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Recoverable Palladium Catalysts for Suzuki–Miyaura Cross-Coupling Reactions Based on Organic-Inorganic Hybrid Silica Materials Containing Imidazolium and Dihydroimidazolium Salts

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Abstract: The systems formed by palladium acetate [$Pd(OAc)_2$] and hybrid silica materials prepared by sol-gel from monosilylated imidazolium and disilylated dihydroimidazolium salts show catalytic activity in Suzuki–Miyaura cross-couplings with challenging aryl bromides and chlorides. They are very efficient as recoverable catalysts with aryl bromides. Recycling is also possible with aryl chlorides, although with lower conversions. *In situ* formation of palladium nanoparticles has been observed in recycling experiments.

Keywords: catalyst recycling; nanoparticles; organic-inorganic hybrid composites; palladium; sol-gel processes; Suzuki–Miyaura reaction

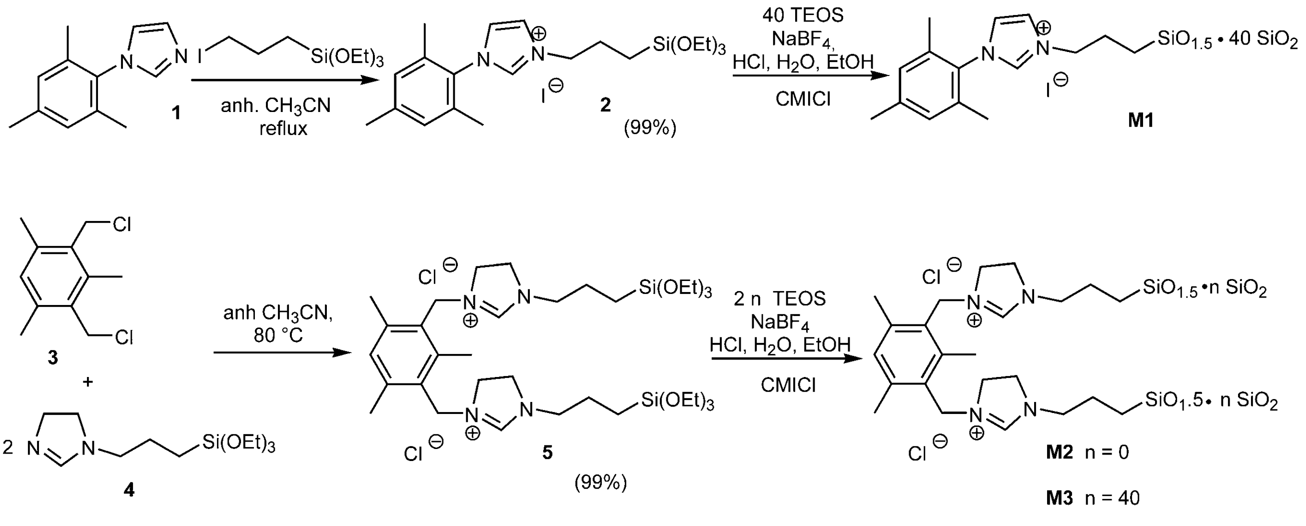
Introduction

The palladium-catalyzed Suzuki–Miyaura cross-coupling[1] reaction constitutes a powerful methodology for C–C bond formation that is widely used in synthetic organic chemistry. On the other hand, the efficient recovery and recycling of homogeneous transition metal catalysts remains a scientific challenge of economic and environmental relevance. One of the most useful strategies for this purpose involves the immobilization of homogeneous catalysts on polymeric organic[2] or inorganic[3] supports. Some of us have described the heterogenization of air- and moisture-stable phosphane-free macrocyclic triolefinic Pd(0) complexes by covalent anchoring to a cross-linked polystyrene[4] or silica matrix.[5] We have tested the activity of these supported versions as recyclable catalysts in Suzuki–Miyaura coupling and telomerization reactions. These heterogenized macrocyclic complexes were only active with aryl iodides and we then turned to other phosphane-free palladium systems based on bipyridin-2-ylmethane-type ligands for the more challenging bromides and chlorides. We have found that hybrid silica materials covalently Si–C bonded to di(2-pyridyl)methylamine-palladium dichloride complex are efficient recyclable catalysts for Heck and Sonogashira reactions with aryl bromides and for Suzuki–Miyaura couplings with aryl bromides and chlorides.[6] N-heterocyclic carbenes (NHC) derived from imidazolium and dihydroimidazolium salts are another class of ancillary ligands that allow the formation of versatile, stable and efficient Pd catalytic systems for C–C bond forming reactions.[7] Although several Pd-NHC complexes are described in the literature, in some cases they are formed *in situ* from the corresponding salt and a palladium source.[8] There are few precedents of immobilization of Pd-NHC complexes in a silica matrix[7e,f,9] for Suzuki, Heck and Sonogashira reactions. We describe here the preparation of organic-inorganic hybrid silica materials containing imidazolium and dihydroimidazolium salts from mono- and disilylated monomers and the activity and recyclability in Suzuki–Miyaura cross-coupling of catalytic systems formed by a Pd(II) salt and these hybrid silicas.

Results and Discussion

The synthesis of the monomers **2** and **5** and hybrid materials **M1**, and **M2** and **M3** derived thereof are summarized in Scheme 1. 1-Mesitylimidazole,[10,11] **1**, was reacted with (3-iodopropyl)triethoxysilane[12] in refluxing anhydrous acetonitrile under argon for 24 h to afford the hygroscopic silylated imidazolium salt **2** in 99% yield. The co-gelification of **2** with tetraethyl orthosilicate (TEOS) (1:40) in ethanolic hydrochloric acid solution at 40 °C with sodium tetrafluoroborate[13] as a promoter for hydrolytic condensation of alkoxysilanes and 1-cetyl-3-methylimidazolium chloride (CMICl) as cationic surfactant[13] ($[\mathrm{CMICl}]_0/[\mathrm{NaBF_4}]_0/[\mathrm{TEOS}]_0/[\mathbf{2}]_0/[\mathrm{H_2O}]_0/[\mathrm{HCl}]_0/[\mathrm{EtOH}]_0 = 1.0{:}0.5{:}3.8{:}0.09{:}643{:}32{:}21$) afforded material **M1**. The reaction of commercial bis(chloromethyl)mesitylene **3**, with commercial 1-(3-triethoxysilyl)propyl-4,5-dihydro-1*H*-imidazole, **4**, in anhydrous acetonitrile at 80 °C under argon for 24 h gave the salt **5** in 99% yield as an hygroscopic white solid. This disilylated monomer **5** was hydrolyzed at 40 °C in the absence of TEOS under acidic conditions in presence of the same cationic surfactant[13] ($[\mathrm{CMICl}]_0/[\mathrm{NaBF_4}]_0/[\mathbf{5}]_0/[\mathrm{H_2O}]_0/[\mathrm{HCl}]_0/[\mathrm{EtOH}]_0 = 1.0{:}0.5{:}0.8{:}630{:}31{:}20$) but as no gel or precipitate was formed in acidic medium, aqueous 6.5 M NaOH solution was added until pH 7 to promote polycondensation and to afford material **M2**. The co-gelification of **5** with TEOS (1:80) under analogous acidic conditions[13] ($[\mathrm{CMICl}]_0/[\mathrm{NaBF_4}]_0/[\mathrm{TEOS}]_0/[\mathbf{5}]_0/[\mathrm{H_2O}]_0/[\mathrm{HCl}]_0/[\mathrm{EtOH}]_0 = 1.0{:}0.5{:}3.7{:}0.046{:}641{:}32{:}20$) gave **M3**. In this case no base was added.

The materials were characterized by solid state ^{29}Si NMR, ^{13}C NMR for **M2**, surface area BET measurements, IR and elemental analysis (see Supporting Information). **M2** prepared from disilylated **5** without TEOS shows a very low surface area (2 $\mathrm{m^2\,g^{-1}}$) resulting from the voluminous organic fragment in the material as already observed before.[14] **M1** and **M3** present higher values (506 and 266 $\mathrm{m^2\,g^{-1}}$, respectively). **M1** and **M3** have pore diameters of 3.1–2.7 and 4.3–4.2 nm and pore volumes of 0.307–0.364 and 0.262–0.253 $\mathrm{cm^3\,g^{-1}}$, respectively. **M1** presents a nitrogen sorption isotherm of type IV according to IUPAC, superimposed with the isotherm of smaller mesopores (Figure 1 b). Accordingly, the BJH calculation for the pore-size distribution of **M1** from the desorption data reveals a bimodal distribution centered at 2.0 and 3.1 nm whereas **M3** presents a pore-size distribution centered at 2.1 nm. In both cases the desorption branches of the isotherm are sharp indicating periodic pore structure. Powder X-ray diffraction (p-XRD) of **M1** exhibits a 2D hexagonal *p6mm* mesopore structure (MCM-41 type) as expected[13] (Figure 1 a) with three diffraction peaks attributable to the d_{100}, d_{110} and d_{200} planes (4.1, 2.5 and 2.1 nm, respectively). This indexation clearly shows the existence of a hexagonal mesoporous phase. Contrarily, **M3** exhibits a worm-like mesoporous organization while **M2** is even less organized with no mesoporosity at all (see Supporting Information). This is mainly due to the increasing ratio of the organic moiety to silica which may interact with the surfactant disfavouring the formation of periodic mesoporous structures. Moreover in the case of **M2** NaOH was added to favour the solid formation of the material. The basic catalyst may alter and disrupt the supramolecules of the surfactant and thus leading to a non-ordered material. The results of elemental analyses of N reveal that the materials **M1**, **M2**, and **M3** contain 0.585, 7.432 and 0.828 mmol N/g, respectively. The solid state ^{29}Si NMR spectra of **M1** and **M3** show two groups of chemical shifts: T units at around −55 to −68 ppm, re-



Scheme 1. Synthesis of hybrid silica materials **M1**–**M3**.

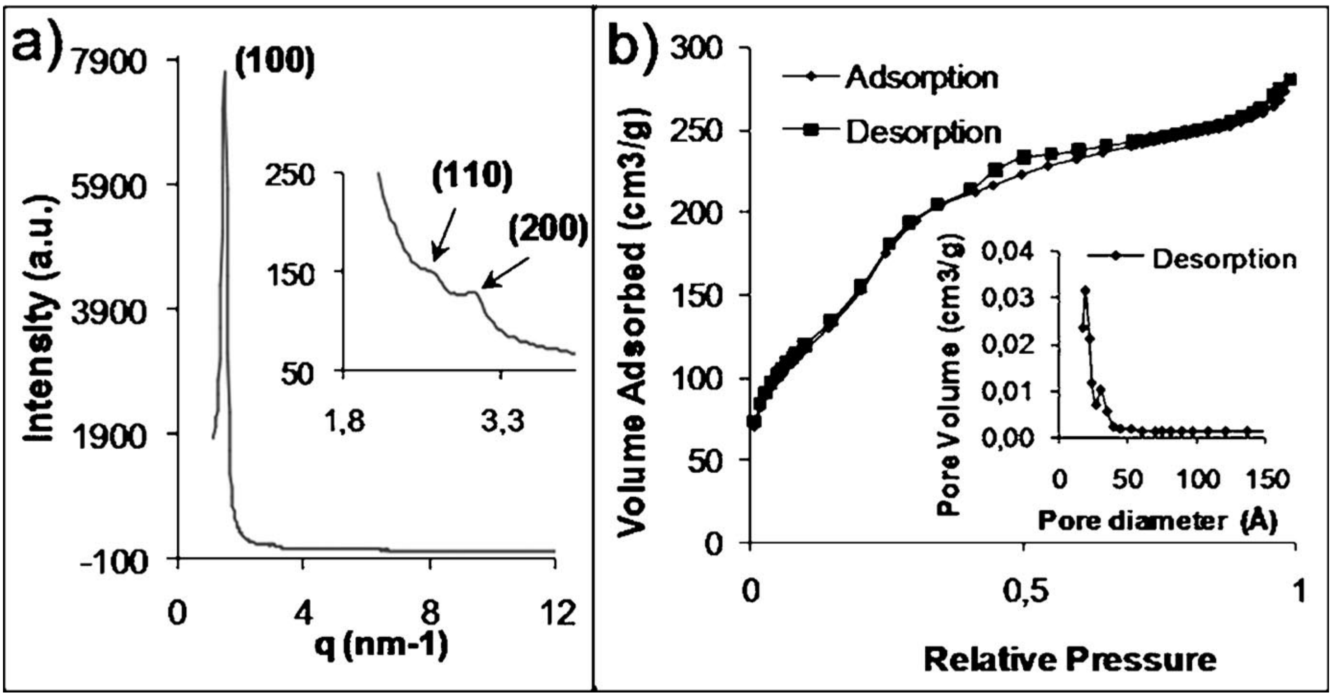
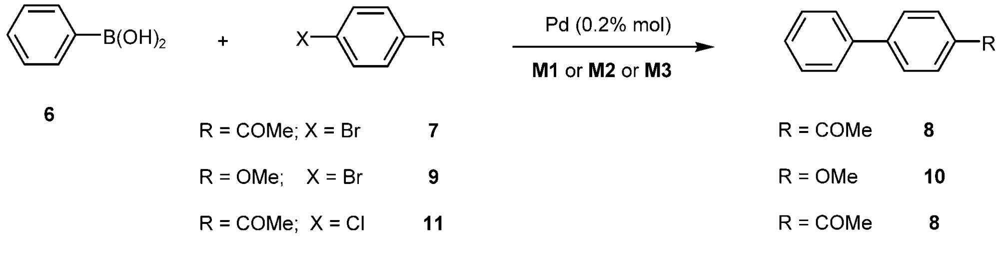


Figure 1. a) *p*-XRD of **M1**; b) N_2 sorption isotherm of **M1** and plot of the pore size distribution.

sulting from the hydrolysis-condensation of the corresponding monomers **2** and **5**, and Q units ranging from −96 to −110 ppm formed from TEOS. As expected, **M2** spectrum shows only T^2 and T^3 units at −57.3 and −65.6 ppm showing that no Si−C bond cleavage occurred during the hydrolysis process.

Mixtures of $Pd(OAc)_2$ (0.2% mol) and these materials (0.2–0.4% mol) were tested as catalytic systems in the Suzuki cross-couplings of phenylboronic acid **6** (1.5 equiv.) with *p*-bromoacetophenone **7**, *p*-bromoanisole **9** and *p*-chloroacetophenone **11** to give the corresponding biaryls **8** and **10** (Scheme 2 and Table 1).

The three materials **M1–M3** gave efficient and fast reactions with the activated aryl bromide **7** giving almost quantitative isolated yields of **8** in 0.5–1 h under the conditions indicated in Table 1 (A: K_2CO_3, DMF-H_2O 95:5, 110 °C) (entries 1–3). The same conditions were assayed for the deactivated aryl bromide **9** and material **M2** (entry 4), incomplete conversion of **9** being obtained (74%) after 24 h. The formation of a small amount of biphenyl (8% GC yield) by homocoupling of phenylboronic acid **6** was observed. The use of degassed solvents and a nitrogen atmosphere improved the conversion to 88% (entry 5). A similar result (90% conversion at 24 h) was obtained when the base was changed to Cs_2CO_3 and the solvent was anhydrous and degassed dioxane at the same temperature (110 °C) (conditions B, entry 6), although biphenyl formation could not be completely avoided. Contrarily, the reaction performed in degassed THF-H_2O 80:20 at 90 °C in the presence of potassium carbonate was clearly more sluggish (conditions C, entry 7). The 33% conversion achieved after 3 h was not increased after prolonged heating. Material **M3** gave superior performance for the same reaction and a quantitative yield of the coupling product **10** was achieved after 5 h (conditions A: K_2CO_3, DMF-H_2O 95:5, 110 °C) (entry 8). Material **M1** was also tested under two sets of conditions A and B (entries 9 and 10). The use of potassium carbonate in DMF-H_2O



Scheme 2. Suzuki cross-couplings catalyzed by PdX_2/**M** systems.

Table 1. Suzuki cross-couplings between phenylboronic acid **6** and aryl halides **7**, **9** and **11** with Pd/**M** systems[a] (Scheme 3).

Entry	ArX	**M** (% mol)	Conditions[b]	*t* [h]	Ph-Ar (%)	Ph-Ph (%)
1	**7**	**M1** (0.4)	A	1	**8** (99)[c]	–
2	**7**	**M2** (0.2)	A	0.5	**8** (96)[c]	–
3	**7**	**M3** (0.2)	A	1	**8** (100)[c]	–
4	**9**	**M2** (0.2)	A	24	**10** (74)[d]	8
5	**9**	**M2** (0.2)	A[e]	24	**10** (88)[d]	–
6	**9**	**M2** (0.2)	B[f]	24	**10** (90)[d]	3
7	**9**	**M2** (0.2)	C[e]	3	**10** (33)[d,g]	–
8	**9**	**M3** (0.2)	A	5	**10** (100)[c]	–
9	**9**	**M1** (0.4)	A[e]	5	**10** (94)[d]	–
10	**9**	**M1** (0.4)	B[f]	5	**10** (63)[d]	–
11	**11**	**M3** (0.2)	D	24	**8** (34)[h]	11
12	**11**	**M3** (0.2)	E	24	**8** (46)[h]	8
13[i]	**11**	**M3** (0.2)	D	24	**8** (37)[h]	8

[a] $Pd(OAc)_2$ (0.2% mol) was used, except for entry 13.

[b] A: K_2CO_3, DMF-H_2O 95:5, 110 °C; B: Cs_2CO_3, dioxane, 110 °C; C: K_2CO_3, THF-H_2O 80:20, 90 °C; D: K_2CO_3, DMF-H_2O 95:5, 150 °C; E: Cs_2CO_3, DMF-H_2O 95:5, 150 °C.

[c] Isolated yields.

[d] Conversion of **9** (GC, undecane).

[e] Degassed.

[f] Anhydrous and degassed.

[g] The conversion was not improved after prolonged heating (24 h).[h] GC yield of **8** (undecane).

[i] $PdCl_2$ (0.2% mol) was used.

Table 2. Recyclability of Pd/**M** systems for the reaction of phenylboronic acid **6** with *p*-bromoacetophenone **7** to give **8** (see Scheme 2).[a]

Cycle	**M1**		**M2**		**M3**	
	t [h]	%[b]	*t* [h]	%[b]	*t* [h]	%[b]
1	1	99	0.5	96	1	100
2	1	83	4.5	94	1	99
3	1	87	4.5	95	1	98
4	1	91	4.5	97	1	99
5	1	87	4.5	99	1	97

[a] Conditions: $Pd(OAc)_2$ (0.2%), **M** (0.2 or 0.4%), K_2CO_3, DMF-H_2O 95:5, 110 °C.

[b] Isolated yields.

Table 3. Recyclability of Pd/**M** systems for the reaction of phenylboronic acid **6** with *p*-bromoanisole **9** to give **10** (see Scheme 2).[a]

Cycle	**M2**				**M3**	
	Conditions A[b]		Conditions B[b]		Conditions A	
	t [h]	%[c]	*t* [h]	%[c]	*t* [h]	%[d]
1	24	88	24	90	5	100
2	24	67	24	31	5	65
3					5	68
4					5	54
5					24	85

[a] Conditions A: $Pd(OAc)_2$ (0.2%), **M** (0.2%), K_2CO_3, DMF-H_2O 95:5, 110 °C. Conditions B: $Pd(OAc)_2$ (0.2%), **M** (0.2%), Cs_2CO_3, dioxane, 110 °C.

[b] Degassed solvents.

[c] Conversion of **9** (GC).

[d] Isolated yields of **10**.

95:5 gave higher conversions than cesium carbonate in dioxane for the same temperature (110 °C) and the same reaction time (5 h).

The reaction of **6** with the more challenging aryl chloride **11** was undertaken under three different conditions (entries 11–13). The system $Pd(OAc)_2$/**M3** with two different bases (potassium and cesium carbonate) in DMF-H_2O 95:5 at 150 °C (conditions D and E) gave moderate yields of **8** after 24 h, formation of biphenyl being a competitive process for the consumption of phenylboronic acid. The use of palladium chloride instead of palladium acetate under conditions D gave similar results (entry 11 *vs* entry 13).

The reusability of the catalytic systems Pd/**M** for aryl bromides and chlorides (Scheme 2) is shown in Table 2, Table 3 and Table 4.

The systems $Pd(OAc)_2$/**M** were found to be excellent recyclable catalysts for the Suzuki reaction of phenylboronic acid **6** with *p*-bromoacetophenone **7.** The dihydroimidazolium salt-based materials **M2** and **M3** gave slightly better performance than the imidazolium based material **M1**, as no decrease in activity was observed after five cycles and almost quantitative yields of the coupling product **8** were isolated (Table 2).

For the Suzuki coupling of phenylboronic acid **6** with deactivated aryl bromide **9** Pd/**M3** remains superior to Pd/**M2** system (Table 3), the former giving

Table 4. Recyclability of Pd/**M3** system for the reaction of phenylboronic acid **6** with *p*-chloroacetophenone **11** to give **8** (see Scheme 2).[a]

Cycle	Conditions D[b]		Conditions D[c]	
	t [h]	%[d]	*t* [h]	%[d]
1	24	34	24	37
2	24	12	24	25
3	24	13	24	10

[a] Conditions D: PdX_2 (0.2%), **M3** (0.2%), K_2CO_3, DMF-H_2O 95:5, 150 °C.

[b] $Pd(OAc)_2$ was used.

[c] $PdCl_2$ was used.

[d] GC yield of **8**.

faster reactions. Although a decrease of activity is observed upon recycling, by increasing the reaction time high isolated yields of **10** could be achieved in the fifth cycle. For material **M2** only two cycles were tested under the conditions previously mentioned in entries 5 and 6 of Table 1. Although similar conversions are attained in the first run, the solvent system DMF-H_2O 95:5 is clearly superior to dioxane in terms of reusability.

Only Pd/**M3** systems were tested as recyclable catalysts for the Suzuki coupling of phenylboronic acid **6** with the aryl chloride **11**, introducing the palladium either as $Pd(OAc)_2$ or as $PdCl_2$ (Table 4) under the conditions D previously mentioned in entries 11 and 13 of Table 1. Although the yields are modest, the reusability of this system has been proved with this challenging substrate. In most cases described in the literature for NHC-based supported catalysts[9,15] only recycling experiments with aryl iodides or aryl bromides are reported. Even if phosphane ligands are more prone to oxidation, silica sol-gel entrapped dichlorobis(triphenylphosphane)palladium has been described[16] as an efficient catalyst in Suzuki cross-couplings, although significant amounts of homocoupling products are also obtained and the recycling of the catalyst is only reported for the reaction of phenylboronic acid with 4-bromotoluene.

ICP determination of the amount of Pd in products **8** and **10** which were isolated from entries 3 and 8 of Table 1 gave respectively 6.4 and 22.9 ppm. When the catalyst **M3** was filtered off from the hot reaction mixture of the first cycle of Table 3 after 5 min (50% GC conversion of **9**) and the remaining filtrate was made to react at the same temperature, the conversion rose up to 79% after 30 min (the conversion was 95% after 30 min for the first cycle without catalyst filtration) and up to 89% after 5 h. Thus, a homogeneous pathway is mainly operating in the catalysis.

High-resolution transmission electron microscopy (HR-TEM) of the grey solid material Pd/**M3** recovered after the 5th cycle of the reaction of Table 2 revealed Pd nanoparticles of 3.1 nm (Figure 2). Electron diffraction (ED) of the sample showed the pattern characteristic of face-centered cube (fcc) Pd(0) (d-spacings found = 0.224, 0.194, 0.139, 0.117 nm). Furthermore, the worm-like porous structure of the material is maintained (Figure 2b). Similar generation of Pd nanoparticles from $Pd(OAc)_2$ and tetralkylammo-

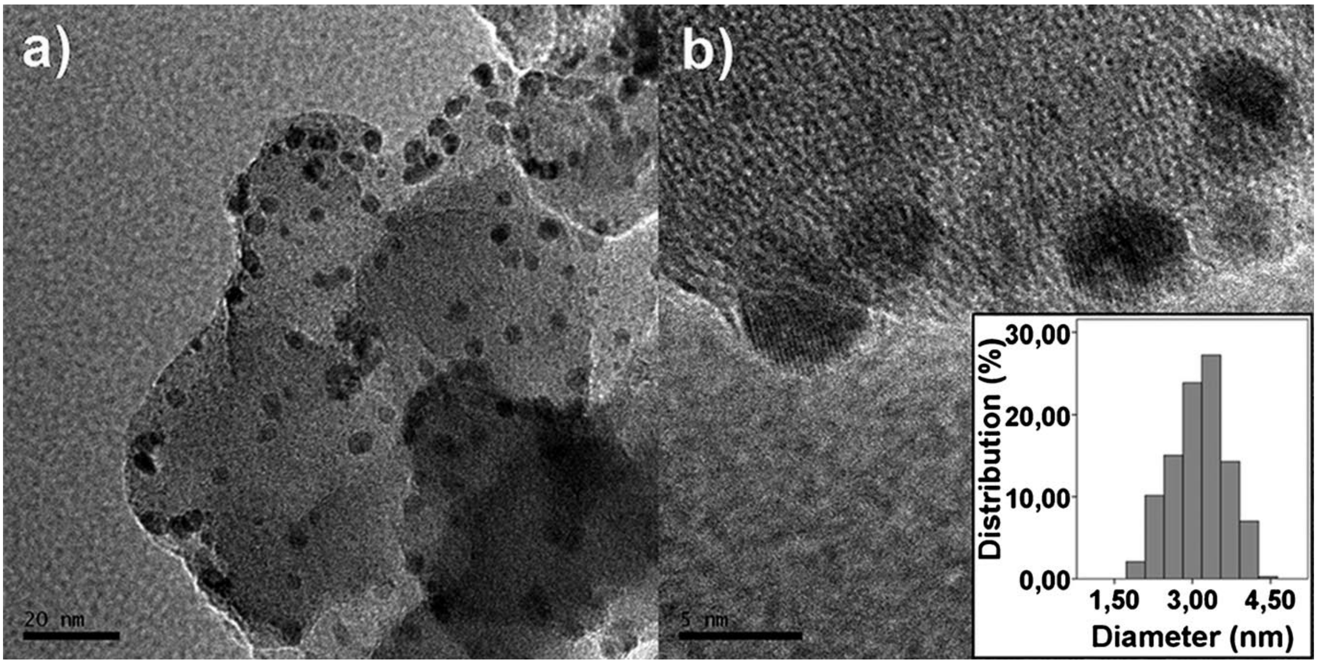


Figure 2. a) and b) HR-TEM micrographs of Pd nanoparticles. The inset in b) shows the particle size distribution (385 particles; mean particle size: 3.1 ± 0.5).

nium or imidazolium salts and from Pd-N-heterocyclic carbenes has already been reported.[17] The role of palladium nanoparticles (as catalyst precursors or formed *in situ* from homogeneous or supported complexes during the course of the reaction) in C−C coupling reactions has recently been reviewed.[18] Some reports describe the catalytic activity in Suzuki coupling of silica-supported Pd nanoparticles.[19] In some of these cases, the silica support is functionalized with coordinating amino, phosphino or thiol groups, which undoubtedly should contribute to metal nanoparticles stabilization. However, only aryl iodides and bromides are reported as successful, the reaction coupling with aryl chlorides either fails or is not mentioned. The recycling experiments refer only to aryl iodides or to activated aryl bromides.

Carbenes and bulky electron-rich aliphatic phosphanes appear to be the best ligands in homogeneous palladium catalysis for the activation of challenging aryl chlorides in C−C coupling reactions[20] by promoting the *in situ* formation of coordinatively unsaturated species PdL_n ($n=1$ or 2), which function as the actual highly catalytic species. The high donicity of these ligands favour the oxidative addition to the C−Cl bond and contribute to the stabilization of these intermediate species. These basic aliphatic phosphanes are readily oxidized to their corresponding phosphane oxides, which can prevent the easy recovery and reuse of the catalytic systems. For this reason carbenes seem more appropriate than aliphatic phosphanes for supported palladium catalysts. Homogeneous N-heterocyclic carbene-palladium complexes for C−C coupling with aryl chlorides are, in most cases, formed *in situ* from a palladium source and the corresponding imidazolium or dihydroimidazolium salt. Some authors have observed the formation of palladium(0) nanoparticles from the decomposition of Pd-NHC complexes[9b,c] or from the C−C coupling reactions performed in imidazolium-based ionic liquids.[17] Stabilization of transition-metal nanoparticles in imidazolium (and dihydroimidazolium) salts probably relies on the intrinsic charge of these salts which creates an electrostatic colloid-type protection.[17b] Nevertheless, Finke[21] has shown some evidence for the formation of N-heterocyclic carbenes in the generation of Ir(0) nanoparticles in imidazolium-based ionic liquid media.[17b] He concluded that the Ir(0) nanoclusters react with imidazolium-based IL to form surface-attached carbenes, at least as transient species, that should contribute to stabilize the nanoclusters.

The *in situ* generation of palladium nanoparticles in reactions catalyzed by recyclable supported palladium complexes should be more evident than in homogeneous catalytic versions, as darkening of the recovered material is observed in successive cycles in the former case.[6] However, Pd(0) nanoparticle formation has not always been claimed before for NHC-based supported catalysts.[7f,9,15] A reaction cycle for C−C couplings with supported Pd catalysts may be complex and present a considerable number of processes involving Pd colloids on the support or in the solution, molecular Pd(0) and Pd(II) species supported or in the solution. The dissolution and redeposition of palladium has been proven by several authors[18] for supported catalysts and seems to be effective in our case. Undoubtedly, both the inorganic matrix and the organic moiety of our hybrid materials have a contribution to the nanoparticle stabilization and prevent metal agglomeration. The imidazolium and dihydroimidazolium salts should facilitate a good dispersion of metal nanoparticles in the material. The structuring and high porosity of the materials should facilitate diffusion of reactants but surely the structure of the organic ligand present in the hybrid material is a more important point for its catalytic activity and recyclability.[6]

Conclusions

In summary, we have prepared hybrid materials from monosilylated imidazolium and disilylated dihydroimidazolium salts in acidic conditions using $NaBF_4$ and CMICl. **M1** and **M3** are mesostructured materials (hexagonal and worm-like organization). Mixtures of $Pd(OAc)_2$ and these hybrid materials were efficient recyclable catalysts for Suzuki cross-couplings with aryl bromides. The activity and recyclability with activated aryl chlorides are modest. *In situ* formation of Pd nanoparticles in recycling experiments has been observed by HR-TEM. Further work to test these systems in other palladium C−C bond forming reactions is in progress.

Experimental Section

General Remarks

When required, experiments were carried out with standard high vacuum and Schlenk techniques. Solvents were dried and distilled just before use. The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX250. HR-MS have been determined at Servei d'Anàlisi Química at the Universitat Autònoma de Barcelona with an ESI hybrid quadrupole time of flight microTOFQ spectrometer of Bruker Daltonics. IR data were obtained in a Perkin–Elmer (System 2000 FT-IR) spectrophotometer. The CP-MAS ^{13}C and ^{29}Si solid state NMR spectra of **M1** and **M2** were recorded on a Bruker AV-400-WB and on a Bruker FT-AM 400 in the case of **M3**. Surface areas were determined by the Brunauer–Emmett–Teller (BET) method on a Micromeritics Tristar 3000 analyzer, and the average pore diameter was calculated by the BJH method. Elemental analyses have been performed at the Serveis Cientificotècnics of the Universitat de Barcelona. The content of palladium was determined at the Serveis

Cientificotècnics of the Universitat de Barcelona by inductively coupled plasma (ICP). Transmission electron microscopy (TEM) observations of **M1** were carried out in Montpellier with a JEOL 1200 EXII (100 kV). High resolution transmission electron microscopy (HR-TEM) observations were carried out at the Servei de Microscòpia of the Universitat Autònoma de Barcelona with a JEOL JEM 2011 (200 kV). X-ray diffraction experiments were carried out on solid powders in 1 mm diameter glass capillaries, in the Laboratoire des Colloïdes, Verres et Nanomatériaux (UMR5587), Université de Montpellier II, France, working in a transmission configuration. A copper rotating anode X-ray source (functioning at 4 kW) with a multilayer focusing "Osmic" monochromator giving high flux (10^8photons/sec) and punctual collimation was employed. An "Image plate" 2D detector was used. Diffraction curves were obtained giving diffracted intensity as a function of the wave vector q. Diffracted intensity was corrected by exposition time, transmission and intensity background coming from diffusion by an empty capillary.

Synthesis of 1-Mesityl-3-(3-(triethoxysilyl)propyl)-1*H*-imidazol-3-ium Iodide (2)

A solution of 1-mesitylimidazole **1** (0.101 g, 0.542 mmol) and (3-iodopropyl)triethoxysilane (0.181 g, 0.545 mmol) in anhydrous CH_3CN (3 mL) was stirred under argon at reflux temperature for 24 h. The solvent was evaporated to afford **2** as a hygroscopic solid; yield: 0.278 g (99%). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.63$–0.70 (m, 2H), 1.22 (t, 9H, $J = 7.0$ Hz), 2.00–2.10 (m, 8H), 2.34 (s, 3H), 3.83 (q, 6H, $J = 7.0$ Hz), 4.74 (t, 2H, $J = 7.0$ Hz), 7.01 (s, 2H), 7.17 (s, 1H), 7.68 (s, 1H), 10.07 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 6.6$, 17.5, 18.1, 20.8, 24.3, 51.8, 58.4, 123.5, 123.6, 129.6, 130.3, 133.9, 136.6, 140.9; HR-MS: $m/z = 391.2404$ (calcd. for $C_{21}H_{35}N_2O_3Si$: 391.2411).

Synthesis of 3,3′-(2,4,6-Trimethyl-1,3-phenylene)bis(methylene)bis{1-[3-(triethoxysilyl)propyl]-4,5-dihydro-1*H*-imidazol-3-ium} Chloride (5)

A solution of commercial 2,4-bis(chloromethyl)mesitylene **3** (0.318 g, 1.44 mmol) and commercial 1-[3-(triethoxysilyl)-propyl]-4,5-dihydro-1*H*-imidazole **4** (0.8 mL, 0.804 g, 2.87 mmol) in anhydrous CH_3CN (4 mL) was stirred under argon at 80 °C for 24 h. The solvent was evaporated to afford **5** as a white hygroscopic solid; yield: 1.094 g (99%). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.41$–0.48 (m, 4H), 1.09 (t, 18H, $J = 7.0$ Hz), 1.58 (quint., 4H, $J = 7.8$ Hz), 2.20 (s, 6H), 2.33 (s, 3H), 3.58 (t, 4H, $J = 7.4$ Hz), 3.68 (q, 12H, $J = 7.0$ Hz), 3.85–4.12 (m, 8H), 4.63 (s, 4H), 6.88 (s, 1H), 9.46 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 7.3$, 16.8, 18.4, 20.2, 21.2, 47.0, 48.3, 49.6, 50.5, 58.6, 127.7, 131.8, 139.3, 157.8; HR-MS: $m/z = 729.4201$ (calcd. for $C_{35}H_{66}ClN_4O_6Si_2$: 729.4209).

Synthesis of Material M1

1-Cetyl-3-methylimidazolium chloride (1.962 g, 5.72 mmol), sodium tetrafluoroborate (0.333 g, 2.972 mmol), hydrochloric acid (15 mL of conc. HCl, 0.181 mol HCl, 0.624 mol of water) and distilled and deionized water (55 mL, 3.053 mol) were mixed and stirred together at 40 °C. In a few minutes an emulsion was formed. A solution of the silylated monomer **2** (0.278 g, 0.536 mmol) and TEOS (4.566 g, 0.0219 mol) in absolute ethanol (7 mL, 0.120 mol) was added over the emulsion and stirred together at 40 °C overnight. The resulting powder was filtered, washed twice with water and three times with ethanol. The solid **M1** was obtained after template removal by Soxhlet extraction with acetone overnight, powdering and drying under vacuum at 70 °C during 6 h; yield: 1.369 g. S_{BET}: 506 m^2g^{-1}; pore diameter: 3.1–2.7 nm; pore volume: 0.307–0.364 cm^3g^{-1}; IR (KBr): $\nu = 3406$, 1627, 1090 (broad), 960, 803, 470 cm^{-1}; ^{29}Si CP-MAS NMR: $\delta = -66.3$ (T^3), −100.5 (Q^3), −109.6 (Q^4); anal. (%) found: N 0.82

Synthesis of Material M2

1-Cetyl-3-methylimidazolium chloride (2.003 g, 5.839 mmol), sodium tetrafluoroborate (0.333 g, 2.972 mmol), hydrochloric acid (15 mL of conc. HCl, 0.181 mol HCl, 0.624 mol of water) and distilled and deionized water (55 mL, 3.053 mol) were mixed and stirred together at 40 °C. In a few minutes an emulsion was formed. A solution of the disilylated monomer **5** (3.436 g, 4.486 mmol) in absolute ethanol (7 mL, 0.120 mol) was added over the emulsion and stirred together at 40 °C for one day. As no solid was formed, a 6.5 M NaOH aqueous solution was added (25 mL, until pH 7). After stirring the mixture overnight, the resulting powder was filtered, washed twice with water and three times with ethanol. The solid **M2** was obtained after template removal by Soxhlet extraction with acetone overnight, powdering and drying under vacuum at 70 °C during 6 h; yield: 2.141 g. S_{BET}: 2 m^2g^{-1}; IR (KBr): $\nu = 3410$, 2939, 1653, 1454, 1305, 1252, 1200, 1098 (broad), 915, 782, 696, 464 cm^{-1}; ^{13}C CP-MAS NMR: $\delta = 16.7$, 35.1, 42.9, 125.2, 135.1, 153.9; ^{29}Si CP-MAS NMR: $\delta = -57.3$ (T^2), −65.6 (T^3); anal. (%) found: N 10.41

Synthesis of Material M3

1-Cetyl-3-methylimidazolium chloride (6.803 g, 19.833 mmol), sodium tetrafluoroborate (1.105 g, 9.862 mmol), hydrochloric acid (52 mL of conc. HCl, 0.63 mol HCl, 2.16 mol of water) and distilled and deionized water (190 mL, 10.55 mol) were mixed and stirred together at 40 °C. In a few minutes an emulsion was formed. A solution of the disilylated monomer **5** (0.702 g, 0.916 mmol) and TEOS (15.561 g, 0.0732 mol) in absolute ethanol (23 mL, 0.394 mol) was added over the emulsion and stirred together at 40 °C for 3 days. The resulting powder was filtered, washed twice with water and three times with ethanol. The solid **M3** was obtained after template removal by Soxhlet extraction with acetone overnight, powdering and drying under vacuum at 90 °C overnight; yield: 4.875 g. S_{BET}: 266 m^2g^{-1}; pore diameter: 4.3–4.2 nm; pore volume: 0.262–0.253 cm^3g^{-1}; IR (KBr): $\nu = 3408$, 1653, 1020 (broad), 956, 801, 468 cm^{-1}; ^{29}Si CP-MAS NMR: $\delta = -61.5$ (T^3), −95.9 (Q^3), −105.3 (Q^4); anal. (%) found: N 1.16

Suzuki Cross-Coupling between 6 and 7 to give 8; Typical Procedure

K_2CO_3 (0.829 g, 6 mmol) was added to a stirred mixture of **M3** (0.029 g, 0.207 mmol ligand/g, 0.006 mmol), $Pd(OAc)_2$ (0,0013 g, 0.006 mmol), **6** (0.560 g, 4.5 mmol) and **7** (0.609 g, 3 mmol) in DMF/H_2O (95:5) (6 mL) which was then heated at 110 °C for 1 h (GLC monitoring). Product **8** was precipitated by the addition of water to the crude mixture. The filtered solid was washed with water and then taken up in ethyl acetate. Insoluble **M3** was filtered. The filtrate was dried with anhydrous sodium sulfate and the solvent was evaporated to give pure **8**; yield: 0.587 g (100%).

The material **M3** was washed successively with water, ethanol and diethyl ether, then it was dried and reused in the next run. Mp of **8**: 120–121 °C, Lit.[22] mp 120.5 °C; ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 2.65$ (s, 3H), 7.40–7.51 (m, 3H), 7.63 (d, 2H, $J = 6.7$ Hz), 7.69 (d, 2H, $J = 8.4$ Hz), 8.04 (d, 2H, $J = 8.4$ Hz); IR (ATR): $\nu = 3067$, 2994, 1674, 1594, 1357, 1257, 955, 835, 761 cm^{-1}.

Compound **10** was obtained by an analogous procedure. Mp 84–85 °C, Lit.[23] mp 84–85 °C; ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 3.88$ (s, 3H), 7.02 (d, 2H, $J = 8.8$ Hz), 7.34 (tt, 1H, $J = 7.3$ Hz, $J = 1.7$ Hz), 7.45 (t, 2H, $J = 7.3$ Hz), 7.54–7.61 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) $\delta = 55.7$, 114.5, 127.0, 127.1, 128.5, 129.0, 134.1, 141.1, 159.5; IR (ATR): $\nu = 3003$, 2938, 1604, 1521, 1463, 1247, 1183, 1034, 833, 758, 686 cm^{-1}.

Supporting Information

Characterization data for materials **M1** (^{29}Si CP-MAS NMR, IR, TEM, BET, *p*-XRD), **M2** (^{29}Si CP-MAS NMR, ^{13}C CP-MAS NMR, IR, *p*-XRD), and **M3** (^{29}Si CP-MAS NMR, IR, *p*-XRD, BET) are given in the Supporting Information.

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