b</sup> E:Z is 42:58

also be used successfully. Although in most cases only *E* isomers are formed (entries 1–8, Table 1) in the case of ethylvinylether the *E/Z* ratio is nearly 1 presumably because of the unhindered nature of the substrate.

The Heck-coupling reaction involving arylbromides was more effective in DMF (Tables S3–S4, Supplementary data). A large variety of arylbromides, including those that are sterically hindered as well as those containing electron-releasing substituents could be used (Table 2 entries 2–4, 9). Difficult substrates such as 1-bromonaphthalene could also be used. Similarly the versatility of SnPPd can be gauged by the fact that substrates such as 2-bromopyridine, 2,6-dibromopyridine, as well as bromo-substituted benzaldehydes could be used.

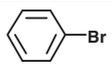
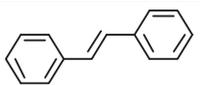
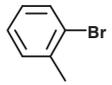
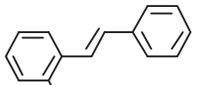
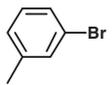
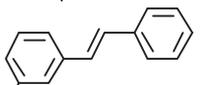
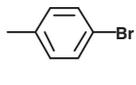
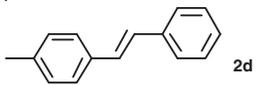
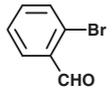
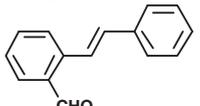
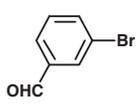
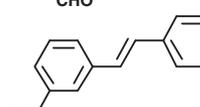
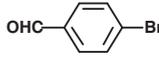
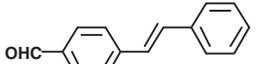
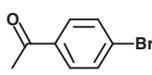
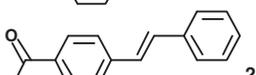
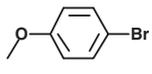
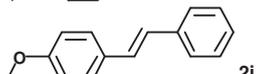
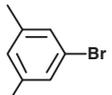
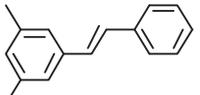
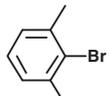
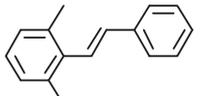
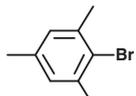
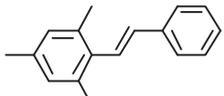
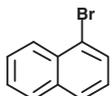
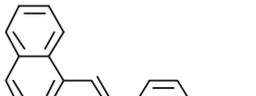
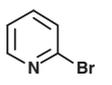
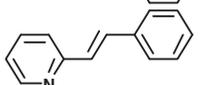
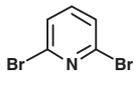
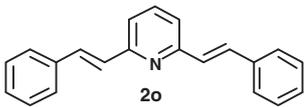
Aryl chlorides were also tested as substrates with mixed results. Firstly, the reactions required longer times and higher temperatures (Table 3). Secondly, using 4-chloro-1-nitrobenzene as the substrate resulted in only 35% of the Heck-coupled product (entry 9, Table 3). The major product was the Buchwald product involving dimethylamination of the substrate, 4-dimethylamino-1-nitrobenzene.<sup>19</sup> However, in spite of this, a number arylchlorides do undergo Heck reaction under these conditions (entries 1–11, Table 3). For example, coupling of 2-chlorobenzaldehyde reacts with styrene to give the Heck-coupled product in about 90% yield (entry 5, Table 3).

SnPPds were tested in recycling experiments involving the coupling of 4-bromotoluene and styrene as a representative example (entry 4, Table 2) by adopting the in situ recycling methodology (Table S5, Supplementary data).<sup>13</sup> It was found that the reaction could be recycled up to 8 cycles, beyond which the recyclability was not tested. The fate of the catalyst was examined after the catalysis. The catalyst particles showed virtually no change in the dimension of the nanoparticles except for a slight increase from 3.0 to 3.6 nm even after 8 consecutive cycles (Fig. 1).

During this whole process formation of the palladium black was not observed indicating the efficacy of the sterically bulky dendrimer-like organostannoxane, SnP in stabilizing PdNPs.

The nature of SnPPd was further examined to rule out any molecular species. The <sup>31</sup>P NMR of SnPPd was flat (Supplementary data) consistent with the absence of molecular complexes. A negative mercury<sup>20</sup> and -thiophene poisoning effect<sup>21</sup> was observed indicating that the nanoparticles are encapsulated effectively by the organostannoxane ligand. Finally, the solutions of the nanoparticles in many solvents including dimethylformamide and dioxane were always clear and no indication of any palladium black formation was observed. Prevention of formation of the latter is one of the challenges in this area.

**Table 2**  
Heck-coupling reaction of different aryl bromides with styrene under optimized conditions

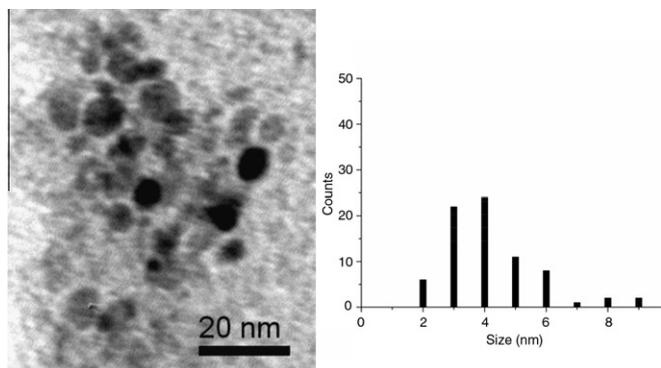
Entry	ArX	Ar-  -Ph	Time (h)	Yield (%)	TON 10 <sup>4</sup> mol <sup>-1</sup>	TOF 10 <sup>3</sup> mol <sup>-1</sup> h <sup>-1</sup>
1		 2a	4	99	10.6	2.65
2		 2b	8	84	8.98	1.12
3		 2c	8	89	9.52	1.19
4		 2d	6	99	10.6	1.76
5		 2e	5	90	10.6	1.93
6		 2f	4	99	10.6	2.65
7		 2g	4	99	9.63	2.65
8		 2h	5	99	10.6	2.12
9		 2i	8	90	9.63	1.2
10		 2j	9	99	10.6	1.18
11		 2k	12	90	9.63	0.80
12		 2l	14	87	9.3	0.66
13		 2m	7	95	10.2	1.45
14		 2n	9	85	9.09	1.01
15		 2o	14	70	7.49	0.53

Reactions and Conditions: (a) ArX (1 equiv), Styrene (1.25 equiv), K<sub>2</sub>CO<sub>3</sub> (2 equiv), PdNPs (9.6 × 10<sup>-4</sup> mol %) and solvent (5 mL) at 100 °C. (b) Yields reported are the isolated yields and progress of the reaction was monitored by TLC.

**Table 3**  
Heck-coupling reaction of different aryl chlorides with styrene under optimized conditions

Entry	ArX	Ar-Ph	Time (h)	Yield (%)	TON $10^4 \text{ mol}^{-1}$	TOF $10^3 \text{ mol}^{-1} \text{ h}^{-1}$
1			15	87	9.3	6.203
2			24	33	3.53	1.47
3			20	52	5.58	2.78
4			24	70	7.49	3.12
5			12	90	9.63	8.02
6			22	45	4.81	2.18
7			15	76	8.13	5.41
8			32	15	1.6	0.5
9			10	35	3.74	3.74
10			48	75	8.02	1.67
11			36	30	3.21	8.91

Reaction and Conditions: (a) ArX (1 equiv), Styrene (1.25 equiv),  $\text{K}_2\text{CO}_3$  (2 equiv), PdNPs ( $9.6 \times 10^{-4} \text{ mol} \%$ ) and solvent (5 mL) at  $100^\circ\text{C}$ . (b) Yields reported are the isolated yields and progress of the reaction was monitored by TLC.



**Figure 1.** TEM of PdNPs after the 8 cycles of the Heck-coupling reaction along with the particle size distribution.

### Acknowledgments

We are thankful to the Department of Science and Technology (DST), New Delhi, for the financial support. R.S.N. thanks the Council of Scientific and Industrial Research, India for Senior Research Fellowship. V.C. is thankful to the DST for a J.C. Bose National fellowship. We thank the electron microscopy facility

of the Department of Metallurgical Engineering and Materials Science, IIT Kanpur, for TEM measurements.

### Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.05.006.

### References and notes

- (a) Srimani, D.; Sawoo, S.; Sarkar, A. *Org. Lett.* **2007**, *9*, 3639; (b) Ranu, B. C.; Chattopadhyay, K.; Adak, L. *Org. Lett.* **2007**, *9*, 4595; (c) Adak, L.; Chattopadhyay, K.; Ranu, B. C. *J. Org. Chem.* **2009**, *74*, 3982; (d) Srimani, D.; Bej, A.; Sarkar, A. *J. Org. Chem.* **2010**, *75*, 4296.
- (a) Beletskaya, I. P.; Kashin, A. N.; Litvinov, A. E.; Tyurin, V. S.; Valetsky, P. M.; van Koten, G. *Organometallics* **2006**, *25*, 154; Astruc, D. *Organometallic Chemistry and Catalysis*; Springer-Verlag: Berlin, 2007; Astruc, D. *Nanoparticles and Catalysis*; WILEY, GmbH & Co: Weinheim, 2008.
- (a) Yoon, B.; Wai, C. M. *J. Am. Chem. Soc.* **2005**, *127*, 17174; (b) Baruch, A. R.-B.; Tvelikhovsky, D.; Schwarze, M.; Schomäcker, R.; Fanun, M.; Blum, J. *J. Mol. Catal. A: Chem.* **2010**, *323*, 65; (c) Zhang, G.; Zhou, H.; Hu, J.; Liu, M.; Kuang, Y. *Green Chem.* **2009**, *11*, 1428.
- (a) Luo, C.; Zhang, Y.; Wang, Y. *J. Mol. Catal. A: Chem.* **2005**, *229*, 7; (b) Meier, M. A. R.; Filali, M.; Gohy, J.-F.; Schubert, U. S. *J. Mater. Chem.* **2006**, *16*, 3001; (c) Ranu, B. C.; Dey, R.; Chattopadhyay, K. *Tetrahedron Lett.* **2008**, *49*, 3430.
- (a) Okamoto, K.; Akiyama, R.; Yoshida, H.; Yoshida, T.; Kobayashi, S. *J. Am. Chem. Soc.* **2005**, *127*, 2125; (b) Ornelas, C.; Diallo, A. K.; Ruiz, J.; Astruc, D. *Synth. Catal.* **2009**, *351*, 2147; (c) Evangelisti, C.; Panziera, N.; D'Alessio, A.; Bertinetti,

- L.; Botavina, M.; Vitulli, G. *J. Catal.* **2010**, *272*, 246; (d) Bandari, R.; Höche, T.; Prager, A.; Dirnberger, K.; Buchmeiser, M. R. *Chem. Eur. J.* **2010**, *16*, 4650.
6. (a) Crooks, R. M.; Zhao, M.; Sun, L.; Chechic, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181; (b) Rahim, E. H.; Kamounah, F. S.; Frederiksen, J.; Christensen, J. B. *Nano Lett.* **2001**, *1*, 499; (c) Diallo, A. K.; Ornelas, C.; Salmon, L.; Aranzaes, J. R.; Astruc, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8644; (d) Ornelas, C.; Aranzaes, J. R.; Salmon, L.; Astruc, D. *Chem. Eur. J.* **2008**, *14*, 50.
7. (a) Richardson, J. M.; Jones, C. W. *J. Catal.* **2007**, *251*, 80; (b) Budroni, G.; Corma, A.; Garcia, H.; Primo, A. *J. Catal.* **2007**, *251*, 345; (c) Demel, J.; Čejka, J.; Štěpnička, P. *J. Mol. Catal. A: Chem.* **2007**, *274*, 127; (d) Köhler, K.; Heidenreich, R. G.; Soomro, S. S.; Pröckl, S. S. *Adv. Synth. Catal.* **2008**, *350*, 2930.
8. (a) Kogan, V.; Aizenshtat, Z.; Popovitz-Biro, R.; Neumann, R. *Org. Lett.* **2002**, *4*, 3529; (b) De Bruyn, M.; Neumann, R. *Adv. Synth. Catal.* **2007**, *349*, 1624.
9. (a) Dupont, J.; de Souza, R. F. Z. *Suarez, P. A. Chem. Rev.* **2002**, *102*, 3667; (b) Migowski, P.; Dupont, J. *Chem. Eur. J.* **2007**, *13*, 32; (c) Dupont, J.; Scholten, J. D. *Chem. Soc. Rev.* **2010**, *39*, 1780.
10. (a) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989; (b) Zapf, A.; Beller, M. *Chem. Eur. J.* **2001**, *7*, 2908; (c) Fu, G. C. *Acc. Chem. Res.* **2008**, *41*, 1555.
11. Son, S. U.; Jang, Y.; Yoon, K. Y.; Kang, E.; Hyeon, T. *Nano Lett.* **2004**, *4*, 1147.
12. (a) Jansat, S.; Gómez, M.; Philippot, K.; Muller, G.; Guiu, E.; Claver, C.; Castillón, S.; Chaudret, B. *J. Am. Chem. Soc.* **2004**, *126*, 1592; (b) Favier, I.; Gómez, M.; Muller, G.; Axet, R.; Castillón, S.; Claver, C.; Jansat, S.; Chaudret, B. *Adv. Synth. Catal.* **2007**, *349*, 2459.
13. (a) Tamura, M.; Fujihara, H. *J. Am. Chem. Soc.* **2003**, *125*, 15742; (b) Sawai, K.; Tatumi, R.; Nakahodo, T.; Fujihara, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 6917.
14. (a) Wu, L.; Li, B.-L.; Huang, Y.-Y.; Zhou, H.-F.; He, Y.-M.; Fan, Q.-H. *Org. Lett.* **2006**, *8*, 3605; (b) Wu, L.; Li, Z.-W.; Zhang, F.; He, Y.-M.; Fan, Q.-H. *Adv. Synth. Catal.* **2008**, *350*, 846.
15. (a) Badetti, E.; Caminade, A.-M.; Majoral, J.-P.; Moreno-Mañas, M.; Sebastián, R. M. *Langmuir* **2008**, *24*, 2090; (b) Naka, K.; Itoh, H.; Chujo, Y. *Nano Lett.* **2002**, *2*, 1183; (c) Li, X.; Du, Y.; Dai, J.; Wang, X.; Yang, P. *Catal. Lett.* **2007**, *118*, 151.
16. Chandrasekhar, V.; Narayanan, R. S.; Thilagar, P. *Organometallics* **2009**, *28*, 5883.
17. (a) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009; de Meijere, A.; Diederich, F. *Metal-Catalyzed Cross-Coupling Reactions*; WILEY GmbH & Co. KGaA: Weinheim, Germany, 2004.
18. Pd content was determined spectrophotometrically using newfuchsine dye at  $\lambda = 374$  nm; (b) West, P. W.; Amis, E. S. *Ind. Engg. Chem.* **1946**, *18*, 400.
19. Agarwal, A.; Chauhan, P. M. S. *Synth. Commun.* **2004**, *34*, 2925.
20. Phan, N. T. S.; Van der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609.
21. Eberhard, M. R. *Org. Lett.* **2004**, *6*, 2125.