

Proximity Effect using a Nanocage Structure: Polyhedral Oligomeric Silsesquioxane-Imidazolium Tetrachloropalladate Salt as a Precatalyst for the Suzuki–Miyaura Reaction in Water

Lucia Anna Bivona,^[a, b] Francesco Giacalone,^[a] Esther Carbonell,^[b] Michelangelo Gruttadauria,^{*[a]} and Carmela Aprile^{*[b]}

A polyhedral oligomeric silsesquioxane-imidazolium tetrachloropalladate salt (POSS-Imi-PdCl₄) was prepared by the reaction of a polyhedral oligomeric silsesquioxane-imidazolium chloride salt (POSS-Imi-Cl) with PdCl₂ and used as a pre-catalyst for the Suzuki–Miyaura reaction in water at 100 °C at a low loading (0.08–0.16 mol%). Biphenyl compounds were isolated in high to excellent yields. A comparison of the POSS-based catalyst with the corresponding catalyst without the nanocage structure (i.e., 1-butyl-3-methylimidazolium tetrachloropalladate) highlighted the role of the POSS structure to reach higher yields in the Suzuki–Miyaura reaction. This result is ascribed to a proximity effect of the imidazolium moieties linked to the nanocage structure. Fresh and used catalytic materials were characterised by using X-ray photoelectron spectroscopy and TEM.

Introduction

The palladium-catalysed Suzuki–Miyaura cross-coupling reaction has emerged as an important and efficient tool in organic synthesis because it is one of the most convenient modern methods for C–C bond formation.^[1] The main advantages of this process are represented by the mild reaction conditions employed^[2] and the tolerance toward a wide range of functional groups. In particular, this reaction is an important strategy for the synthesis of polymers but also in the field of pharmaceutical and natural products.^[3]

Traditionally, the Suzuki–Miyaura reaction proceeds by using Pd complexes with N- and P-containing ligands. It has been well established that ionic liquids (ILs) are interesting solvents and/or ligands in which to conduct the Suzuki–Miyaura reaction with Pd salts under "ligand-free" conditions. This process eliminates the need for toxic solvents and expensive P-containing ligands. Moreover, in ILs it is possible to use Pd^{II} as a precatalyst for the C–C coupling reaction, which avoids the use of reducing reagents.^[4] To obtain greener conditions, special at-

[a]	Dr. L. A. Bivona, Dr. F. Giacalone, Prof. M. Gruttadauria Dipartimento di Scienze e Tecnologie Biologiche
	Chimiche e Farmaceutiche (STEBICEF) Sezione di Chimica, Università di Palermo Viale delle Scienze s/n, Ed. 17, I-90128 Palermo (Italy)
[b]	E-mail: michelangelo.gruttadauria@unipa.it Dr. L. A. Bivona, Dr. E. Carbonell, Prof. C. Aprile Laboratory of Applied Material Chemistry (CMA)
	61 rue de Bruxelles, 5000 Namur (Belgium) E-mail: carmela.aprile@unamur.be
	Supporting information and the ORCID identification number(s)

 Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/ cctc.201600155. tention has been paid to the use of eco-friendly and cheap solvents or co-solvents, such as water.^[5] Tetrachloropalladate salts are useful Pd pre-catalysts. Imidazolium tetrachloropalladate salts were employed as pre-catalysts at 1 mol % loading in Suzuki-Miyaura reactions in 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide at 100 °C, which resulted in high conversions.^[6] Other imidazolium tetrachloropalladate salts of the type $[IL]_2[PdX_4]$ (IL = imidazolium cation, X = Cl, Br) were used as catalyst precursors at 1 mol% loading in the Suzuki-Miyaura reaction in *i*PrOH or *i*PrOH/H₂O 1:1 at 40 °C.^[7] In situ ESI-MS experiments showed evidence of [(IL)_xPd₃] cluster formation if complexes of the type [IL]₂[PdX₄] were used as catalyst precursors.^[8] Other anionic Pd complexes of the type [IL]2[PdX4] have been reported and used as pre-catalysts in the Suzuki-Miyaura reaction,^[9] in the oxidative Heck reaction^[10] and other catalytic applications.^[11] Recently, inorganic–organic hybrid materials have attracted great interest thanks to their excellent performance in terms of thermal and mechanical stability. Nanostructured polyhedral oligomeric silsesquioxanes (POSS) are a class of organic-inorganic hybrid compounds with the general formula $(RSiO_{3/2})_n$ that consist of an inorganic silica-like core surrounded by organic groups.^[12] In general, their structure can be expressed by the formula $T_n R_m$, in which T indicates the number of Si atoms and R denotes the organic substituents. Typical POSS derivatives have a cube-octameric structure (T₈R₈). Recently, increased interest in POSS nanostructures has been attributed to their high performances, which come from a combination of inorganic and organic characteristics. As the organic peripheries can be functionalised easily, POSS can be designed for multi-functional nanocomposites. To date, they have been applied widely in many materials, such



as biomaterials,^[13] hybrid electrochromic devices,^[14] solar cells,^[15] models of silica-supported catalysts,^[16] additives in the synthesis of periodic mesoporous organosilicas,^[17] polymer nanocomposites^[18] and in catalysis.^[19] In particular, there are very few examples of POSS-stabilised Pd nanoparticles used as catalysts.^[20]

In recent years, we have been involved in investigations in the development of new Pd-based catalysts^[21] and, in addition, we have presented a silsesquioxane-based nanostructure functionalised with imidazolium chloride (POSS-Imi-Cl) as an efficient catalyst for chemical fixation of CO_2 .^[22] In this case, the catalyst displayed an improved catalytic performance with respect to unsupported 1-butyl-3-methylimidazolium chloride and such enhanced activity was ascribed to the proximity effect generated by the increased local concentration of imidazolium species that surround the inorganic silsesquioxane core.

As imidazolium-based ILs have been employed as homogeneous supports for Pd-based catalysts and to take advantage of our synthetic strategy for the synthesis of POSS-Imi-Cl, we envisaged a new approach for Pd-based POSS imidazolium salts as pre-catalysts for Suzuki–Miyaura reactions. In this paper, we describe the synthesis of a new imidazolium tetrachloropalladate salt immobilised on a POSS nanocage and its use as a pre-catalyst at a low catalytic loading in the Suzuki– Miyaura reaction in water. We also describe an improved catalytic performance with respect to the corresponding unsupported pre-catalyst.

Results and Discussion

Polyhedral oligomeric silsesquioxane functionalised with imidazolium moieties was synthesised in a two-step procedure.[22] We started from the commercially available T₈R₈ octavinyl-substituted silsesquioxane (POSS-vinyl; Scheme 1). POSS-vinyl was reacted with 3-chloro-1-propanethiol through a thiol-ene reaction in presence of 2,2-azobisisobutyronitrile (AIBN) as a radical source to give POSS-CI (Scheme 1). Then, POSS-CI was reacted with 1-methylimidazole to produce the imidazolium-functionalised silsesquioxane (POSS-Imi-Cl; Scheme 1). POSS-Cl and POSS-Imi-Cl were fully characterised (¹H, ¹³C and ²⁹Si magicangle spinning cross-polarisation (MAS-CP) NMR spectroscopy, FTIR spectroscopy and elemental analysis). POSS-Imi-PdCl₄ was synthesised by the treatment of POSS-Imi-Cl with $PdCl_2$ in water. Tetrachloropalladate-based ILs can be synthesised by the treatment of the appropriate imidazolium salt with PdCl₂ or PdCl₂(cod) (cod = cyclooctadiene) in acetonitrile.^[11c] However, because of the low solubility of POSS-Imi-Cl in acetonitrile, the reaction was performed in water. The final product was characterised by elemental analysis, ¹H and ¹³C NMR spectroscopy, thermogravimetric analysis (TGA), TEM and X-ray photoelectron spectroscopy (XPS). ¹H and ¹³C NMR spectra in D₂O, although not resolved as the precursor POSS-Imi-Cl (see Supporting Information), showed all the expected signals. However, different from the ¹H NMR spectrum of POSS-Imi-Cl, which did not show the signal of the proton at the C-2 position of the imidazolium ring because of its exchange with D₂O, the ¹H NMR spectrum of POSS-Imi-PdCl₄ showed the signal of this proton clearly. After heating the samples to 95 °C, NMR spectroscopy showed a partial exchange of the above-mentioned proton but did not show any significant modification of the POSS-Imi-Cl structure. TGA was performed under oxygen flow to 900 °C with a heating rate of 10 °C min⁻¹ (Figure 1). Under these conditions, the residue is constituted by SiO_2 and Pd_1^{0} which is in excellent agreement with the structure of POSS-Imi-PdCl₄.



Figure 1. TGA of POSS-Imi-PdCl₄ under oxygen flow.

POSS-Imi-PdCl₄ was then used as a catalyst for the Suzuki– Miyaura reaction between phenylboronic acid and a set of aryl bromides. The reactions were performed in water at 100 °C for 4 h using K₂CO₃ as the base in the presence of 0.16 mol % catalyst (Table 1). All the biphenyls were obtained in high or excellent yields. The reactions can even be performed at a lower temperature (50 °C) as demonstrated by the quantitative yield obtained in the case of 4-bromobenzaldehyde and the high yield (85%) obtained with 4-bromoanisole (entries 11 and 12).

To investigate the role of the silsesquioxane nanocage, additional catalytic tests were performed using the corresponding imidazolium-based catalyst without the silsesquioxane nanocage (i.e., 1-butyl-3-methylimidazolium tetrachloropalladate; bmim₂PdCl₄; Table 2). These catalytic tests were performed using different aryl bromides and two catalyst loadings (0.16



Scheme 1. Synthesis of the POSS-Imi-PdCl₄ pre-catalyst.

www.chemcatchem.org



	B(OH) ₂ + Br	$(0.16 \text{ mol}\%) = K_2CO_3, H_2O = 100 \text{°C}, 4h$		R		
Entry	Biphenyl	Conv. ^[b] [%]	Yield ^[c] [%]	TON ^[d]		
1	СНО	99	97	606		
2		99	99	619		
3		99	99	619		
4		80	76	475		
5		95	95	594		
6		93	88	550		
7	С-СН3	88	79	494		
8		99	99	619		
9	H ₃ C	99	99	619		
10		77	69	431		
11 ^[e]	С—С—сно	99	99	619		
12 ^[e]		85	85	531		
[a] Reaction conditions: aryl bromide (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (2.1 mmol), H_2O (1.0 mL), catalyst (0.16 mol%, 1.2 mg). [b] Calculated from the ¹ H NMR spectra (Figures S20–S31). [c] Isolated yield obtained after passing the residue through a short pad of silica gel.						

[d] Turnover number (TON) calculated as mmol product/mmol catalytically active sites. [e] Reaction performed at 50 $^\circ$ C.

and 0.08 mol%). If $bmim_2PdCl_4$ was employed in a 0.16 mol% loading, the conversions and yields were much lower than those obtained using POSS-Imi-PdCl₄ (Table 2, entries 1–4 vs. Table 1, entries 4–7).

The difference between the POSS-based catalyst and $\text{bmim}_2\text{PdCl}_4$ was even more evident if the catalysts were employed at a lower loading (0.08 mol%; Table 2, entries 5–8).

4-Bromoanisole and 4-bromotoluene gave drastically lower conversions if the reactions were performed in the presence of $pmim_2PdCl_4$ (Table 2, entries 5–8). Notably, the POSS-Imi-PdCl₄ catalyst worked well even at 0.08 mol% loading, a catalyst loading much lower than other [IL]₂[PdCl₄] catalytic systems reported previously.^[6,7]

To collect more information about the role of the POSS-Imi-Cl nanocage, we performed the Suzuki–Miyaura reaction between phenylboronic acid and 4-bromoanisole using Na_2PdCl_4 or Na_2PdCl_4 in the presence of bmimCl or POSS-Imi-Cl (Table 3). Again, the effect of the imidazolium-POSS nanocage was evident.



[a] Reaction conditions: aryl bromide (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (2.1 mmol), H_2O (1.0 mL), catalyst (0.16 or 0.08 mol%). [b] Calculated from ¹H NMR spectra (Figures S32–S39). [c] Isolated yield obtained after passing the residue through a short pad of silica gel. [d] TON calculated as mmol product/mmol catalytically active sites.



Finally, we checked the less reactive 4-chloronitrobenzene in the presence of POSS-Imi-PdCl₄ and $bmim_2PdCl_4$ (Scheme 2). Under such mild conditions (0.16 mol%, 100 °C, 4 h), a 15% conversion was obtained in the presence of POSS-Imi-PdCl₄ (Figure S40). However, no product was observed if the same reaction was catalysed by $bmim_2PdCl_4$.

The two catalysts (POSS-Imi-PdCl₄ and $bmim_2PdCl_4$) were characterised by XPS before and after the Suzuki reaction (Fig-



Scheme 2. Suzuki–Miyaura reaction between phenylboronic acid and 4-chloronitrobenzene.

ChamCatCham	2016	0	160E 1601	
ChemCatChem	2010,	ŏ,	1085 - 1091	



Figure 2. Pd 3d core-level XPS spectra of fresh a) POSS-Imi-PdCl₄ and b) $\text{bmim}_2\text{PdCl}_4$.

ures 2 and 3 and Table 4). As expected, the fresh catalysts showed the presence of Pd^{II} species, although, in the case of POSS-Imi-PdCl₄, a small amount of Pd^{0} was observed (entries 1 and 2). However, after the reaction, both catalysts showed practically the same amount of Pd^{0} (entries 3 and 4 and Figure 3). To disclose if the presence of Pd^{0} is imputable only to the C–C coupling reaction mechanism, the POSS-Imi-PdCl₄ and bmim₂PdCl₄ catalysts were heated at 100 °C in water for 4 h. For POSS-Imi-PdCl₄, approximately 17% of the Pd⁰ species was observed, whereas approximately 29% of the Pd⁰ species was observed for bmim₂PdCl₄ (entries 5 and 6, Figure S19).

Such reduced species could be ascribed to the thermal decomposition of the tetrachloropalladate anion that takes place under the reaction conditions independent of the Suzuki– Miyaura catalytic cycle.^[24]

We wondered if the presence of sulfur atoms in the alkyl chains in the POSS nanocage may have a role in the stabilisation of the Pd species. To shed some light on this question, the high-resolution S2p core-level XPS spectrum of POSS-Imi-PdCl₄ was analysed. To make a comparison, we prepared POSS-

the Suzuki–Miyaura reaction. ^[a]							
Entry	Catalyst	Pd ^{II} [eV]	Pd⁰ [eV]	Pd" [%]	Pd ⁰ [%]		
1	POSS-Imi-PdCl₄ (fresh)	337.4	335.7	93	7		
2	bmim₂PdCl₄ (fresh)	337.2	-	99	trace		
3	POSS-Imi-PdCl₄ (after reaction)	336.8	334.6	13	87		
4	bmim₂PdCl₄ (after reaction)	336.9	334.9	12	88		
5 ^[b]	POSS-Imi-PdCl₄ (after heating)	336.6	335.0	83	17		
6 ^[b]	bmim₂PdCl₄ (after heating)	336.9	334.6	71	29		

Table 4. XPS data of POSS-Imi-PdCl₄ and bmim₂PdCl₄ before and after

[a] The reference peak (C1s) is set at BE=284.6 eV. FWHM fit parameters are fixed between 0.5 and 3.5 eV for all of the signals. [b] After heating at 100 $^\circ$ C in water for 4 h.

S-PdCl₂ (Scheme 3 and Supporting Information), which lacks imidazolium units, and XPS was performed (Figure 4).

The S2p core-level XPS spectrum of POSS-Imi-PdCl₄ (Figure 4a) can be resolved into a doublet (from the S2p_{3/2} and S2p_{1/2} components that originate from the spin–orbit splitting effect contributions). However, the presence of different sulfur moieties in POSS-S-PdCl₂ is shown in Figure 4b. At least two different doublets can be thus resolved. The peak at a binding energy (BE) of 161.9 eV (16%), can be ascribed to the presence of a S \rightarrow Pd interaction, as reported previously.^[25] This interaction is absent in POSS-Imi-PdCl₄, which indicates that, in this case, the sulfur atoms play a minor role to stabilise Pd species.

A TEM investigation on the silsesquioxane-based catalyst before and after the Suzuki–Miyaura reaction was performed as well (Figure 5). TEM analysis after the Suzuki–Miyaura reaction confirmed the presence of Pd⁰. The Pd nanoparticles are well distributed and have an average dimension of 3 nm. TEM analysis after the same Suzuki–Miyaura reaction performed in the presence of bmim₂PdCl₄ also shows Pd nanoparticles with an average dimension of 3 nm. The only difference between the two catalysts could be ascribed to a slightly better dispersion of the Pd nanoparticles in the POSS-based compound.

Neither TEM nor XPS analyses provide a clear explanation for the improved catalytic performance of POSS-Imi-PdCl₄ compared to $\text{bmim}_2\text{PdCl}_4$. This higher catalytic activity could be ascribed to a proximity effect^[26] displayed by POSS-Imi-PdCl₄ (Figure 6a), in which the reaction is highly favoured by the local concentration of imidazolium moieties. Probably, a kind



Scheme 3. Structures of POSS-S and POSS-S-PdCl₂.

www.chemcatchem.org



Figure 3. Pd3d core-level XPS spectra of a) POSS-Imi-PdCl₄ and b) $bmim_2PdCl_4$ after the Suzuki–Miyaura reaction.

of phase-transfer catalysis caused by the imidazolium units linked to the silica nanocage is operative. The imidazolium units could create a local environment in which the reactants are better dissolved with respect to the aqueous phase. Indeed, ILs that contain imidazolium, phosphonium, ammonium and pyridinium cations have been shown to act as phasetransfers catalysts for fluorination, nucleophilic substitutions, etherification and benzoin condensation reactions.^[27] Recently, it was described that an imidazolium-based organic–inorganic hybrid silica enhanced the asymmetric Michael addition of 1,3dicarbonyl compounds to nitroalkenes in brine at 0.5 mol% loading by acting as a phase-transfer catalyst.^[28] These effects cannot be operative if the bmim₂PdCl₄ catalyst is used because of the absence of the nanocage (Figure 6 b).

Conclusions

For the first time, a proximity effect has been observed in the Suzuki–Miyaura reaction between arylbromides and phenylbor-



CHEMCATCHEM

Full Papers

Figure 4. S2p core-level XPS spectra of a) POSS-Imi-PdCl₄ and b) POSS-S-PdCl₂.

onic acid in water in the presence of a polyhedral oligomeric silsesquioxane-imidazolium tetrachloropalladate salt (POSS-Imi-PdCl₄) as a pre-catalyst. POSS-Imi-PdCl₄ was prepared by reaction of a polyhedral oligomeric silsesquioxane-imidazolium chloride salt with PdCl₂ and used in water at 100 °C at a low loading (0.08–0.16 mol%).

The catalytic activity of this pre-catalyst was compared with that of the corresponding pre-catalyst without the nanocage structure (1-butyl-3-methylimidazolium tetrachloropalladate). X-ray photoelectron spectroscopy and TEM did not evidence any particular stabilising role of the POSS structure. Therefore, the enhanced catalytic activity can be ascribed to a phasetransfer catalysis preformed by imidazolium units linked to the silica nanocage. The proximity of these units creates a local environment in which the reactants are better dissolved with respect to the aqueous phase.



Figure 5. TEM images of a) fresh POSS-Imi-PdCl₄, and b) POSS-Imi-PdCl₄ and c) bmim₂PdCl₄ after the Suzuki reaction between 4-bromotoluene and phenylboronic acid.



Figure 6. Schematic representation of Suzuki–Miyaura reaction in water catalysed by a) POSS-Imi-PdCl₄ and b) $bmim_2PdCl_4$. Route a shows that the reaction is highly favoured by local concentration of imidazolium moieties.

Experimental Section

General methods

All of the substrates and solvents were purchased from Sigma Aldrich and Fischer and used without further purification. Liquidstate ¹H and ¹³C NMR spectroscopy were performed by using a JEOL ECX-400 spectrometer operated at 9.4 T (399.9 MHz for ¹H and 100.5 MHz for ¹³C). Chemical shifts were referenced to the residual ¹H and ¹³C signals of the deuterated solvents. Liquid-state ²⁹Si NMR spectra were recorded by using a Bruker Avance-500 spectrometer operated at 11.7 T (99.3 MHz for $^{\rm 29}{\rm Si}{\rm)}.$ Combustion chemical analysis (C, H, N) was performed by using a Thermo Finnigan-FlashEA 1112 apparatus. TEM images were taken by using a PHILIPS TECNAI 10 instrument at 80 kV. Samples were dispersed in ethanol and deposited on a carbon-coated copper grid. XPS was performed by using a Thermo Scientific K-Alpha spectrometer equipped with a monochromatised Al anode (1486.6 eV): X-ray source: 12 kV, 1.8 mA; X-ray spot size: 200 mm. A flood gun (electrons and Ar ions at very low energy) was used to avoid possible charging effects. The analyser was operated at constant pass energy (CAE) to ensure a constant energy resolution over the whole spectrum. The analyser was operated at 200 eV pass energy for survey spectra and at 40 eV for high-resolution individual spectra. Pressure in the chamber was approximately 10⁻⁷ mbar. Analysis of the peaks was performed by using the software Thermo Avantage, based on a non-linear least squares fitting program using a weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley and Sherwood.^[29] Full width at half maximum (FWHM) values were fixed for all the signals. POSS-Imi-Cl was synthesised using a slight modification of a previous procedure.^[22]

Synthesis of POSS-Cl

POSS-vinyl (300 mg, 0.474 mmol) was added to anhydrous toluene (1.6 mL) under a N_2 atmosphere. AIBN (30 mg, 0.183 mmol) was added to the POSS-vinyl solution, and the reaction mixture was heated to 40 °C. Then, the linker 3-chloropropanethiol (0.400 mL, 4.108 mmol, 8.67 equiv.) was slowly added to the mixture, and the reaction was stirred for 6 h at 60 °C. After cooling the reaction to RT, the supernatant was removed under reduced pressure, and the

gel was solubilised in dichloromethane (0.5 mL) and precipitated with hexane (3×25 mL) at 0 °C. Finally, the gel was dried under reduced pressure to give POSS-Cl as a transparent viscous gel. Yield: 99%; ¹H NMR (400 MHz, CDCl₃): δ = 3.66 (t, 16 H, *J* = 6.2 Hz), 2.68 (t, 16 H, *J* = 8.7 Hz), 2.63 (t, 16 H, *J* = 8.7 Hz), 2.04 (m, 16 H), 1.04 ppm (t, 16 H, *J* = 8.7 Hz); ¹³C NMR (100 MHz, CDCl₃): δ = 43.8, 32.4, 29.1, 26.3, 13.2 ppm; ²⁹Si MAS NMR (99 MHz): δ = -68 ppm; elemental analysis calcd (%) for C₄₀H₈₀Cl₈O₁₂S₈Si₈ (1517.88): C 31.65, H 5.31, S 16.90; found: C 32.09, H 5.28, S 16.27.

Synthesis of POSS-Imi-Cl

POSS-CI (670 mg, 0.441 mmol) was dissolved in toluene (7.2 mL), and 1-methylimidazole (0.422 mL, 5.294 mmol, 12.00 equiv.) was added. The reaction was stirred for 4 days at 90°C, which resulted in the precipitation of a brown gel. After this time, the reaction mixture was cooled, and the supernatant was removed. The solid was washed with dichloromethane (6×20 mL) by stirring at RT and then dried under reduced pressure. Finally, it was lyophilised overnight in milliQ water (2 mL) to give POSS-Imi-Cl as a brown viscous solid. Yield: 68%; ¹H NMR (500 MHz, D₂O): δ = 7.37 (d, 8H, J = 2.0 Hz), 7.31 (d, 8H, J=2.0 Hz), 4.18 (t, 16H, J=6.9 Hz), 3.75 (s, 24H); 2.54 (t, 16H, J=8.9 Hz), 2.44 (t, 16H, J=7.0 Hz), 2.03 (m, 16H), 0.86 ppm (t, 16H, J=7.0 Hz); ¹³C NMR (125 MHz, D₂O): δ = 135.7, 123.4, 121.8, 47.9, 35.4, 28.4, 26.5, 25.2, 12.6 ppm; ²⁹Si MAS NMR (99 MHz): $\delta = -60.2$, -69.9 ppm; elemental analysis calcd (%) for $C_{72}H_{128}Cl_8N_{16}O_{12}S_8Si_8$ (2174.71): N 10.31, C 39.77, H 5.93, S 11.79; found: N 9.32, C 34.54, H 6.28, S 9.47.

Synthesis of POSS-Imi-PdCl₄

In a round-bottomed flask, POSS-Imi-Cl (70.5 mg, 0.0324 mmol) was dissolved in water (1.0 mL). PdCl₂ was added (23.06 mg, 0.1300 mmol, Imi/PdCl₂=2:1), and the reaction mixture was heated at 80 °C for 1 h. The orange mixture was cooled and stirred at RT for 16 h. After this time, the supernatant was removed under reduced pressure to give POSS-Imi-PdCl₄ as an orange powder in quantitative yield. ¹H NMR (500 MHz, D₂O): δ = 8.86 (8H), 7.59 (8H), 7.53 (8H), 4.42 (16H) 3.96 (24H) 3.01 (16H), 2.42 (16H), 2.24 (16H) 1.65 ppm (16H); ¹³C NMR (100 MHz, D₂O): δ = 136.3, 124.0, 122.3, 48.2, 35.6, 33.0, 32.1, 27.9, 13.2 ppm; elemental analysis calcd (%) for C₇₂H₁₂₈Cl₁₆N₁₆O₁₂Pd₄S₈Si₈ (2884.02): N 7.77, C 29.98, H 4.47, S 8.89; found: N 6.48, C 25.63, H 4.88, S 7.16.

Synthesis of Bmim₂PdCl₄

An aqueous solution of 1-butyl-3-methylimidazolium chloride (90.7 mg, 0.5209 mmol) was prepared in a volumetric flask (2.0 mL). Then, this solution (0.1302 mmol, 0.5 mL) and PdCl₂ (11.45 mg, 0.065 mmol) were added into a round-bottomed flask and heated at 80 °C for 1 h. The red mixture was cooled to RT and stirred for 16 h (as the procedure reported for the previous catalyst). Finally, the supernatant was removed under reduced pressure to give Bmim₂PdCl₄ as a red solid in quantitative yield. ¹H NMR (400 MHz, CD₃OD): δ =9.08 (s, 2 H), 7.72 (d, 2 H, *J*=2.0 Hz), 7.64 (d, 2 H, *J*=2.0 Hz), 4.32 (t, 4 H, *J*=8 Hz), 4.02 (s, 6 H), 1.95 (m, 4 H, *J*=8 Hz), 1.04 ppm (t, 6 H, *J*=8 Hz); ¹³C NMR (100 MHz, CD₃OD): δ =136.6, 123.7, 122.4, 49.4, 35.3, 31.8, 19.0, 12.3 ppm; elemental analysis calcd (%) for C₁₆H₃₀Cl₄N₄Pd (526.67): C 36.49, H 5.74, N 10.64; found: C 36.85, H 5.45, N 10.73.



Typical procedure for the Suzuki-Miyaura reaction

Catalyst (0.16 or 0.08 mol%), phenylboronic acid (1.100 mmol), K₂CO₃ (2.100 mmol), aryl bromide (1.000 mmol) and water (1.0 mL) were placed in a round-bottomed flask. The reaction mixture was stirred at 100 °C. After 4 h, the reaction mixture was cooled, water was added, and the mixture was extracted with dichloromethane (3×30 mL). The organic phase was dried with Na₂SO₄, filtered and concentrated under reduced pressure. The residue was passed through a short silica gel pad (petroleum ether/ethyl acetate).

Acknowledgements

The authors acknowledge the Università di Palermo and the University of Namur. L.B. gratefully acknowledges the Università di Palermo and University of Namur for a co-funded PhD fellowship. E.C. acknowledges the FNRS for a postdoctoral researcher (CR) grant. The authors acknowledge Dr. Luca Fusaro and Dr. Pierre Louette for their support in the NMR and XPS measurements, respectively.

Keywords: cage compounds · C–C coupling · palladium · phase-transfer catalysis · supported catalysts

- a) N. T. S. Phan, M. Van Der Sluys, C. W. Jones, Adv. Synth. Catal. 2006, 348, 609–679; b) A. Zapf, M. Beller, Chem. Commun. 2005, 431–440.
- [2] K. W. Anderson, S. L. Buchwald, Angew. Chem. Int. Ed. 2005, 44, 6173– 6177; Angew. Chem. 2005, 117, 6329–6333.
- [3] a) C. Torborg, M. Beller, Adv. Synth. Catal. 2009, 351, 3027–3043; b) F. Babudri, G. M. Farinola, F. Naso, J. Mater. Chem. 2004, 14, 11–34; c) Z. Peng, A. R. Gharavi, L. Yu, J. Am. Chem. Soc. 1997, 119, 4622–4632; d) J. Sakamoto, M. Rehahn, G. Wegner, A. D. Schlüter, Macromol. Rapid Commun. 2009, 30, 653–687.
- [4] a) J. Durand, E. Teuma, F. Malbosc, Y. Kihn, M. Gómez, *Catal. Commun.* 2008, 9, 273–275; b) D. Zhao, Z. Fei, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* 2004, 43, 2197–2205; c) F. McLachlan, C. J. Mathews, P. J. Smith, T. Welton, *Organometallics* 2003, 22, 5350–5357; d) V. Calò, A. Nacci, A. Monopoli, *Eur. J. Org. Chem.* 2006, 3791–3802; e) S. Navalón, M. Álvaro, H. García, *ChemCatChem* 2013, 5, 3460–3480.
- [5] a) D. N. Korolev, N. A. Bumagin, *Tetrahedron Lett.* 2006, 47, 4225–4229;
 b) D. Badone, M. Baroni, R. Cardamone, A. Ielmini, U. Guzzi, *J. Org. Chem.* 1997, 62, 7170–7173; c) N. E. Leadbeater, M. Marco, *Org. Lett.* 2002, 4, 2973–2976; d) G. A. Molander, B. Biolatto, *J. Org. Chem.* 2003, 68, 4302–4314.
- [6] H. Song, N. Yan, Z. Fei, K. J. Kilpin, R. Scopelliti, X. Li, P. J. Dyson, Catal. Today 2012, 183, 172–177.
- [7] E. Silarska, A. M. Trzeciak, J. Pernak, A. Skrzypczak, Appl. Catal. A 2013, 466, 216–223.
- [8] W. Zawartka, A. Gniewek, A. M. Trzeciak, J. J. Ziółkowski, J. Pernak, J. Mol. Catal. A 2009, 304, 8–15.
- [9] X. Yang, Z. Fei, T. J. Geldbach, A. D. Phillips, C. G. Hartinger, Y. Li, P. J. Dyson, Organometallics 2008, 27, 3971 – 3977.
- [10] E. Silarska, A. M. Trzeciak, J. Mol. Catal. A 2015, 408, 1-11.
- [11] a) J. E. L. Dullius, P. A. Z. Suarez, S. Einloft, R. F. de Souza, J. Dupont, J. Fischer, A. De Cian, *Organometallics* **1998**, *17*, 815–819; b) C. K. Lee, H. H. Peng, I. J. B. Lin, *Chem. Mater.* **2004**, *16*, 530–536; c) W. Zawartka, A. M. Trzeciak, J. J. Ziółkowski, T. Lis, Z. Ciunik, J. Pernak, *Adv. Synth. Catal.* **2006**, *348*, 1689–1698; d) C.-M. Zhong, Y.-J. Zuo, H.-S. Jin, T.-C. Wang, S.-Q. Liu, *Acta Crystallogr. Sect. E* **2006**, *62*, m2281–m2283.
- [12] a) P. P. Pescarmona, T. Maschmeyer, Aust. J. Chem. 2001, 54, 583-596;
 b) D. B. Cordes, P. D. Lickiss, F. Rataboul, Chem. Rev. 2010, 110, 2081-2173.
- [13] a) M. Lo Conte, S. Staderini, A. Chambery, N. Berthet, P. Dumy, O. Renaudet, A. Marra, A. Dondoni, *Org. Biomol. Chem.* **2012**, *10*, 3269–3277;
 b) K. Tanaka, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2013**, *86*, 1231–1239.

[14] M. Čolović, I. Jerman, M. Gaberšček, B. Orel, Sol. Energy Mater. Sol. Cells 2011, 95, 3472–3481.

CHEMCATCHEM

Full Papers

- [15] W. Zhang, J. Li, S. Jiang, Z.-S. Wang, Chem. Commun. 2014, 50, 1685– 1687.
- [16] B. J. Hendan, H. C. Marsmann, Appl. Organomet. Chem. 1999, 13, 287– 294.
- [17] M. Seino, W. Wang, J. E. Lofgreen, D. P. Puzzo, T. Manabe, G. A. Ozin, J. Am. Chem. Soc. 2011, 133, 18082–18085.
- [18] a) Y.-C. Sheen, C.-H. Lu, C.-F. Huang, S.-W. Kuo, F.-C. Chang, *Polymer* 2008, 49, 4017–4024; b) E. Ayandele, B. Sarkar, P. Alexandridis, *Nanomaterials* 2012, 2, 445.
- [19] a) S. Sakugawa, K. Wada, M. Inoue, J. Catal. 2010, 275, 280–287; b) E. S. Cozza, V. Bruzzo, F. Carniato, E. Marsano, O. Monticelli, ACS Appl. Mater. Interfaces 2012, 4, 604–607; c) M. Janssen, J. Wilting, C. Müller, D. Vogt, Angew. Chem. Int. Ed. 2010, 49, 7738–7741; Angew. Chem. 2010, 122, 7904–7907; d) S. Tang, R. Jin, H. Zhang, H. Yao, J. Zhuang, G. Liu, H. Li, Chem. Commun. 2012, 48, 6286–6288; e) Y. Leng, J. Liu, C. Zhang, P. Jiang, Catal. Sci. Technol. 2014, 4, 997–1004.
- [20] a) C.-H. Lu, F.-C. Chang, ACS Catal. 2011, 1, 481–488; b) S. E. Létant, J. Herberg, L. N. Dinh, R. S. Maxwell, R. L. Simpson, A. P. Saab, Catal. Commun. 2007, 8, 2137–2142; c) V. Ervithayasuporn, K. Kwanplod, J. Boonmak, S. Youngme, P. Sangtrirutnugul, J. Catal. 2015, 332, 62–69.
- [21] a) V. Campisciano, V. La Parola, L. F. Liotta, F. Giacalone, M. Gruttadauria, *Chem. Eur. J.* 2015, *21*, 3327–3334; b) L. A. Bivona, F. Giacalone, L. Vaccaro, C. Aprile, M. Gruttadauria, *ChemCatChem* 2015, *7*, 2526–2533; c) C. Petrucci, G. Strappaveccia, F. Giacalone, M. Gruttadauria, F. Pizzo, L. Vaccaro, *ACS Sustainable Chem. Eng.* 2014, *2*, 2813–2819; d) M. Massaro, S. Riela, G. Lazzara, M. Gruttadauria, S. Milioto, R. Noto, *Appl. Organomet. Chem.* 2014, *28*, 234–238; e) C. Pavia, F. Giacalone, L. A. Bivona, A. M. P. Salvo, C. Petrucci, G. Strappaveccia, L. Vaccaro, C. Aprile, M. Gruttadauria, *J. Mol. Catal. A* 2014, *387*, 57–62; f) C. Pavia, E. Ballerini, L. A. Bivona, F. Giacalone, C. Aprile, L. Vaccaro, M. Gruttadauria, *Adv. Synth. Catal.* 2013, *355*, 2007–2018; g) M. Gruttadauria, L. F. Liotta, A. M. P. Salvo, F. Giacalone, V. La Parola, C. Aprile, R. Noto, *Adv. Synth. Catal.* 2011, *353*, 2119–2130.
- [22] L. A. Bivona, O. Fichera, L. Fusaro, F. Giacalone, M. Buaki-Sogo, M. Gruttadauria, C. Aprile, *Catal. Sci. Technol.* 2015, *5*, 5000 – 5007.
- [23] a) S. Gil, J. Garcia-Vargas, L. Liotta, G. Pantaleo, M. Ousmane, L. Retailleau, A. Giroir-Fendler, *Catalysts* 2015, *5*, 671; b) W. K. Jóźwiak, T. P. Maniecki, *Thermochim. Acta* 2005, *435*, 151–161.
- [24] K. Okitsu, Y. Mizukoshi, H. Bandow, T. A. Yamamoto, Y. Nagata, Y. Maeda, J. Phys. Chem. B 1997, 101, 5470–5472.
- [25] a) J. C. Love, D. B. Wolfe, M. L. Chabinyc, K. E. Paul, G. M. Whitesides, J. Am. Chem. Soc. 2002, 124, 1576–1577; b) J. C. Love, D. B. Wolfe, R. Haasch, M. L. Chabinyc, K. E. Paul, G. M. Whitesides, R. G. Nuzzo, J. Am. Chem. Soc. 2003, 125, 2597–2609; c) S. Santra, K. Dhara, P. Ranjan, P. Bera, J. Dash, S. K. Mandal, Green Chem. 2011, 13, 3238–3247.
- [26] a) A. Dahan, M. Portnoy, J. Am. Chem. Soc. 2007, 129, 5860-5869; b) T. Okano, M. Iwahara, J. Kiji, Synlett 1998, 09, 243-244.
- [27] a) V. Kumar, I. J. Talisman, O. Bukhari, J. Razzaghy, S. V. Malhotra, RSC Adv. 2011, 1, 1721–1727; b) S. S. Shinde, H. M. Chi, B. S. Lee, D. Y. Chi, Tetrahedron Lett. 2009, 50, 6654–6657; c) J. Bender, D. Jepkens, H. Hüsken, Org. Process Res. Dev. 2010, 14, 716–721; d) A. Perosa, P. Tundo, M. Selva, S. Zinovyev, A. Testa, Org. Biomol. Chem. 2004, 2, 2249–2252; e) G. D. Yadav, S. P. Tekale, Org. Process Res. Dev. 2010, 14, 722–727; f) N. M. T. Lourenço, C. A. M. Afonso, Tetrahedron 2003, 59, 789–794; g) L.-W. Xu, Y. Gao, J.-J. Yin, L. Li, C.-G. Xia, Tetrahedron Lett. 2005, 46, 5317–5320; h) D. W. Kim, C. E. Song, D. Y. Chi, J. Am. Chem. Soc. 2002, 124, 10278–10279.
- [28] X. Xu, T. Cheng, X. Liu, J. Xu, R. Jin, G. Liu, ACS Catal. 2014, 4, 2137– 2142.
- [29] a) D. A. Shirley, *Phys. Rev. B* **1972**, *5*, 4709–4714; b) P. M. A. Sherwood in *Practical Surface Analysis* (Ed.: M. P. S. D. Briggs), Wiley, New York, **1990**, 190.

Received: February 8, 2016 Revised: February 25, 2016 Published online on April 26, 2016