

A Practical Heterogeneous Catalyst for the Suzuki, Sonogashira, and Stille Coupling Reactions of Unreactive Aryl Chlorides**

Myung-Jong Jin* and Dong-Hwan Lee

Transition-metal-catalyzed coupling reactions have contributed greatly to the straightforward and facile construction of carbon–carbon bonds.^[1] Significant progress in this area has been achieved with a variety of homogeneous palladium catalysts.^[2,3] However, homogeneous catalysis suffers from the problematic separation of the expensive catalyst from the product for re-use.^[4] Moreover, the homogeneous palladium catalysts tend to lose their catalytic activity because of palladium metal aggregation and precipitation.^[5] These problems are of particular environmental and economic concern in large-scale syntheses. Heterogenization of the existing homogeneous palladium catalysts could be an attractive solution to this problem.^[6] There has been considerable interest in the development of heterogeneous catalytic systems that can be efficiently re-used whilst keeping the inherent activity of the catalytic center.

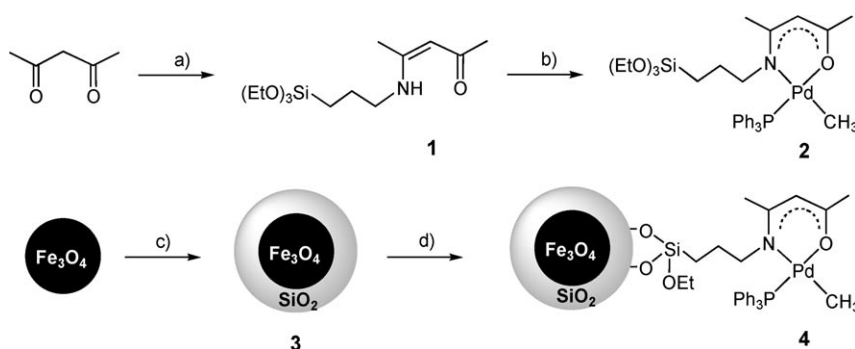
Aryl iodides and bromides have been widely employed as substrates in heterogeneous coupling reactions.^[7–9] From a practical point of view, the use of aryl chlorides is highly desirable because they are readily available and inexpensive. However, they are much more difficult to activate than aryl iodides and bromides.^[2a] The activation of aryl halides is particularly challenging for heterogeneous catalysts, and although there have been many reports of heterogeneous reactions in the literature, successful examples using deactivated aryl chlorides are quite rare.^[10] Therefore, the development of high-performance catalysts for practical catalytic coupling reactions is of ongoing interest.

Magnetite Fe₃O₄ nanoparticles have recently emerged as promising supports for immobilization because Fe₃O₄-supported catalysts can be separated from the reaction medium by an external permanent magnet.^[11] This circumvents time-consuming and laborious separation steps, and allows for practical continuous catalysis. In particular, Fe₃O₄ nanoparticles coated with a thin layer of silica have

beneficial properties, such as invariant catalytic activity and stability.^[12]

We have previously reported the use of a (β-oxoiminato)(phosphanyl)palladium complex as an efficient catalyst in coupling reactions.^[3f] In this context, we have prepared triethoxysilyl-functionalized palladium complex **2**, which can be anchored easily onto the surface of the silica. Commercially available Fe₃O₄ nanoparticles, with an average diameter of 20 nm, were coated with a thin layer of silica using a sol-gel process to give silica-coated Fe₃O₄ (**3**; SiO₂@Fe₃O₄).^[13] The silica shell has plenty of hydroxyl groups for potential derivatization with different functional groups, and also protects the magnetite core from abrasion under harsh shaking conditions.

The silylated palladium complex **2** was successfully immobilized on the surface of robust SiO₂@Fe₃O₄ (**3**) (Scheme 1). Schiff-base condensation of 2,4-pentanedione with (3-aminopropyl)triethoxysilane under microwave heating afforded **1** in only 3 min in quantitative yield. Deprotonation of **1** with EtOTf in tetrahydrofuran, followed by treatment with [Pd(μ-Cl)₂Me₂(PPh₃)₂],^[14] led to the formation of **2**. Magnetic-nanoparticle-supported (β-oxoiminato)-(phosphanyl)palladium complex **4** was obtained by reaction



Scheme 1. Synthesis of magnetic nanoparticle-supported (β-oxoiminato)(phosphanyl) palladium complex **4**. a) NH₂(CH₂)₃Si(OEt)₃, microwave heating; b) EtOTf, [Pd(μ-Cl)₂Me₂(PPh₃)₂], tetrahydrofuran, RT; c) tetraethyl orthosilicate; d) **2**, toluene, 100 °C, 12 h.

of **2** with **3** in refluxing toluene (see the Supporting Information). Palladium catalyst Pd–SiO₂@Fe₃O₄ (**4**), with a loading of 0.21 mmol of palladium per gram, was prepared for this study, and the palladium content was confirmed by inductively coupled plasma atomic emission spectrometry (ICP-AES). TEM images of **4** show the core-shell structure of the particles, and the silica coating, which has a uniform thickness of 7 nm (Figure 1). Herein, we report the use of a highly active and magnetically recyclable catalyst **4** in the

[*] Prof. M.-J. Jin, Dr. D.-H. Lee
Department of Chemical Science and Engineering, Inha University
Incheon 402-751 (South Korea)
Fax: (+82) 32-872-0959
E-mail: mjjin@inha.ac.kr

[**] This work was supported by National Research Foundation of Korea Grant funded by the Korean Government (2009-0072013).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.200905626>.

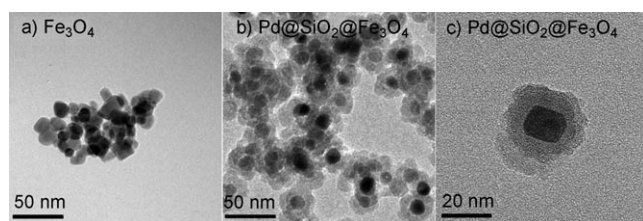


Figure 1. TEM images of a) aggregated Fe_3O_4 ; b) aggregated $\text{Pd@SiO}_2\text{@Fe}_3\text{O}_4$ (**4**); c) individual $\text{Pd-SiO}_2\text{@Fe}_3\text{O}_4$ (**4**).

Suzuki, Sonogashira, and Stille reactions of unreactive aryl chlorides in aqueous conditions.

First, the Suzuki coupling of various substituted aryl chlorides with arylboronic acids was investigated in the presence of catalyst **4** (Table 1). Suzuki couplings are typically conducted in organic solvents or in aqueous–organic mixed-solvent systems. Recently, the use of water as an environmentally benign solvent has received considerable attention from the viewpoint of green chemistry.^[15]

Table 1: Suzuki coupling of aryl chlorides with arylboronic acids.^[a]

$\text{R}^1\text{-C}_6\text{H}_4\text{-Cl} + (\text{HO})_2\text{B-C}_6\text{H}_4\text{-R}^2 \xrightarrow[\text{K}_2\text{CO}_3, \text{TBAB, H}_2\text{O}]{\text{4 (0.5 mol\%), 60 }^\circ\text{C}} \text{R}^1\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-R}^2$		
5a , 88 % (10 h) ^[b,c] 93 % (4 h)	5b , 95 % (3 h)	5c , 92 % (3 h)
5d , 91 % (3 h)	5e , 83 % (10 h) ^[b,c] 94 % (5 h)	5f , 93 % (5 h)
5g , 87 % (5 h)	5h , 89 % (6 h)	5i , 87 % (6 h)
5j , 82 % (6 h)	5k , 90 % (6 h)	5l , 93 % (5 h)
5m , 92 % (5 h)	5n , 91 % (5 h)	5o , 84 % (5 h)
5p , 86 % (8 h)	5q , 77 % (15 h) ^[c]	5r , 71 % (15 h) ^[c]

[a] Aryl chloride (1.0 mmol), arylboronic acid (1.2 mmol), **4** (0.5 mol %), K_2CO_3 (2.0 mmol), TBAB (0.5 mmol), H_2O (2 mL), 60 °C; yield of isolated product. [b] **4** (1.0 mol %), without TBAB. [c] 80 °C.

The heterogeneous reaction was initially carried out in neat water at 80 °C, and resulted in satisfactory yields (**5a** and **5e**). A phase transfer agent, tetrabutylammonium bromide (TBAB), was added to enhance the reactivity of the reaction in water. As a consequence, we were able to lower the catalytic loading to 0.5 mol %, and the reaction temperature

to 60 °C. Outstanding catalytic activities were observed for the coupling reactions of chlorobenzene and activated aryl chlorides with phenylboronic acid, such as 1-chloro-4-nitrobenzene, 4-chlorobenzonitrile, and 1-chloro-2-nitrobenzene (**5a–d**). High levels of reactivity were also observed for the coupling of deactivated aryl chlorides with phenylboronic acid, including 4-chloroanisole, 4-chlorotoluene, 4-chlorophenol, 2-chloroanisole, and 2-chlorotoluene (**5e–i**). Coupling reactions in which one coupling partner contains a nitrogen donor are typically difficult to accomplish.^[16] It is therefore noteworthy that catalyst **4** successfully promoted the coupling reactions of 2- and 3-chloroaniline (**5j** and **5k**, respectively), both of which bear a free amino group. 1-Chloronaphthalene (**5l**) and 9-chloroanthracene (**5m**) were also efficiently coupled with phenylboronic acid in excellent yields; similar catalytic activities were observed in the coupling of deactivated aryl chlorides with substituted phenylboronic acids (**5n–p**). Sterically hindered substrate 2-chloro-1,3-dimethylbenzene also successfully coupled in good yield (**5q** and **5r**), although a higher temperature and longer reaction time were required. All of the coupling reactions, regardless of the substituent, proceeded cleanly and highly efficiently in water under mild heating. To the best of our knowledge, catalyst **4** shows the highest catalytic activity reported to date for the heterogeneous Suzuki coupling of deactivated aryl chlorides.

Next, we considered the Sonogashira coupling reaction of various aryl chlorides with alkynes in the presence of catalyst **4** (Table 2). Typically, reactions with aryl chlorides require high catalyst loadings, elevated reaction temperatures, prolonged reaction times, and either CuI as a co-catalyst or large

Table 2: Sonogashira coupling of aryl chlorides with alkynes.^[a]

$\text{R}^1\text{-C}_6\text{H}_4\text{-Cl} + \text{C}\equiv\text{C-R}^2 \xrightarrow[\text{piperidine, TBAB, H}_2\text{O}]{\text{4 (0.5 mol\%), 60 }^\circ\text{C}} \text{R}^1\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-R}^2$		
6a , 94 % (5 h)	6b , 91 % (6 h)	6c , 96 % (4 h)
6d , 95 % (4 h)	6e , 93 % (4 h)	6f , 93 % (6 h)
6g , 91 % (6 h)	6h , 86 % (6 h)	6i , 81 % (6 h)
6j , 83 % (6 h)	6k , 88 % (6 h)	6l , 94 % (6 h)
6m , 82 % (6 h)	6n , 81 % (15 h) ^[b]	6o , 74 % (15 h) ^[b]
6p , 92 % (5 h)	6q , 87 % (8 h)	6r , 90 % (8 h)

[a] Aryl chloride (1.0 mmol), alkyne (1.2 mmol), **4** (0.5 mol %), piperidine (2.0 mmol), TBAB (0.5 mmol), H_2O (2 mL), 60 °C; yield of isolated product. [b] 80 °C.

amounts of amine as a co-solvent.^[6b,17] Gratifyingly, we were able to perform efficient copper-free Sonogashira coupling reactions of aryl chlorides in the presence of only 0.5 mol % of **4** at 60 °C. It was observed that the couplings of chlorobenzene, 1-chloronaphthalene, and activated aryl chlorides with phenylacetylene, all proceeded in excellent yields (**6a–e**). This catalytic system was also effective for the couplings of deactivated aryl chlorides (**6f–j**), with the reactions proceeding to completion in 6 h under mild conditions. Furthermore, aryl chlorides were coupled with electron-rich 2- or 4-ethynyltoluene with great success (**6k–m**). As expected, the sterically hindered and deactivated 2-chloro-1,3-dimethylbenzene also smoothly underwent the coupling reaction (**6n** and **6o**). The scope of the alkyne was successfully extended to include substrates such as propargyl alcohol, 1-octyne and (triisopropylsilyl)acetylene (**6p–r**). It is noteworthy that this is the first successful example of a heterogeneous Sonogashira reaction of aryl chlorides in aqueous solvent.

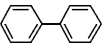
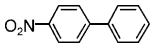
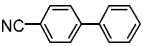
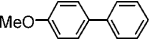
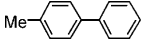
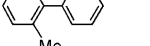
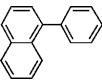
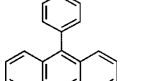
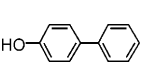
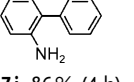
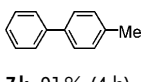
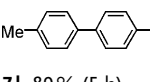
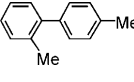
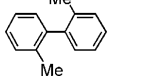
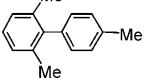
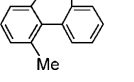
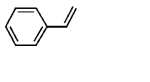
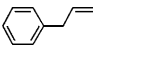
Encouraged by these results, we performed the Stille coupling of a variety of aryl chlorides with organostannanes in the presence of 0.5 mol % of **4** at 50 °C (Table 3). The Stille coupling of aryl chlorides in water under mild heating has not been reported to date. The coupling reactions of chlorobenzene, activated 1-chloro-4-nitrobenzene, and 4-chlorobenzonitrile, with tributylphenylstannane took place in 3 h, with complete conversion and in high yields (**7a–c**). In the coupling of 1-chloro-4-nitrobenzene, the catalyst was found to maintain high activity, even at 25 °C (**7b**). Deactivated aryl

chlorides bearing electron-donating substituents were found to furnish the biaryl products in high yields (**7d–f**). 1-Chloronaphthalene and 9-chloroanthracene both coupled well with tributylphenylstannane (**7g** and **7h**). Importantly, the catalyst was found to be active for the coupling reactions of unprotected 4-chlorophenol and 2-chloroaniline (**7i** and **7j**). Furthermore, the catalyst system worked efficiently for the coupling reactions of aryl chlorides with electron-rich arylstannanes (**7k–n**). Satisfyingly, sterically hindered 2-chloro-1,3-dimethylbenzene was successfully coupled, albeit over more-prolonged reaction times (**7o** and **7p**). One of the most useful applications of the Stille reaction is the ability to couple vinyl- and allylstannanes.^[2a] We obtained similar success in the reaction of chlorobenzene with tributylvinylstannane or allyltributylstannane at 50 °C (**7q** and **7r**). To our knowledge, this is also the first reported heterogeneous Stille coupling of aryl chlorides.

A structural feature of catalyst **4** is the monodentate electron-rich phosphine and bulky imine ligands on the palladium atom. Mechanistically, oxidative activation of the substrate to the catalytically active palladium(0) species is a key step for less reactive aryl chlorides. The superior activity observed for this catalyst suggests that these two independent ligands cooperatively facilitate the oxidative addition, as well as the reductive elimination step.

A long catalyst lifetime and the ability to easily recycle the catalyst are highly desirable for industrial applications. The separation of heterogeneous catalysts, commonly performed by filtration, results in reduced catalyst retention. An attractive advantage of catalyst **4** is its easy separation using external magnets, which minimizes the loss of catalyst during separation (Figure 2a). The recycle efficiency of **4** was investigated in the coupling reactions of 4-chloroanisole with phenylboronic acid and phenylacetylene, respectively (see the Supporting Information). After each run, the catalyst was recovered by simple decantation, and then re-used in the following run. The catalytic activity of **4** remained unchanged over ten reaction cycles. After the reaction, the solution was analyzed for palladium metal using ICP-AES. The results indicated that less than 0.06% of the starting palladium catalyst had leached out from the catalyst surface. Furthermore, the filtered solution did not exhibit any further reactivity. No obvious agglomeration of palladium(0) to form visible nanoparticles was observed on the support surface after the tenth reaction (Figure 2b). The facile recycling of **4** in these coupling reactions is probably due to

Table 3: Stille coupling of aryl chlorides with organostannanes.^[a]

$\text{R}^1\text{-C}_6\text{H}_4\text{-Cl} + (\text{Bu})_3\text{Sn-R}^2 \xrightarrow[\text{CsF, EtOH-H}_2\text{O}]{\text{4 (0.5 mol\%), 50 }^\circ\text{C}}$		
$\text{R}^1\text{-C}_6\text{H}_4\text{-R}^2$		
 7a , 95 % (3 h)	 7b , 92 % (5 h) ^[b] 96 % (2 h)	 7c , 94 % (2 h)
 7d , 92 % (3 h)	 7e , 94 % (3 h)	 7f , 92 % (4 h)
 7g , 91 % (4 h)	 7h , 92 % (4 h)	 7i , 89 % (3 h)
 7j , 86 % (4 h)	 7k , 91 % (4 h)	 7l , 89 % (5 h)
 7m , 92 % (5 h)	 7n , 86 % (6 h)	 7o , 81 % (12 h) ^[c]
 7p , 72 % (12 h) ^[c]	 7q , 87 % (5 h)	 7r , 90 % (5 h)

[a] Aryl chloride (1.0 mmol), organostannane (1.2 mmol), **4** (0.5 mol %), CsF (2.0 mmol), EtOH/H₂O (2 mL, 1:1), 50 °C; yield of isolated product. [b] 25 °C. [c] 70 °C.

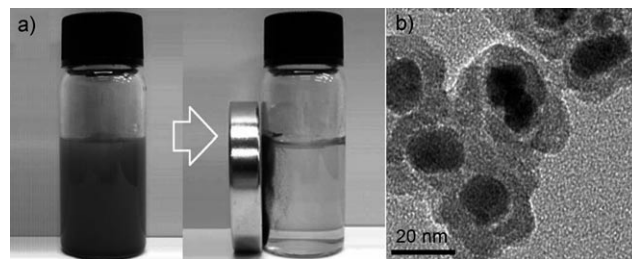


Figure 2. a) Photographs showing the magnetic separation of catalyst **4**; b) TEM image of catalyst **4** after the 10th reaction cycle.

the high durability of the silica-coated Fe_3O_4 support, along with the robust nature of the free palladium complex. As well as the high activity and broad substrate scope of **4**, the successful recycling of this catalyst allows for a more economic and environmentally friendly process.

In conclusion, we have developed a highly active, easily recoverable, and practical heterogeneous catalyst for the Suzuki, Sonogashira and Stille coupling reactions. A wide range of unreactive aryl chlorides were coupled successfully under mild conditions. In particular, the performance of the catalyst was fully retained during the re-use process. These represent the first widely applicable coupling reactions of aryl chlorides using a heterogeneous catalyst.

Received: October 7, 2009

Revised: November 6, 2009

Published online: December 30, 2009

Keywords: aryl chlorides · cross-coupling · magnetic properties · palladium · supported catalysts

- [1] a) *Metal-Catalyzed Cross-Coupling Reactions, Vol. 2* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**; b) M. Beller, C. Bolm, *Transition Metals for Organic Synthesis*, 2nd ed., Wiley-VCH, Weinheim, **2004**.
- [2] For reviews, see: a) A. F. Littke, G. C. Fu, *Angew. Chem.* **2002**, *114*, 4350; *Angew. Chem. Int. Ed.* **2002**, *41*, 4176; b) U. Christmann, R. Vilar, *Angew. Chem.* **2005**, *117*, 370; *Angew. Chem. Int. Ed.* **2005**, *44*, 366; c) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem.* **2005**, *117*, 4516; *Angew. Chem. Int. Ed.* **2005**, *44*, 4442; d) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem.* **2007**, *119*, 2824; *Angew. Chem. Int. Ed.* **2007**, *46*, 2768; e) R. Martin, S. L. Buchwald, *Acc. Chem. Res.* **2008**, *41*, 1461; f) G. C. Fu, *Acc. Chem. Res.* **2008**, *41*, 1555.
- [3] a) K. W. Anderson, S. L. Buchwald, *Angew. Chem.* **2005**, *117*, 6329; *Angew. Chem. Int. Ed.* **2005**, *44*, 6173; b) B. Saito, G. C. Fu, *J. Am. Chem. Soc.* **2007**, *129*, 9602; c) O. Diebolt, P. Braunstein, S. P. Nolan, C. S. J. Cazin, *Chem. Commun.* **2008**, 3190; d) J. R. Naber, S. L. Buchwald, *Adv. Synth. Catal.* **2008**, *350*, 957; e) K. L. Billingsley, S. L. Buchwald, *Angew. Chem.* **2008**, *120*, 4773; *Angew. Chem. Int. Ed.* **2008**, *47*, 4695; f) D.-H. Lee, J.-Y. Jung, I. M. Lee, M.-J. Jin, *Eur. J. Org. Chem.* **2008**, 356.
- [4] a) C. E. Garrett, K. Prasad, *Adv. Synth. Catal.* **2004**, *346*, 889; b) C. J. Welch, J. Albaneze-Walker, W. R. Leonard, M. Biba, J. DaSilva, D. Henderson, B. Laing, D. J. Mathre, S. Spencer, X. Bu, T. Wang, *Org. Process Res. Dev.* **2005**, *9*, 198.
- [5] a) M. T. Reetz, J. G. de Vries, *Chem. Commun.* **2004**, 1559; b) J. G. de Vries, *Dalton Trans.* **2006**, 421; c) D. Astruc, *Inorg. Chem.* **2007**, *46*, 1884.
- [6] For reviews, see: a) N. T. S. Phan, M. V. D. Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609; b) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133.
- [7] For Suzuki coupling reactions, see: a) A. Garcia-Bernabé, C. C. Tzschucke, W. Bannwarth, R. Haag, *Adv. Synth. Catal.* **2005**, *347*, 1389; b) S. Schweizer, J.-M. Becht, C. L. Drian, *Adv. Synth. Catal.* **2007**, *349*, 1150; c) J. D. Webb, S. MacQuarrie, K. McEleney, C. M. Crudden, *J. Catal.* **2007**, *252*, 97; d) K. Köhler, R. G. Heidenreich, S. S. Soomro, S. S. Pröckl, *Adv. Synth. Catal.* **2008**, *350*, 2930; e) H. Qiu, S. M. Sarkar, D.-H. Lee, M.-J. Jin, *Green Chem.* **2008**, *10*, 37; f) K. Sawai, R. Tatum, T. Nakahodo, H. Fujihara, *Angew. Chem.* **2008**, *120*, 7023; *Angew. Chem. Int. Ed.* **2008**, *47*, 6917; g) G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, *J. Am. Chem. Soc.* **2009**, *131*, 8262; h) M.-J. Jin, A. Taher, H.-J. Kang, M. Choi, R. Ryoo, *Green Chem.* **2009**, *11*, 309.
- [8] For Sonogashira coupling reactions, see: a) L. Djakovitch, P. Rollet, *Adv. Synth. Catal.* **2004**, *346*, 1782; b) P.-H. Li, L. Wanga, *Adv. Synth. Catal.* **2006**, *348*, 681; c) W. J. Sommer, M. Weck, *Adv. Synth. Catal.* **2006**, *348*, 2101; d) R. Nishio, M. Sugiura, S. Kobayashi, *Chem. Asian J.* **2007**, *2*, 983; e) M. Trilla, R. Pleixalts, M. W. C. Man, C. Bied, J. J. E. Moreau, *Adv. Synth. Catal.* **2008**, *350*, 577.
- [9] For Stille coupling reactions, see: a) J. C. Garcia-Martinez, R. Lezutekong, R. M. Crooks, *J. Am. Chem. Soc.* **2005**, *127*, 5097; b) X. Yang, Z. Fei, D. Zhao, W. H. Ang, Y. Li, P. J. Dyson, *Inorg. Chem.* **2008**, *47*, 3292; c) H. Zhao, Y. Wang, J. Sha, S. Sheng, M. Cai, *Tetrahedron* **2008**, *64*, 7517; d) M. Bernechea, E. de Jesús, C. López-Mardomingo, P. Terreros, *Inorg. Chem.* **2009**, *48*, 4491.
- [10] a) M. Lysén, K. Köhler, *Synlett* **2005**, 1671; b) M. Lysén, K. Köhler, *Synthesis* **2006**, 692; c) R. Sayah, K. Glegola, E. Framery, V. Dufaud, *Adv. Synth. Catal.* **2007**, *349*, 373; d) S. Schweizer, J.-M. Becht, C. L. Drian, *Org. Lett.* **2007**, *9*, 3777; e) D.-H. Lee, J.-H. Kim, B.-H. Jun, H. Kang, J. Park, Y.-S. Lee, *Org. Lett.* **2008**, *10*, 1609; f) A. Komáromi, Z. Novák, *Chem. Commun.* **2008**, 4968.
- [11] a) A. Hu, G. T. Yee, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 12486; b) A.-H. Lu, E. L. Salabas, F. Schüth, *Angew. Chem.* **2007**, *119*, 1242; *Angew. Chem. Int. Ed.* **2007**, *46*, 1222; c) M. Kawamura, K. Sato, *Chem. Commun.* **2007**, 3404; d) G. Chouhan, D. Wang, H. Alper, *Chem. Commun.* **2007**, 4809; e) K. M. Yeo, S. I. Lee, Y. T. Lee, Y. K. Chung, I. S. Lee, *Chem. Lett.* **2008**, *37*, 116; f) B. Brandt, W. Ludwig, J.-H. Fischer, J. Libuda, F. Zaera, S. Schauerer, *J. Catal.* **2009**, 265, 191.
- [12] a) R. Abu-Reziq, H. Alper, D. Wang, M. L. Post, *J. Am. Chem. Soc.* **2006**, *128*, 5279; b) C. Ó Dálaigh, S. A. Corr, Y. Gun'ko, S. J. Connon, *Angew. Chem.* **2007**, *119*, 4407; *Angew. Chem. Int. Ed.* **2007**, *46*, 4329; c) L. M. Rossi, F. P. Silva, L. L. R. Vono, P. K. Kiyohara, E. L. Duarte, R. Itri, R. Landers, G. Machado, *Green Chem.* **2007**, *9*, 379; d) A. Gole, N. Agarwal, P. Nagaria, M. D. Wyatt, C. J. Murphy, *Chem. Commun.* **2008**, 6140; e) Y. Deng, D. Qi, C. Deng, X. Zhang, D. Zhao, *J. Am. Chem. Soc.* **2008**, *130*, 28; f) J. Ge, T. Huynh, Y. Hu, Y. Yin, *Nano Lett.* **2008**, *8*, 931; g) Y. Jiang, J. Jiang, Q. Gao, M. Ruan, H. Yu, L. Qi, *Nanotechnology* **2008**, *19*, 075714; h) A. Schätz, M. Hager, O. Reiser, *Adv. Funct. Mater.* **2009**, *19*, 2109; i) L. Kong, X. Lu, E. Jin, S. Jiang, X. Bian, W. Zhang, C. Wang, *J. Solid State Chem.* **2009**, *182*, 2081.
- [13] J. Lee, Y. Lee, J. K. Youn, H. B. Na, T. Yu, H. Kim, S.-M. Lee, Y.-M. Koo, J. H. Kwak, H. G. Park, H. N. Chang, M. Hwang, J.-G. Park, J. Kim, T. Hyeon, *Small* **2008**, *4*, 143.
- [14] F. T. Ladipo, G. K. Anderson, *Organometallics* **1994**, *13*, 303.
- [15] a) C.-J. Li, *Chem. Rev.* **2005**, *105*, 3095; b) A. Chanda, V. V. Fokin, *Chem. Rev.* **2009**, *109*, 725.
- [16] a) N. Kudo, M. Perseghini, G. C. Fu, *Angew. Chem.* **2006**, *118*, 1304; *Angew. Chem. Int. Ed.* **2006**, *45*, 1282; b) K. L. Billingsley, K. W. Anderson, S. L. Buchwald, *Angew. Chem.* **2006**, *118*, 3564; *Angew. Chem. Int. Ed.* **2006**, *45*, 3484.
- [17] R. Chinchilla, C. Najera, *Chem. Rev.* **2007**, *107*, 874.