ChemPubSoc Europe

DOI: 10.1002/cctc.201500417

CHEMCATCHEM
Full Papers

Electrostatic Grafting of a Palladium N-Heterocyclic Carbene Catalyst on a Periodic Mesoporous Organosilica and its Application in the Suzuki–Miyaura Reaction

Fatemeh Rajabi,*[a, b] Dirk Schaffner,[a] Sascha Follmann,[a] Christian Wilhelm,[a] Stefan Ernst,[a] and Werner R. Thiel*[a]

Dedicated to Prof. Dr. F. Preuss on the occasion of his 80th birthday

A periodic mesoporous organosilica material functionalized with a Pd N-heterocyclic carbene complex was synthesized by applying an electrostatic grafting method. The resulting hybrid material was characterized by solid-state ^{29}Si and ^{13}C cross-polarization magic-angle spinning NMR spectroscopy, XRD, thermogravimetric analysis, and BET measurements. The hybrid was applied as a catalyst for the Suzuki–Miyaura cross-coupling between aryl chlorides and phenylboronic acid under heterogeneous and aerobic conditions. The supported catalyst exhibited excellent activity and stability and it could be reused at least six times without any loss of activity. Atomic absorption spectroscopy detected no Pd contamination in the products, and leaching tests verified that the reaction was truly heterogeneous.

Introduction

Pd-catalyzed cross-coupling reactions are applied widely in organic synthesis.[1] Among Pd-catalyzed coupling reactions, the Suzuki–Miyaura coupling reaction is an extremely powerful tool for the generation of biaryl compounds, which are important structural units in polymers, liquid crystals, chiral ligands, natural products, and pharmaceuticals.[2] Significant efforts have been made to develop more efficient Pd catalysts for the Suzuki–Miyaura reaction.[3] In particular, Pd species that bear N-heterocyclic carbene (NHC) ligands have attracted a lot of interest in this context.[4] The strong σ-donor capability of the NHC ligand facilitates the oxidative addition step in the catalytic cycle. Advancements in this field over the last 25 years have been documented in numerous publications and reviews.[5]

Although a large number of homogeneous Pd-NHC complexes are found in the literature, their separation and recovery from the reaction mixture and their reuse are still challenges.[6] A possible strategy to solve such problems is the immobilization of homogeneous catalysts on well-designed organic or inorganic supports by covalent anchoring.[7] After the catalytic transformation is completed, such a catalyst can be separated by simple filtration, which minimizes the cost of the work-up and saves the noble metal and the often expensive ligands. This strategy has been applied for the immobilization of Pd-NHC catalysts[8] and other Pd catalysts applied for the Suzuki–Miyaura reaction.[9] As organic supports tend to undergo swelling and shrinking in the presence of organic solvents, mesoporous silica-type materials, such as SBA-15[10] and MCM-41,[11] have been widely applied as supports. The synthesis protocols that lead to such materials allow their porosity and other surface properties to be fine-tuned. They offer large specific surface areas in combination with reactive Si–OH groups for the covalent attachment of organic groups on their surfaces.[12] However, organic substrates have to undergo diffusion from the liquid phase into the pores, and the products have to do the reverse. Thereby, the solvation of substrates and products will be influenced strongly by the nature of the porous material. Polar porous materials will disturb the solvation of typical organic molecules, and surfaces that possess a more nonpolar nature should be more compatible.[13] Recently, we were able to show this effect by reducing the number of free Si–OH groups in an MCM-41-based epoxidation catalyst by trimethylsilylation and we found an enhancement of activity and recyclability.[14]

In this context, so-called periodic mesoporous organosilicas (PMOs) that are materials with ordered pores consisting of organosilica groups instead of a neat silica framework[15] have increasingly been used as catalyst supports during the last few years. Such materials allow a further fine-tuning of the pore properties in terms of polarity and polarizability. PMOs have found a broad variety of applications in catalysis,[16] gas adsorption,[17] energy conversion,[18] organo-optoelectronics,[19] and drug delivery.[20] Additionally, PMOs show a largely enhanced

---

[a] Dr. F. Rajabi, D. Schaffner, S. Follmann, C. Wilhelm, Prof. Dr. S. Ernst, Prof. Dr. W. R. Thiel
Fachbereich Chemie
Technische Universität Kaiserslautern
Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern (Germany)
E-mail: thiel@chemie.uni-kl.de

[b] Dr. F. Rajabi
Department of Science
Payame Noor University
19395-4697, Tehran (Iran)
E-mail: f_rajabi@pnu.ac.ir

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201500417.

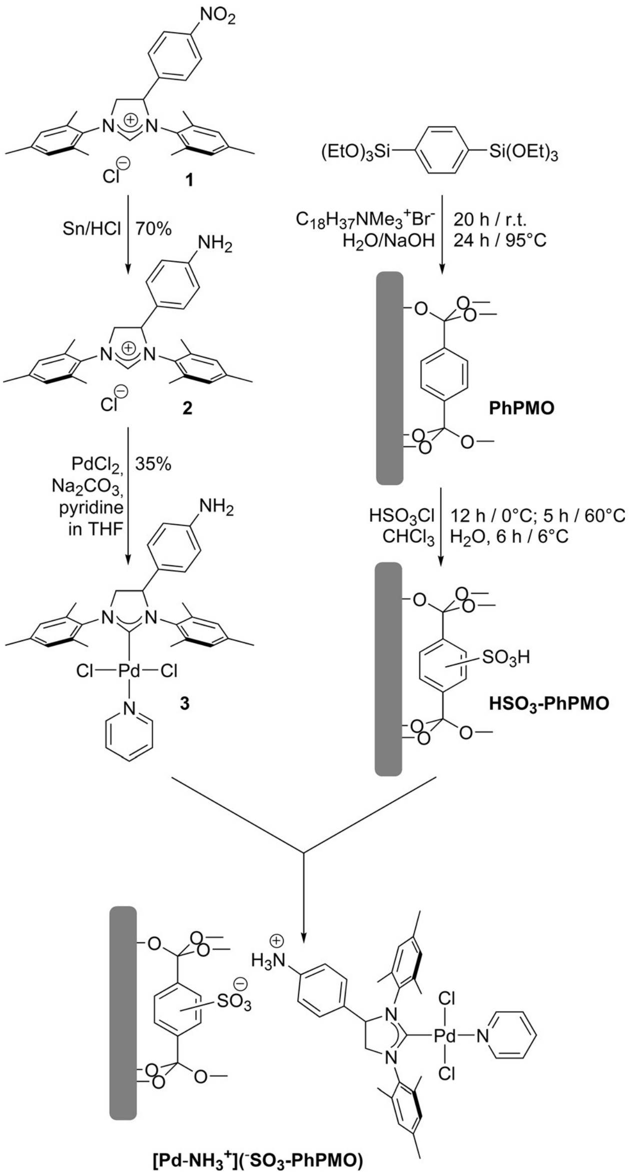
resistance against hydrolysis compared to similarly structured neat silica materials, a feature that is of special interest for reactions that are performed in aqueous media.

Recently, we published a strategy on how to introduce a nitrophenyl unit into the backbone of a saturated imidazolinium salt and found that the derived Pd^{II}-NHC complex showed a fairly high catalytic activity in the Suzuki–Miyaura cross-coupling of unactivated aryl chlorides and various aryl boronic acids.[21] Herein, we describe the synthesis and characterization of a new heterogeneous cross-coupling catalyst by the immobilization of such a functionalized Pd-NHC complex on the surface of a PMO support. In contrast to many other studies on Pd catalysts that are anchored covalently on the surface of a support material, we chose an electrostatic grafting method, which allows the catalyst to interact more flexibly on the surface. Recently, this strategy was beneficial, for example, for the olefin hydrogenation activity of a grafted, phosphane-coordinated Pd catalyst and for the olefin epoxidation activity of phosphomolybdic acid attached to a PMO.[22]

Results and Discussion

The ligand precursor 4-(4-nitrophenyl)-1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydro-3*H*-imidazolium chloride (**1**) is accessible from 4-nitroacetophenone in good yields in just five steps.[18a] To allow the electrostatic immobilization, the nitro group of **1** was converted into an amino unit with Sn/HCl in yields of 70% (Scheme 1). Milder ways to hydrogenate the nitro group such as reduction with $NH_4(HCOO)$ or H_2 in the presence of Pd/C failed.

The formation of **2** was confirmed clearly by ^{1}H NMR spectroscopy. The presence of the electron-donating NH_2 group results in a shift of the resonances of the aminophenyl unit by ≈1.0 ppm to higher field ($\delta = 6.50$ and 7.04 ppm; for the NMR spectra see the Supporting Information) compared to **1**. A broad peak at $\delta = 5.41$ ppm is assigned to the protons of the NH_2 group. As already found in the ^{1}H NMR spectrum of **1**, the two mesityl groups of the dihydroimidazolium salt **2** are hindered in rotation around the C–N bonds, which leads to four resonances for the aromatic mesityl protons and six resonances for the aliphatic mesityl protons. The same doubling of the number of the mesityl resonances is observed in the ^{13}C NMR spectrum. The reaction of **2** with $PdCl_2$, pyridine, and K_2CO_3 in THF gave the Pd-NHC complex **3** as a yellow solid in 35% yield after work-up. In the ^{1}H NMR spectrum of **3**, the resonance at $\delta = 9.65$ ppm typical for the NC(H)N fragment of an imidazolium salt disappeared. The three other resonances of the NHC-ring hydrogen atoms are shifted slightly to higher field compared to **2**. The resonances of the coordinated pyridine ligand are found at $\delta = 8.29$, 7.82, and 7.29 ppm (*o*-H, *p*-H, *m*-H). In the ^{13}C NMR spectrum, the resonance of the carbene carbon atom is observed at $\delta = 180.7$ ppm. Again the rotation around the C–N bonds in the NHC ligand is hindered, which leads to a doubled set of resonances in the ^{1}H and the ^{13}C NMR spectra.



Scheme 1. Synthesis of [Pd-NH_3^+]($^-SO_3$-PhPMO).

The phenylene-bridged PMO (PhPMO) support was synthesized according to a published protocol (Scheme 1).[23] The treatment of PhPMO with chlorosulfonic acid resulted in a partial sulfonation of the phenylene units (HSO_3-PhPMO). The spectroscopic data of the product were in agreement with those in the literature. To determine the specific number of acid sites on the surface, HSO_3-PhPMO was titrated with 0.01 M $NaOH_{(aq)}$/phenolphthalein, which showed that there are 0.78 mmol acid groups per g of HSO_3-PhPMO.

For the electrostatic grafting, compound **3** was stirred with HSO_3-PhPMO for 24 h in toluene under reflux conditions. After washing the product with water and dichloromethane, the resulting hybrid Pd catalyst [Pd-NH_3^+]($^-SO_3$-PhPMO) was dried under vacuum.

The surface properties of the materials were investigated by N_2 physisorption. The isotherms of PhPMO, HSO_3-PhPMO, and [Pd-NH_3^+]($^-SO_3$-PhPMO) are shown in Figure 1. The isotherms are of type IV with a type H4 hysteresis according to the IUPAC classification.[24] The corresponding parameters are summarized

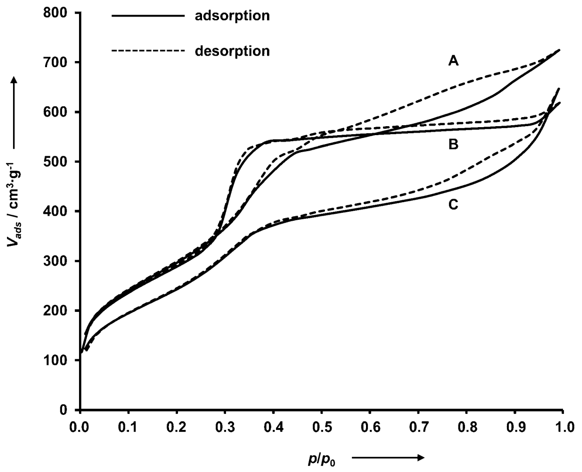


Figure 1. N_2 physisorption isotherms of A) PhPMO, B) HSO_3-PhPMO, and C) [Pd-NH_3^+]($^-SO_3$-PhPMO).

Table 1. Pore parameters of PhPMO, HSO_3-PhPMO, and [Pd-NH_3^+]($^-SO_3$-PhPMO).

Sample	S_{BET} [$m^2 g^{-1}$]	Total pore volume [$cm^3 g^{-1}$]	Mean pore diameter [nm]
PhPMO	891	0.90	2.64
HSO_3-PhPMO	954	1.07	2.89
[Pd-NH_3^+]($^-SO_3$-PhPMO)	766	0.86	2.65

in Table 1. According to these data, the total pore volume and the mean pore diameter are increased after the sulfonation of PhPMO. This can either be explained by the removal of some residual template molecules from the pores or by an ongoing condensation of the framework caused by the strong acid HSO_3Cl. The shapes of the isotherms before and after the loading of **3** are quite similar. As expected, the BET surface area, the total pore volume, and the mean pore diameter become smaller after the formation of [Pd-NH_3^+]($^-SO_3$-PhPMO) because of the ongoing filling of the pores. Generally, it can be considered that the structural features of the support material are not severely altered during the functionalization process.

The mesoporous materials HSO_3-PhPMO and [Pd-NH_3^+]($^-SO_3$-PhPMO) were further investigated by powder XRD, and he measured XRD patterns are presented in Figure 2. For HSO_3-PhPMO, there is a well resolved peak at around $2\theta = 1.90°$, which is typical for the (1 0 0) reflection of hexagonal PMO materials. This shifts slightly ($2\theta = 1.95°$) after the introduction of the Pd complex. Further sharp reflections in the range of $10° < 2\theta < 40°$ are characteristic of phenylene-based PMOs and can be assigned to a periodicity in the pore walls with a spacing of 7.6 Å.[25] Evidently, the structural integrity of the materials is maintained during the functionalization process.

More information about the thermal stability of the hybrid materials HSO_3-PhPMO and [Pd-NH_3^+]($^-SO_3$-PhPMO) can be extracted from the thermogravimetric analysis (TGA) data (Figure 3). Two distinct weight losses occur during the course of the applied temperature ramp: physisorbed water is released at around 80–120 °C. The amount of water is a little higher for [Pd-NH_3^+]($^-SO_3$-PhPMO), probably because of the higher degree of hydration of the ion pair. The material itself decomposes between 550 and 630 °C. Here the decomposition of [Pd-NH_3^+]($^-SO_3$-PhPMO) sets in at slightly lower temperatures. For differential thermogravimetric analysis data, see the Supporting Information.

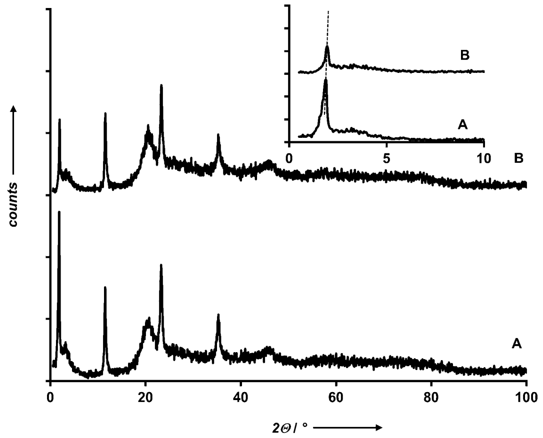


Figure 2. Powder XRD patterns of A) HSO_3-PhPMO and B) [Pd-NH_3^+]($^-SO_3$-PhPMO). The inset shows the (1 0 0) reflection typical of hexagonally structured mesoporous materials.

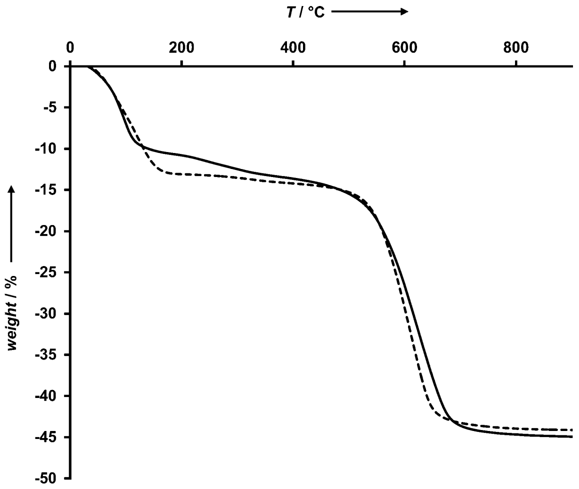


Figure 3. TGA plot of HSO_3-PhPMO (continuous line) and [Pd-NH_3^+]($^-SO_3$-PhPMO) (dashed line).

Solid-state ^{29}Si and ^{13}C NMR spectroscopy was performed to gain more structural information about the materials. In the solid-state ^{29}Si NMR spectrum of [Pd-NH_3^+]($^-SO_3$-PhPMO) there are signals exclusively in the range of $\delta = -60$ to -80 ppm, which can be assigned to so-called T species (Figure 4). These are Si atoms that carry one organic group and three O atoms (R–SiO_3). The absence of Q signals, Si atoms bound to four O atoms, indicates that the Si–C bonds remain unchanged during the functionalization processes.

Compared to the ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR spectrum of HSO_3-PhPMO that shows only one intense peak at $\delta = 131.3$ ppm, the number of resonances increases significantly in the spectrum of [Pd-NH_3^+]($^-SO_3$-PhPMO)

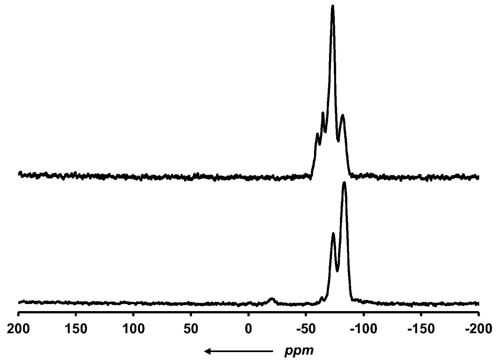


Figure 4. Solid-state ^{29}Si NMR spectra of HSO_3-PhPMO (bottom) and [Pd-NH_3^+]($^-SO_3$-PhPMO) (top).

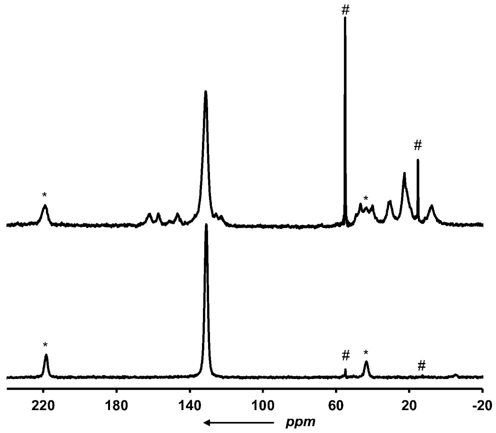


Figure 5. Solid-state ^{13}C CP-MAS NMR spectra of HSO_3-PhPMO (bottom) and [Pd-NH_3^+]($^-SO_3$-PhPMO) (top); the resonances marked with an asterisk * are rotational side bands, and those marked with # are caused by ethanol adsorbed in the pores.

Table 2. Suzuki–Miyaura cross-coupling of chlorobenzene and phenylboronic acid catalyzed by [Pd-NH_3^+]($^-SO_3$-PhPMO).[a]

Entry	Solvent	Base	Catalyst loading [mol %]	Yield [%]
1	H_2O	Na_2CO_3	0.1	60
2	H_2O	K_2CO_3	0.1	55
3	EtOH	K_2CO_3	0.1	48
4	*i*PrOH	K_2CO_3	0.1	95
5	*i*PrOH	Na_2CO_3	0.1	92
6	*i*PrOH/H_2O (1:1)	K_2CO_3	0.1	68
7	*i*PrOH	K_2CO_3	0.05	95
8	*i*PrOH	K_2CO_3	0.02	95
9	*i*PrOH	K_2CO_3	0.01	83
10	*i*PrOH	K_2CO_3	0.015	95
11	*i*PrOH	K_2CO_3	0.015	95[b]
12	*i*PrOH	K_2CO_3	0.015	95[c]
13	*i*PrOH	K_2CO_3	0.015	85[d]
14	*i*PrOH	K_2CO_3	0.015	70[e]

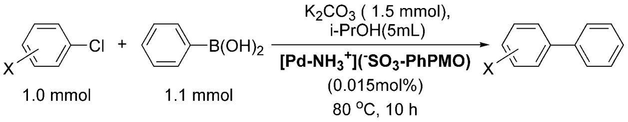
[a] Reaction conditions: solvent (5 mL), PhCl (1 mmol), $PhB(OH)_2$, (1.1 mmol), base (1.5 mmol), 18 h, heating to reflux, isolated yields; [b] reaction time: 10 h; [c] reaction time: 10 h, temperature 80 °C; [d] reaction time: 6 h; [e] temperature: 50 °C.

(Figure 5): in the aryl region, a series of resonances are found between $\delta = 160$ and 120 ppm. A shift to a lower field in comparison to the spectrum of **3** in solution can be explained by the cationic nature of the anilinium group. A series of further signals at higher field can be assigned to the resonances of the $-CH$, $-CH_2$, and $-CH_3$ groups in [Pd-NH_3^+]($^-SO_3$-PhPMO).

After full characterization of [Pd-NH_3^+]($^-SO_3$-PhPMO), the catalytic performance of the Pd-containing material was studied in the Suzuki–Miyaura cross-coupling under heterogeneous conditions. We used chlorobenzene and phenylboronic acid as substrates as the homogeneous congener of [Pd-NH_3^+]($^-SO_3$-PhPMO) showed high activities for aryl chlorides under mild conditions. To optimize the cross-coupling reaction, various parameters such as catalyst concentration, bases, and solvents were investigated. A combination of K_2CO_3 and *i*PrOH gave the best results (Table 2). Generally the activity of [Pd-NH_3^+]($^-SO_3$-PhPMO) is comparable to that of the homogeneous system. All catalytic experiments were performed under an ambient atmosphere (air), and the catalyst is stable under these conditions.

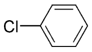
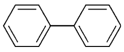
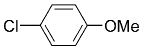
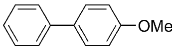
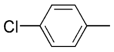
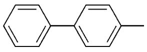
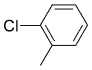
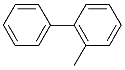
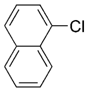
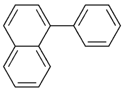
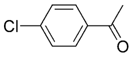
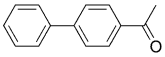
Under the optimized conditions, the catalyst not only showed excellent activity but also reusability. Leaching tests were performed to determine whether the reaction was truly heterogeneous. For this purpose, the catalyst was removed from the catalysis mixture by filtration after half of the reaction time required for the coupling of chlorobenzene and phenyl boronic acid under the given conditions, and the filtrate was allowed to react under the same conditions. No further reaction occurred after the filtration, which suggests that immobilized Pd species are the active site. Atomic absorption spectroscopy (AAS) detected no traces of Pd in solution down to the limit of the method (0.5×10^{-4} mmol L^{-1}), which confirms the high stability of the Pd complex and its strong binding to the surface. In the mechanism of pyridine-enhanced precatalyst preparation stabilization and initiation (PEPPSI) catalysts, a dissociation of the pyridine site is one of the accepted steps. As it is unfavorable for this ligand to recoordinate to an immobilized catalytically active site, we assume that the catalyst is stabilized by interactions with basic surface sites as we do not observe any catalyst decomposition to accompany the catalytic transformation.

With the optimized reaction conditions in hand, we screened the scope of the reaction using aryl chlorides with different functional groups (Scheme 2, Table 3). Substrates that bear electron-withdrawing substituents provided the desired products in perfect yields, and for deactivated substrates the yield was ≥ 90 %. The catalyst again showed excellent recoverability and reusability over six successive runs under the given reaction conditions.



Scheme 2. Suzuki–Miyaura cross-coupling of aryl chlorides and phenylboronic acid catalyzed by [Pd-NH_3^+]($^-SO_3$-PhPMO).

Table 3. Suzuki–Miyaura cross-coupling of aryl chlorides and phenylboronic acid catalyzed by [Pd-NH_3^+]($^-SO_3$-PhPMO).

Entry	Aryl chloride	Product	Yield [%][a]
1			95
2			92
3			90
4			90
5			95
6			98

[a] Isolated yields; reaction conditions as in Table 2, entry 10.

Conclusions

We have synthesized an organic–inorganic hybrid material by the electrostatic anchoring of a Pd N-heterocyclic carbene complex onto the surface of a partially sulfonated periodic mesoporous organosilica material. The derived heterogeneous Pd catalyst is highly active for the Suzuki–Miyaura coupling of aryl chlorides under mild and aerobic conditions. The heterogeneity of the system was examined by a leaching test performed at the reaction temperature of the catalysis, and no leaching was detected. The material stays stable under these conditions and could be reused at least six times without any loss of activity.

Experimental Section

General remarks

Solvents were dried by standard methods. Reagents were purchased from ACROS, Alfa Aesar, or Sigma–Aldrich and used without further purification, unless otherwise noted. NMR spectra in solution were recorded by using a Bruker DPX 400 spectrometer, and solid-state NMR measurements were performed by using a 500 MHz Bruker Avance III widebore NMR spectrometer. Elemental analysis was performed at the Fachbereich Chemie (TU Kaiserslautern). Pd leaching was determined by AAS by using a PERKIN ELMER AAnalyst 300. N_2 physisorption isotherms were measured at 77 K by using a Quantachrome Autosorb 1 sorption analyzer. The specific surface areas were calculated using the BET equation at $P/P_0=0.05$–0.5. TGA was performed by using a Setaram Setsys 16/18.

4-(4-Aminophenyl)-1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydro-3*H*-imidazolium chloride (2)

Compound **1** (4.64 g, 10 mmol) and granulated tin (1.79 g, 15 mmol) were added into a 100 mL round-bottomed flask equipped with a reflux condenser. The flask was placed into cold water, and concd HCl (4 mL) was added dropwise under vigorous stirring followed by heating of the mixture to reflux for 1 h. After cooling the reaction mixture to RT, a solution of NaOH (3.00 g) in water (5 mL) was added slowly with cooling. The mixture was extracted three times with $CHCl_3$ (30 mL), and the combined organic phase was dried over $MgSO_4$. Evaporation of the solvent resulted in a yellow solid (yield: 82%). Elemental analysis calcd (%) for $C_{27}H_{32}ClN_3$ (434.02) C 74.72, H 7.43, N 9.68; found C 74.34, H 7.36, N 9.78%; ^{1}H NMR (400 MHz, [D_6]DMSO): $\delta=9.03$ (s, 1H, H1), 7.13 (d, $^3J=7.5$ Hz, 2H, H5), 7.05, 7.05, 7.03, 6.84 (4 s, 4H, H10), 6.50 (d, 2H, 2H, H6), 5.84 (dd, $2\times{}^3J=11.1$ Hz, 1H, H2), 5.41 (s, 2H, NH_2), 4.81 (dd, $^2J={}^3J=12.3$ Hz, 1H, H3 resp. H3′), 4.62 (dd, $^2J=12.1$, $^3J=10.3$ Hz, 1H, H3 resp. H3′), 2.50, 2.46, 2.40, 2.31, 2.22, 1.80 ppm (6 s, 18H, $6\times CH_3$); ^{13}C NMR (101 MHz, DMSO-d_6): $\delta=158.6$ (C1), 150.1, 139.7, 139.2, 136.0, 135.7, 135.4, 135.3 131.1 (C5), 129.8, 129.6, 129.5, 129.4, 129.2, 119.3 (C4), 113.6 (C6), 66.5 (C2), 55.1 (C3), 20.6, 20.4, 18.0, 17.73 17.6, 17.3 ppm ($6\times CH_3$).

Dichlorido(pyridine)[4-(4-aminophenyl)-1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydro-3*H*-imidazol-2-ylidene]palladium(II) (3)

A mixture of **2** (0.512 g, 1.18 mmol), $PdCl_2$ (0.105 g, 0.59 mmol), and K_2CO_3 (0.326 g, 2.36 mmol) of was stirred in pyridine (6 mL) for three days at 60 °C under an atmosphere of N_2. After cooling the reaction mixture to RT, most of the volatiles were removed under reduced pressure. The solid residue was purified by flash chromatography (SiO_2, hexane/ethyl acetate, 5:1) to give **3** as a yellow solid (yield: 35%). Elemental analysis calcd (%) for $C_{32}H_{37}Cl_2N_4Pd$ (654.98): C 58.68, H 5.69, N 8.55; found C 57.97, H 5.76, N 8.18; ^{1}H NMR (400 MHz, [D_6]DMSO): $\delta=8.29$ (t, $^3J=4.5$ Hz, 2H, Hpy-*o*), 7.81 (t, $^3J=7.4$ Hz, 1H, Hpy-*p*), 7.34 (dd, 2H, Hpy-*m*), 7.04, 7.01, 6.74 (3 s, 3H, H10), 6.94–6.86 (m, 2H+1H, H5+H10), 6.46 (d, $^3J=8.3$ Hz, 2H, H6), 5.28–5.20 (m, 2H+1H, NH_2+H2), 4.35 (dd, $^2J={}^3J=11.5$ Hz, 1H, H3 resp. H3′), 4.11 (dd, $^2J=11.0$, $^3J=8.5$ Hz, 1H, H3 resp. H3′), 2.62, 2.58, 2.51, 2.31, 2.22, 2.00 ppm (6 s, 18H, $6\times CH_3$); ^{13}C NMR (101 MHz, [D_6]DMSO): $\delta=180.7$ (C1), 150.6, 150.5, 149.2, 138.4, 137.7, 137.2, 137.0, 136.7, 135.2, 129.5, 129.3, 129.1, 128.7, 124.4 (C4), 113.4 (C6), 66.4 (C2), 56.6 (C3), 20.59, 20.5, 19.8, 19.6, 19.6, 19.0 ppm ($6\times CH_3$).

Synthesis of [Pd-NH_3^+]($^-SO_3$-PhPMO)

Complex **3** (0.51 g, 0.78 mmol) was dissolved in $CHCl_3$ (5 mL) and added to a suspension of HSO_3-PhPMO (1.00 g) in dry toluene (50 mL). After the mixture was stirred for 12 h at 90 °C, the solid material was collected by filtration, extracted for 24 h with $CHCl_3$ in a Soxhlet apparatus, and dried under vacuum at 50 °C. Based on AAS analysis of a solution obtained by washing the catalyst with nitric acid, a loading of Pd of (0.250 ± 0.001) mmol g^{-1} was determined.

General procedure for the catalytic Suzuki–Miyaura cross-coupling

A 50 mL round-bottomed flask equipped with a magnetic stirring bar was charged with aryl chloride (1.0 mmol), phenylboronic acid (134 mg, 1.1 mmol), K_2CO_3 (207 mg, 1.5 mmol), [Pd-NH_3^+]($^-SO_3$-PhPMO) (60 mg; 0.015 mmol Pd), and isopropyl alcohol (5 mL). The mixture was heated to 80 °C for 10 h under air. After cooling to RT, $CHCl_3$ (20 mL) was added, and the mixture was filtered. The solid residue was washed twice with water (10 mL) and twice with ethyl acetate (10 mL) and then dried under vacuum at 50 °C. After this procedure, the catalyst could be used for the next run. The organic phase was dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. Pure products were obtained by column chromatography on silica.

Acknowledgements

F.R. gratefully acknowledges the Alexander von Humboldt Foundation for a research grant. The state research unit NanoKat is acknowledged for financial support of this work.

Keywords: carbene ligands · cross-coupling · heterogeneous catalysis · mesoporous materials · palladium

[1] a) D. S. Surry, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2008**, *47*, 6338–6361; *Angew. Chem.* **2008**, *120*, 6438–6461; b) A. J. Arduengo, R. L. Harlow, M. J. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
[2] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; b) A. J. Suzuki, *Organomet. Chem.* **1999**, *576*, 147–168.
[3] a) A. Martínez, J. L. Krinsky, I. Peñafiel, S. Castillón, K. Loponov, A. Lapkin, C. Godard, C. Claver, *Catal. Sci. Technol.* **2015**, *5*, 310–319; b) R. Zhong, A. Pöthig, Y. Feng, K. Riener, W. A. Herrmann, F. E. Kühn, *Green Chem.* **2014**, *16*, 4955–4962; c) F. S. Han, *Chem. Soc. Rev.* **2013**, *42*, 5270–5298.
[4] a) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91; b) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; *Angew. Chem.* **2008**, *120*, 3166–3216; c) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445–3478; d) R. H. Crabtree, *Coord. Chem. Rev.* **2013**, *257*, 755–766.
[5] a) F. Glorius, *N-Heterocyclic Carbenes in Transition Metal Catalysis in Topics in Organometallic Chemistry, Vol. 21*, Springer Verlag, Berlin, **2007**; b) S. P. Nolan, *N-Heterocyclic Carbenes*, Wiley-VCH, Weinheim, **2014**.
[6] a) G. C. Fortman, S. P. Nolan, *Chem. Soc. Rev.* **2011**, *40*, 5151–5169; b) C. Allolio, T. Strassner, *J. Org. Chem.* **2014**, *79*, 12096–12105; c) Y. Takeda, Y. Ikeda, A. Kuroda, S. Tanaka, S. Minakata, *J. Am. Chem. Soc.* **2014**, *136*, 8544–8547.
[7] a) M. Stratakis, H. Garcia, *Chem. Rev.* **2012**, *112*, 4469–4506; b) D. Cantillo, C. O. Kappe, *ChemCatChem* **2014**, *6*, 3286–3305.
[8] a) S. Xu, K. Song, T. Li, B. Tan, *J. Mater. Chem. A* **2015**, *3*, 1272–1278; b) R. Zhong, A. Pöthig, S. Haslinger, B. Hofmann, G. Raudaschl-Sieber, E. Herdtweck, W. A. Herrmann, F. E. Kühn, *ChemPlusChem* **2014**, *79*, 1294–1303; c) A. Z. Wilczewska, I. Misztalewska, *Organometallics* **2014**, *33*, 5203–5208; d) K. S. M. Salih, W. R. Thiel in *Palladium-Catalyzed Coupling Reactions—Practical Aspects and Future Developments* (Ed.: Á. Molnár), Wiley-VCH, Weinheim, **2013**, pp. 57–78; e) B. Karimi, D. Enders, *Org. Lett.* **2006**, *8*, 1237–1240.
[9] a) P. Puthiaraj, W.-S. Ahn, *Catal. Commun.* **2015**, *65*, 91–95; b) N. Fukaya, S. Onozawa, M. Ueda, T. Miyaji, Y. Takagi, T. Sakakura, H. Yasuda, *J. Mol. Catal. A* **2014**, *385*, 7–12; c) T. Iwai, T. Harada, K. Hara, M. Sawamura, *Angew. Chem. Int. Ed.* **2013**, *52*, 12322–12326; *Angew. Chem.* **2013**, *125*, 12548–12552; d) G. Borja, A. Monge-Marcet, R. Pleixats, T. Parella, X. Cattoen, M. Wong Chi Man, *Eur. J. Org. Chem.* **2012**, 3625–3635; e) Y. M. A. Yamada, S. Sarkar, Y. Uozumi, *J. Am. Chem. Soc.* **2012**, *134*, 3190–3198.
[10] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548–552.
[11] a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710–712; b) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834–10843.
[12] a) D. E. De Vos, M. Dams, B. F. Sels, P. A. Jacobs, *Chem. Rev.* **2002**, *102*, 3615–3640; b) A. Taguchi, F. Schüth, *Microporous Mesoporous Mater.* **2005**, *77*, 1–45.
[13] a) L.-B. Sun, *Curr. Org. Chem.* **2014**, *18*, 1225–1225; b) H. Zou, R. Wang, X. Li, X. Wang, S. Zeng, S. Ding, L. Li, Z. Zhang, S. Qiu, *J. Mater. Chem. A* **2014**, *2*, 12403–12412; c) F. Zhu, D. Yang, F. Zhang, H. Li, *J. Mol. Catal. A* **2012**, *363–364*, 387–397; d) X. Yang, F. Zhu, J. Huang, F. Zhang, H. Li, *Chem. Mater.* **2009**, *21*, 4925–4933.
[14] S. Shylesh, M. Jia, A. Seifert, S. Adappa, S. Ernst, W. R. Thiel, *New J. Chem.* **2009**, *33*, 717–719.
[15] a) K. J. Shea, D. A. Loy, O. Webster, *J. Am. Chem. Soc.* **1992**, *114*, 6700–6710; b) D. A. Loy, K. J. Shea, *Chem. Rev.* **1995**, *95*, 1431–1442; c) T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* **1999**, *402*, 867–871; d) S. Mann, *Nature* **1993**, *365*, 499–505; e) F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem. Int. Ed.* **2006**, *45*, 3216–3251; *Angew. Chem.* **2006**, *118*, 3290–3328.
[16] a) J. P. G. Pater, P. A. Jacobs, J. A. Martens, *J. Catal.* **1999**, *184*, 262–267; b) Y. Liang, R. Anwander, *Dalton Trans.* **2013**, *42*, 12521–12545; c) P. Van Der Voort, D. Esquivel, E. De Canck, F. Goethals, I. Van Driessche, F. J. Romero-Salguero, *Chem. Soc. Rev.* **2013**, *42*, 3913–3955; d) Q. Yang, J. Liu, L. Zhang, C. Li, *J. Mater. Chem.* **2009**, *19*, 1945–1955; e) A. Molnár in *Palladium-Catalyzed Coupling Reactions - Practical Aspects and Future Developments* (Ed.: Á. Molnár), Wiley-VCH, Weinheim, **2013**, pp. 79–139.
[17] a) H. Hata, S. Saeki, T. Kimura, Y. Sugahara, K. Kuroda, *Chem. Mater.* **1999**, *11*, 1110–1119; b) K. M. Kemner, X. Feng, J. Liu, G. E. Fryxell, L. Q. Wang, A. Y. Kim, M. Gong, S. Mattigod, *J. Synchrotron Radiat.* **1999**, *6*, 633–635; c) D. Y. Zhao, P. D. Yang, Q. S. Huo, B. F. Chmelka, G. D. Stucky, *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 111–121.
[18] a) J. C. Vartuli, S. S. Shih, C. T. Kresge, J. S. Beck, *Stud. Surf. Sci. Catal.* **1998**, *117*, 13–21; b) M. Waki, Y. Maegawa, K. Hara, Y. Goto, Y. Yamada, N. Mizoshita, T. Tani, W.-J. Chun, S. Muratsugu, M. Tada, A. Fukuoka, S. Inagaki, *J. Am. Chem. Soc.* **2014**, *136*, 4003–4011; c) R. Ciriminna, A. Fidalgo, V. Pandarus, F. Béland, L. M. Ilharco, M. Pagliaro, *Chem. Rev.* **2013**, *113*, 6592–6620.
[19] a) Y. Li, A. Keilbach, N. Mizoshita, S. Inagaki, T. Bein, *J. Mater. Chem. C* **2014**, *2*, 50–55; b) M. S. Morey, A. Davidson, G. D. Stucky, *J. Porous Mater.* **1998**, *5*, 195–204; c) B. Johnson-White, M. Zeinali, K. M. Shaffer, C. H. Patterson, P. T. Charles, M. A. Markowitz, *Biosens. Bioelectron.* **2007**, *22*, 1154–1162.
[20] M. Santha Moorthy, S. S. Park, D. Fuping, S. H. Hong, M. Selvaraj, C. S. Ha, *J. Mater. Chem.* **2012**, *22*, 9100–9108.
[21] a) F. Rajabi, J. Trampert, Y. Sun, M. Busch, S. Bräse, W. R. Thiel, *J. Organomet. Chem.* **2013**, *744*, 101–107; b) F. Rajabi, W. R. Thiel, *Adv. Synth. Catal.* **2014**, *356*, 1873–1877.
[22] a) L. Wang, D. Dehe, T. Philippi, A. Seifert, S. Ernst, Z. Zhou, M. Hartmann, R. N. Klupp Taylor, M. Jia, W. R. Thiel, *Catal. Sci. Technol.* **2012**, *2*, 1188–1195; b) J. Wang, Y. Zou, Y. Sun, M. Hemgesberg, D. Schaffner, H. Gao, X. Song, W. Zhang, M. Jia, W. R. Thiel, *Chin. J. Catal.* **2014**, *35*, 532–539.
[23] S. Shylesh, A. Wagener, A. Seifert, S. Ernst, W. R. Thiel, *Angew. Chem. Int. Ed.* **2010**, *49*, 184–187; *Angew. Chem.* **2010**, *122*, 188–191.
[24] a) S. J. Gregg, K. S. W. Sing, *Adsorption, Surface area and Porosity, Vol. 3, 2^{nd} ed.*, Academic Press, San Diego, **1982**, pp. 111–118; b) *Handbook of Heterogeneous Catalysis, Vol. 2, 2^{nd} ed.* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**.
[25] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* **2002**, *416*, 304–307.

Received: April 16, 2015
Revised: May 29, 2015