

Organic–inorganic hybrid materials containing 15-membered azamacrocyclic triolefinic palladium(0) complexes Preparation and activity as recoverable catalysts in Suzuki cross-couplings

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Abstract

The synthesis of a palladium complex and a monosilylated monomer derived from 15-membered azatriolefinic macrocycle are described as well as the preparation of the corresponding hybrid organic–inorganic materials, containing a macrocyclic palladium(0) complex covalently anchored to the silica matrix. The materials were obtained by sol–gel process using different routes: post-synthesis treatment on a mesostructured silica, cogelification of a monosilylated precursor and tetraethylorthosilicate. The activity of the different materials as recoverable catalysts in Suzuki cross-couplings is reported and commented.

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1. Introduction

The immobilization of homogeneous catalysts on polymeric organic [1] or inorganic [2] supports offers the advantages of easy product separation and catalyst recycling. Some of us discovered [3] air and moisture stable phosphane-free macrocyclic triolefinic palladium(0) complexes **1** (Fig. 1), which were found to be active and reusable catalysts [4,5]. Phosphanes are readily oxidized to their corresponding phosphane oxides, which can prevent the easy recovery and recycling of the catalyst. Thus, phosphane-free palladium catalysts offer the advantage of superior stability. The preparation [5,6] of the required 15-membered tri-olefinic azamacrocycles **2** (Fig. 1) and their coordination

properties [5,7] with transition metals have been studied. Then, we studied the heterogenisation of our phosphane-free palladium catalysts. The macrocycle-containing cross-linked polystyrene catalyst was first prepared and tested [4a] in Suzuki cross-couplings of activated substrates in aqueous-organic medium. Then, we turned to inorganic supports. Indeed, the silica based inorganic polymers can present high surface areas. Furthermore, the hybrid organic–inorganic materials formed by catalytic species covalently anchored to silica have chemical, mechanical and thermal stability superior to that of organic polymers. We have previously reported the covalent anchoring [8] of 15-membered azamacrocyclic triolefinic palladium(0) complex onto mesoporous organosilica SBA-15 type and the preparation [9] of a palladium(0)-containing organic–inorganic hybrid material **3** (Fig. 1) from the corresponding disilylated macrocyclic monomer by sol–gel process. The catalytic properties and the recyclability of both materials were tested [8,9].

Herein, we present the synthesis of a palladium(0) complex and a monosilylated monomer derived from 15-membered azatriolefinic macrocycle, as well as the preparation of the

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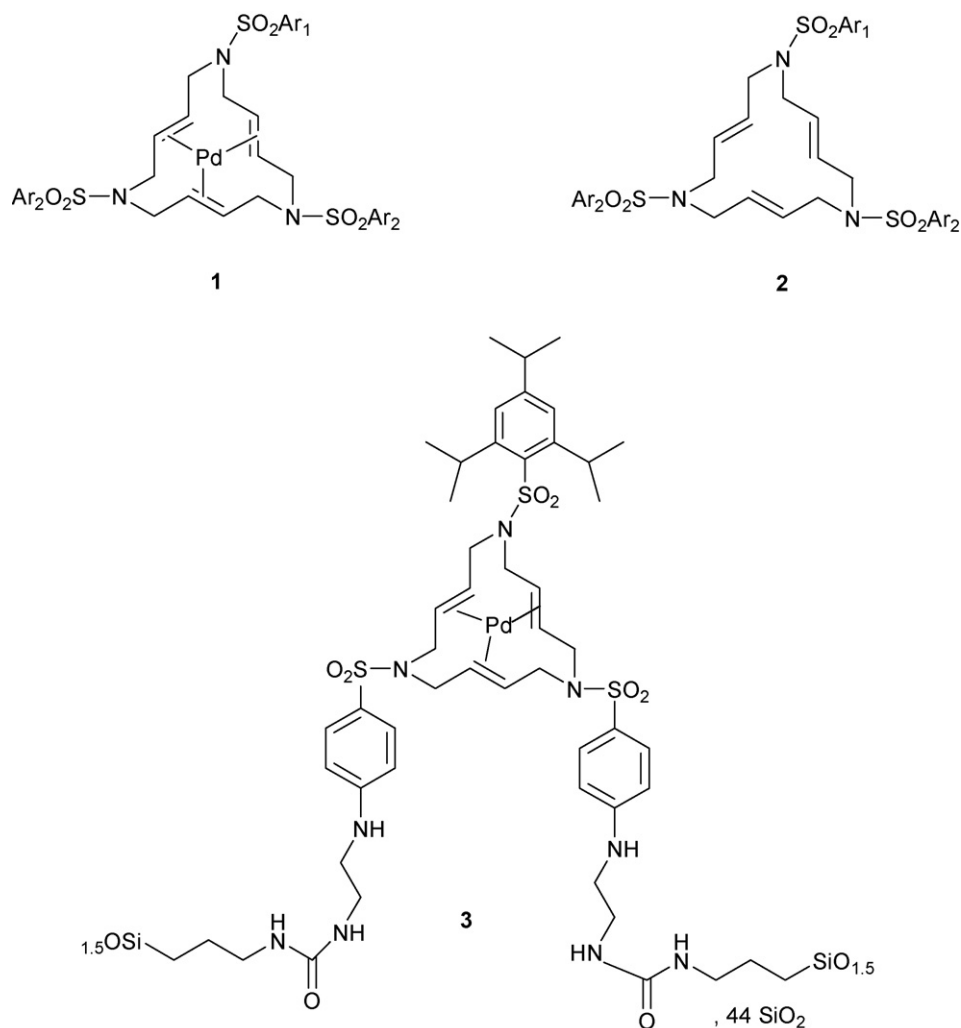


Fig. 1. General formulae for 15-membered azatriolefinic macrocyclic palladium(0) complexes **1**, the corresponding free ligands **2**, and the palladium(0)-containing organic-inorganic hybrid silica material **3**.

corresponding hybrid organic-inorganic materials, containing macrocyclic palladium(0) complex covalently anchored to the silica matrix. The materials were obtained by sol-gel process using different routes: anchoring to a mesostructured silica functionalised by an appropriate group, grafting of monosilylated precursor on mesostructured silica and its cogelification with tetraethylorthosilicate. The activity of the different materials as recoverable catalysts in Suzuki cross-couplings is reported and commented.

2. Experimental

All experiments were carried out with standard high-vacuum and Schlenk techniques. Solvents were dried and distilled just before use. Tetraethylorthosilicate (TEOS), tetrabutylammonium fluoride (TBAF), 4-aminobenzenesulfonamide, cesium carbonate, cinnamyl bromide, and *p*-iodoanisole were purchased from Aldrich; 3-(triethoxysilyl)propyl isocyanate, phenylboronic acid, *p*-methoxyphenylboronic acid, and 2,4,6-triisopropylphenylsulfonamide were purchased from Lancaster. IR data were obtained on the following spectrophotometers:

Perkin-Elmer 1600 FTIR, Perkin Elmer 1720X FTIR, Nicolet 510ZDX FTIR, or Bruker Tensor 27 with ATR Golden Gate. Melting points (mp) were measured with a Buchi B-540 apparatus or with a Kofler Reichardt apparatus and are uncorrected. The solution NMR spectra were recorded on a Bruker DPX-200 or on a Bruker AC-250 (^1H and ^{13}C). Chemical shifts (δ , ppm) were referenced to Me_4Si (^1H , ^{13}C). The abbreviations used are s for singlet, d for doublet, dd for double doublet, t for triplet, q for quartet, sept for septet and m for multiplet. ESI mass spectra were registered at the *Universitat de Girona*, being acquired using a Navigator quadrupole instrument, operating in the positive ion mode (ES+) at a probe tip voltage of 3 kV. MALDI-TOF MS were registered at the *Institut de Biotecnologia i Biomedicina* of the *Universitat Autònoma de Barcelona*, using a Bruker Biflex Reflecton Mode spectrometer, equipped with a pulsed nitrogen laser (337 nm), operating in positive-ion reflector mode, using a 19 kV acceleration voltage and a matrix of α -cyano-4-hydroxycinnamic acid. Elemental analysis have been performed at the *Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona* and at the *Servei de Microanàlisi (CSIC, Barcelona)*. The content of palladium

was determined at the *Universitat de Barcelona* by Inductively Coupled Plasma (ICP). Specific surface areas were determined by Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2010 analyser (using 74 points and starting from 0.01 as value for the relative pressure) and the average pore diameters were calculated by the BJH method. Powder X-ray diffraction patterns were measured on a Bruker D5000 diffractometer equipped with a rotating anode (Institut Européen des Membranes, UMR ENSCM-UMII-CNRS 5625, Montpellier, France).

2.1. Syntheses

Compound **4aa** [10] and bis(dibenzylideneacetone)palladium(0) [11] were prepared as previously reported.

2.1.1. Preparation of

(*E,E,E*)-11-[(4-aminophenyl)sulfonyl]-1,6-bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (**5aab**)

A stirred mixture of **4aa** [10] (0.72 g, 0.8 mmol), 4-aminobenzenesulfonamide (0.14 g, 0.8 mmol), and anhydrous potassium carbonate (0.94 g, 7.1 mmol) in acetonitrile (130 mL) was heated under reflux for 24 h. The salts were filtered off and the solvent was evaporated in vacuo. The crude mixture was purified by column chromatography (silica gel, hexane-ethyl acetate 6:3), affording **5aab** as a white solid (0.47 g, 64%). mp 202–204 °C. IR (KBr): $\nu = 3458, 3371, 2927, 1601, 1565, 1505, 1461, 1363, 1314$ and 1147 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ 1.19–1.25 (m, 36H), 2.87 (sept, $J = 7.0 \text{ Hz}$, 2H), 3.65–3.82 (m, 12H), 4.07 (sept, $J = 6.8 \text{ Hz}$, 4H), 5.72 (m, 6H), 6.65 (d, $J = 8.8 \text{ Hz}$, 2H), 7.13 (s, 4H), 7.54 (d, $J = 8.8 \text{ Hz}$, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): $\delta = 23.5, 24.8, 29.2, 34.1, 48.8, 51.2, 114.1, 123.9, 127.5, 129.2, 129.3, 130.8, 130.9, 150.5, 151.5$ and 153.2. MS (MALDI-TOF): m/z (%) = 933.4 ($[M + K]^+$, 100), 917.3 ($[M + Na]^+$, 20). The presence of peaks attributed to $[M + Na]^+$ and $[M + K]^+$ is a common feature in MALDI-TOF analyses [12]. Anal. Calc. for $\text{C}_{48}\text{H}_{70}\text{N}_4\text{O}_6\text{S}_3$ (895.28): C, 64.40; H, 7.88; N, 6.26. Found: C, 63.90; H, 7.65; N, 6.08.

2.1.2. Preparation of (*E,E,E*)-11-[(4-aminophenyl)sulfonyl]-1,6-bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (**6aab**)

A mixture of **5aab** (0.30 g, 0.3 mmol) and bis(dibenzylideneacetone)palladium(0) (0.2 g, 0.3 mmol) in tetrahydrofuran (20 mL) was stirred under reflux for 6 h. The cooled mixture was filtered and the solvent from filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane-ethyl acetate 5:2), furnishing the complex **6aab** as a white solid (0.17 g, 50%). mp 156–162 °C. IR (KBr): $\nu = 3460, 3380, 2959, 2928, 2869, 1627, 1598, 1562, 1504, 1462, 1425, 1383, 1364, 1315, 1266, 1151, 1049, 939, 907, 829, 766, 750, 675, 586$ and 556 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): $\delta = 1.23$ (m, 36H), 1.70 (dd, $J = 10.7$ and 6.1 Hz , 2H), 2.08 (m, 2H), 2.89 (sept, $J = 7.1 \text{ Hz}$, 2H), 3.17 (m, 4H), 3.82 (m, 2H), 4.07–4.12 (m, 6H), 4.15–4.75

(m, 6H), 6.62 (d, $J = 8.8 \text{ Hz}$, 1.33H), 6.63 (d, $J = 8.8 \text{ Hz}$, 0.67H), 7.15 (s, 4H), 7.51 (d, $J = 8.8 \text{ Hz}$, 1.33H), 7.57 (d, $J = 8.8 \text{ Hz}$, 0.67H). ^{13}C NMR (62.5 MHz, CDCl_3): $\delta = 23.9, 25.2, 29.6, 34.5, 44.2, 45.7, 47.0, 48.3, 48.9, 50.2, 79.1, 79.4, 83.7, 83.8, 84.0, 114.5, 124.3, 126.7, 129.7, 131.7, 150.9, 151.7$ and 153.6. MS (ESI): $m/z = 1000.2$ (only the most intense absorption of the cluster is given) $[M]^+$, 894.5 $[M - \text{Pd} + \text{H}]^+$. Anal. Calc. for $\text{C}_{48}\text{H}_{70}\text{N}_4\text{O}_6\text{S}_3\text{Pd}$ (1001.69): C, 57.56; H, 7.04; N, 5.59; S, 9.60. Found: C, 57.53; H, 7.23; N, 5.49; S, 9.31.

2.1.3. Preparation of 4-(*N'*-(3-triethoxysilylpropyl)ureido)benzenesulfonamide (**10**)

A solution of 4-aminobenzenesulfonamide (2.80 g, 15.9 mmol) and 3-(triethoxysilyl)propyl isocyanate (5.0 mL, 4.7 g, 19.0 mmol) in anhydrous tetrahydrofuran (11 mL) was stirred at room temperature under argon atmosphere for 18 h. The solid formed was filtered, washed and dried under vacuum (6.61 g, 99%). mp 152–154 °C. IR (KBr): $\nu = 3393, 3329, 3193, 2975, 2928, 2887, 1684, 1665, 1596, 1552, 1401, 1338, 1314, 1161, 1158, 1104, 1079, 959, 829, 817, 794, 761, 632, 613, 542$ and 514 cm^{-1} . ^1H NMR (250 MHz, CD_3SOCD_3): $\delta = 0.64$ (m, 2H), 1.18 (t, $J = 7.0 \text{ Hz}$, 9H), 1.70 (m, 2H), 3.10 (td, $J = 12.9$ and 6.2 Hz , 2H), 3.78 (q, $J = 7.0 \text{ Hz}$, 6H), 6.35 (t, $J = 6.0 \text{ Hz}$, 1H), 7.17 (s, 2H), 7.55 (d, $J = 9.0 \text{ Hz}$, 2H), 7.69 (d, $J = 9.0 \text{ Hz}$, 2H), 8.83 (s, 1H). ^{13}C NMR (62.5 MHz, CD_3SOCD_3): $\delta = 8.1, 19.1, 24.1, 42.6, 58.6, 117.6, 127.6, 136.8, 144.6$ and 155.7.

2.1.4. Preparation of (*E,E,E*)-11-[4-(*N'*-(3-triethoxysilylpropyl)ureido)phenylsulfonyl]-1,6-bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (**9aac**)

A degassed mixture of **10** (0.51 g, 1.2 mmol), **4aa** (1.18 g, 1.8 mmol) and anhydrous potassium carbonate (1.34 g, 10.1 mmol) in anhydrous acetonitrile (170 mL) was refluxed for 24 h under argon atmosphere. The mixture was cooled to room temperature, the salts were filtered off and the solvent was evaporated under reduced pressure. The crude mixture was digested with hot and anhydrous pentane. The solid residue (1.12 g) was formed by **9aac** and excess **4aa** (the molar ratio calculated by ^1H NMR spectroscopy was 4.3/1, 0.99 g of **9aac**, 72%). ^1H NMR (250 MHz, CDCl_3) of **9aac**: $\delta = 0.64$ (m, 2H), 1.21 (m, 36 + 9H), 1.66 (m, 2H), 2.87 (sept, $J = 6.8 \text{ Hz}$, 2H), 3.20 (td, $J = 12.9$ and 6.2 Hz , 2H), 3.65–3.85 (m, 12 + 6H), 4.06 (sept, $J = 6.7 \text{ Hz}$, 4H), 5.30 (broad s, 1H), 5.72 (m, 6H), 7.13 (s, 4H), 7.49 (d, $J = 8.9 \text{ Hz}$, 2H), 7.63 (d, $J = 8.8 \text{ Hz}$, 2H).

2.2. Preparation of materials and supported catalysts

2.2.1. Organic–inorganic hybrid silica **7**

Organic–inorganic hybrid silica **7** was prepared by treating SBA-15 [13] (1.25 g, 20.8 mmol) with a solution of (4-triethoxysilyl)benzyl iodide (1.34 g, 3.52 mmol) in toluene (30 mL) heated under reflux for 24 h. After filtration, the solid was washed with toluene, hexane and diethyl ether and then dried at 120 °C under vacuum to give 1.42 g of **7**. Anal. found: Si, 35.80; I, 2.70%.

2.2.2. Organic–inorganic hybrid silica **8**

Material **8** was prepared by treating **7** (1.0 g, 1.67 mmol) with a solution of **6aab** (190 mg, 0.19 mmol) in toluene (25 mL) heated under reflux for 24 h. After filtration, the solid was washed with ethanol and diethyl ether and then dried at 120 °C under vacuum to give 1.10 g of **8** as grey solid. Anal. found: Si, 31.14; N, 0.71; Pd, 1.62%.

2.2.3. Organic–inorganic hybrid silica **11**

To a solution of **9aac** (0.31 g, 0.27 mmol) and TEOS (2.81 g, 13.5 mmol) in THF (13.75 mL) placed in a flask, were added 0.49 mL of water (27.4 mmol) and 0.14 mL (0.14 mmol) of a TBAF solution 1 M in THF. The flask was then placed in a water-bath at 30 °C with stirring. Gelation occurred after 1 h. The wet gel was allowed to age for 5 days at 30 °C. It was then powdered and washed with THF, acetone, and diethyl ether. This treatment was repeated twice and the obtained solid was powdered again and dried for 12 h at 120 °C under vacuum to yield 1.0 g of material **11** as white powder. Anal. Calcd. for C₅₂H₇₆N₅O_{108.5}S₃Si₅₁: C, 15.48; H, 1.90; N, 1.74; S, 2.38; Si, 35.49. Found: C, 13.65; N, 1.24; S, 1.76; Si, 33.66.

2.2.4. Supported palladium(0) catalyst **11Pd(a)**

A stirred mixture of material **11** (20.2 mg, 0.2 mmol macrocycle/g, 0.04 mmol macrocycle), bis(dibenzylidene acetone)palladium(0) (38 mg, 0.06 mmol) and dioxane (1.4 mL) was refluxed for 16 h. The cooled mixture was filtered; the solid was washed successively with tetrahydrofuran and diethyl ether and dried under vacuum (0.198 g). IR (KBr): $\nu = 3426, 1636, 1601, 1547, 1079, 964, 803, 564$ and 461 cm^{-1} . % Pd (ICP): 2.25 (0.21 mmol Pd/g).

2.2.5. Supported palladium(0) catalyst **11Pd(b)**

A mixture of material **11** (0.180 g, 0.2 mmol macrocycle/g, 0.036 mmol macrocycle), bis(dibenzylideneacetone) palladium(0) (0.023 g, 0.04 mmol) and dichloromethane (3 mL) was stirred at room temperature for 6 h. The mixture was filtered, the solid was washed successively with dichloromethane, acetone and diethyl ether and dried under vacuum (0.160 g). IR (KBr): $\nu = 3426, 1636, 1601, 1547, 1079, 964, 803, 564$ and 461 cm^{-1} . % Pd (ICP): 0.74 (0.07 mmol Pd/g).

2.2.6. Organic–inorganic hybrid silica **12**

Material **12** was prepared by treating SBA-15 [13] (0.90 g, 15.0 mmol) with **9aac** (0.31 g, 0.27 mmol) in toluene (30 mL) heated under reflux for 24 h. After filtration, the solid was washed with ethanol, acetone and diethyl ether and then dried at 120 °C under vacuum to give 1.11 g of **12**. Anal. found: Si, 33.70; N, 1.34%.

2.2.7. Supported palladium(0) catalyst **12Pd**

A mixture of material **12** (0.200 g, 0.28 mmol macrocycle/g, 0.06 mmol macrocycle), bis(dibenzylideneacetone) palladium(0) (0.035 g, 0.06 mmol) and dichloromethane (3 mL) was stirred at room temperature for 6 h. The mixture was filtered, the solid was washed successively with dichloromethane, acetone and diethyl ether and dried under vacuum (0.186 g). IR

(KBr): $\nu = 3426, 1654, 1601, 1083, 964, 803, 564$ and 461 cm^{-1} . % Pd (ICP): 2.33 (0.22 mmol Pd/g).

2.3. Catalytic experiments

2.3.1. Suzuki cross-coupling between cinnamyl bromide, **13**, and *p*-methoxyphenylboronic acid, **14**, with hybrid catalyst **8**

A degassed and stirred mixture of cinnamyl bromide, **13** (0.031 g, 0.15 mmol), *p*-methoxyphenylboronic acid, **14** (0.028 g, 0.18 mmol), potassium carbonate (0.16 g, 1.2 mmol), catalyst **8** (0.034 g, 0.15 mmol Pd/g, 0.005 mmol Pd) and anhydrous toluene (3 mL) was heated under nitrogen at 95 °C for 1.5 h. The mixture was cooled to room temperature, filtered and the solid was washed with toluene. The filtrate was washed with water, the organic phase was dried over anhydrous sodium sulphate and the solvent was evaporated under reduced pressure to afford pure **15** [14] (0.030 g, 86%). The palladium content determined by ICP was 119 ppm (0.73% leaching). The filtered solid containing the catalyst was thoroughly washed successively with water, ethanol and diethyl ether; it was dried under vacuum and reused in the next run.

An analogous procedure was followed for this reaction with the other hybrid materials used as catalysts.

2.3.2. Suzuki cross-coupling between *p*-iodoanisole, **16**, and phenylboronic acid, **17**, with hybrid catalyst **8**

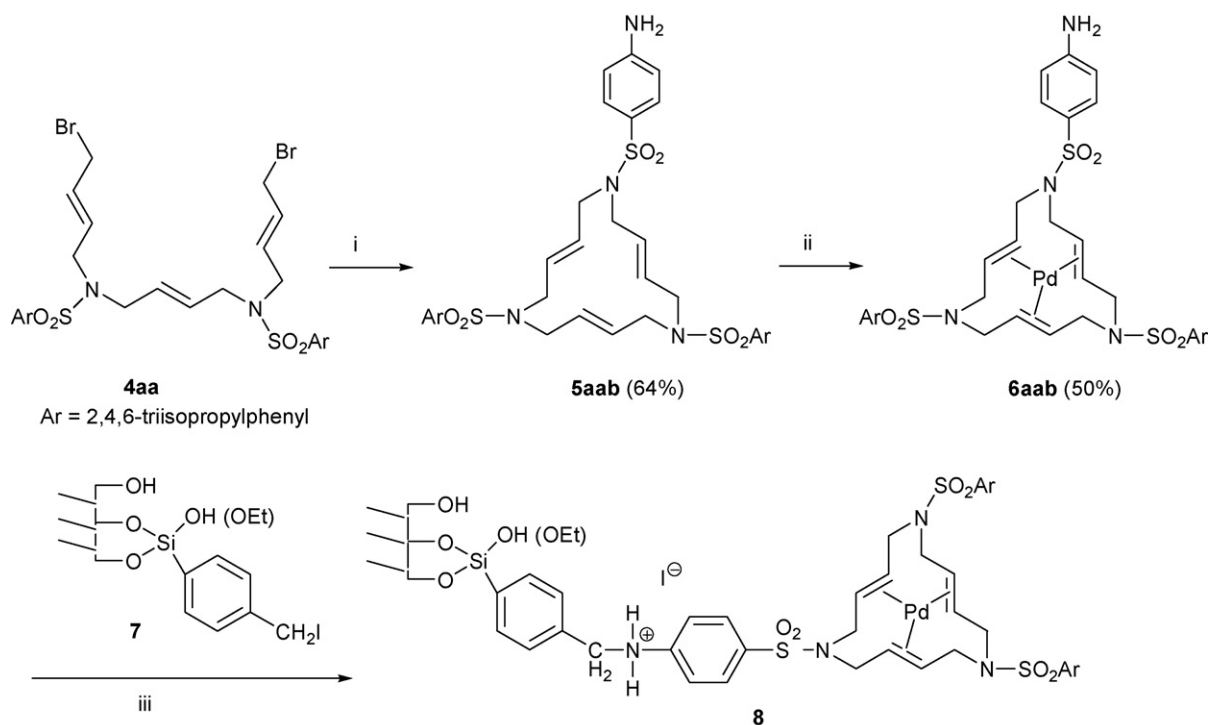
A stirred and degassed mixture of *p*-iodoanisole, **16** (0.105 g, 0.45 mmol), phenylboronic acid, **17** (0.088 g, 0.72 mmol), cesium carbonate (0.580 g, 1.8 mmol), catalyst **8** (0.091 g, 0.15 mmol Pd/g, 0.013 mmol Pd) and degassed dioxane (3 mL) was heated under nitrogen at 100 °C for 5 h. The mixture was cooled to room temperature, filtered and washed with dioxane. The solvent was evaporated and the residue taken in dichloromethane. The solution was washed with water, the organic phase dried with anhydrous sodium sulphate and the solvent evaporated under reduced pressure to afford a mixture of **18** and **16** (0.062 g, the molar ratio **18/16** by ¹H NMR was 19.8/1). ¹H NMR of **18** (250 MHz, CDCl₃): $\delta = 3.83$ (s, 3H), 7.01 (d, $J = 8.8$ Hz, 2H), 7.32–7.37 (m, 1H), 7.45 (apparent t, $J = 7.0$ Hz, 2H), 7.53–7.61 (m, 4H). The palladium content determined by ICP was 1800 ppm (7.9% leaching). The filtered solid containing the catalyst was thoroughly washed successively with water, ethanol and diethyl ether; it was dried under vacuum and reused in the next run.

An analogous procedure was followed for this reaction with the other hybrid materials used as catalysts.

3. Results and discussion

3.1. Synthesis and characterization of the palladium complex **6aab** and the corresponding material **8**

The palladium(0) complex **6aab** was prepared as depicted in Scheme 1: treatment of dibrominated compound **4aa** [10] with 4-aminophenylsulfonamide in acetonitrile afforded



Scheme 1. Preparation of mesostructured hybrid material **8**. *Reagents and conditions*: (i) 4-aminobenzenesulfonamide, K_2CO_3 , refluxing CH_3CN ; (ii) $Pd(dba)_2$, refluxing THF; (iii) refluxing toluene, 24 h.

the macrocycle **5aab**. Subsequent treatment of **5aab** with bis(dibenzylideneacetone)palladium(0) gave **6aab** in 50% yield after purification. Amino groups do not compete with the triolefinic macrocycle for metal coordination if a palladium(0) source is used. Complexation of palladium to the olefins is observed by 1H NMR.

In order to anchor the palladium complex **6aab** on a silica matrix, p-iodobenzyltriethoxysilane was grafted on a mesostructured SBA-15 type silica [13] to give **7**. Then, treatment of **7** with a toluene solution of **6aab** heated under reflux 1 day yielded the desired material **8** by nucleophilic substitution (Scheme 1). The N_2 adsorption–desorption isotherms of materials SBA-15, **7** and **8** are type IV, characteristic of mesoporous materials with a narrow pore size distribution (Fig. 2). A slight decrease

of specific surface and pore volume on going from **7** to **8** is observed as expected. Powder X-ray diffraction patterns of different samples are very similar, which confirms clearly that the mesoporous structure was preserved during the chemical modification reactions. As an example, Fig. 3 shows the XRD pattern corresponding to material **8**. It exhibits an intense diffraction peak corresponding to d_{100} spacing and two others peaks (d_{110} and d_{200} spacing) characteristic of an ordered hexagonal structure. The relevant physicochemical data of SBA-15, **7** and **8** are given in Table 1. The presence of the macrocyclic complex in **8** was confirmed by elemental analyses that gave a Si/N ratio of 21.9; the palladium content of this material, determined by ICP, was found to be 1.55% (0.145 mmol Pd/g).

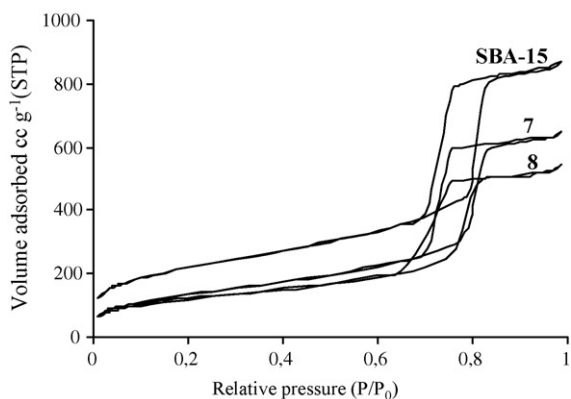


Fig. 2. Nitrogen adsorption isotherms for SBA-15, **7** and **8**.

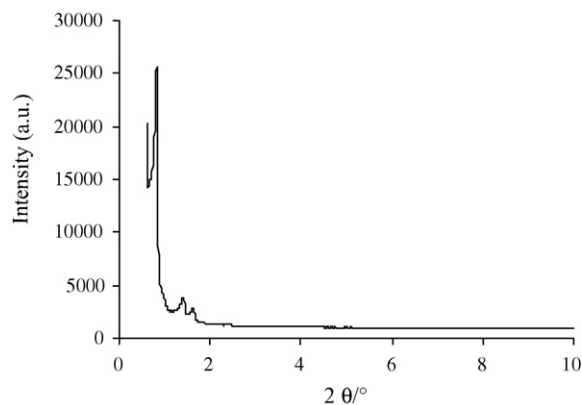


Fig. 3. XRD pattern for **8**.

Table 1
Physicochemical data of materials

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$)	D_p^a (nm)	Si/N
SBA-15	830	1.36	7.8–9.7	–
7	470	1.05	7.5–9.5	–
8	430	0.85	7.3–9.5	21.9
11	436	1.15	40–60	13.5 (0.21) ^b
12	410	0.80	6.2–8.2	11.3 (0.28) ^b

^a Calculated from the desorption branch by using the BJH method.

^b mmol g^{-1} of macrocycle.

3.2. Synthesis and characterization of the precursor **9aac** and the corresponding materials **11**, **11Pd(a)**, **11Pd(b)**, **12**, and **12Pd**

In order to obtain supported catalysts, different routes were achieved to incorporate the triazatriolefinic macrocycle on silica. For that purpose, it was necessary to prepare first an azamacrocycle bearing a $\text{Si}(\text{OR})_3$ hydrolysable group. The reaction of **5aab** with the commercially available 3-(triethoxysilyl)propyl isocyanate did not give rise to **9aac** in a satisfactory yield. The reaction was sluggish and not useful for synthetic purposes (Scheme 2). Steric factors should be probably on the origin of this slow reaction. In contrast, the *p*-aminophenylsulfonamide reacted cleanly with 3-(triethoxysilyl)propyl isocyanate to give **10** in quantitative yield (Scheme 2). Cyclisation to **9aac** was then achieved by reaction between **10** and an excess (1.5 equiv.) of the dibrominated compound **4aa**. The crude mixture containing the macrocycle bearing a hydrolysable triethoxysilyl group **9aac** and the excess of **4aa** was not chromatographed to avoid the hydrolysis of triethoxysilyl group. It was only washed with pentane, and the percentage of **9aac** was calculated from the

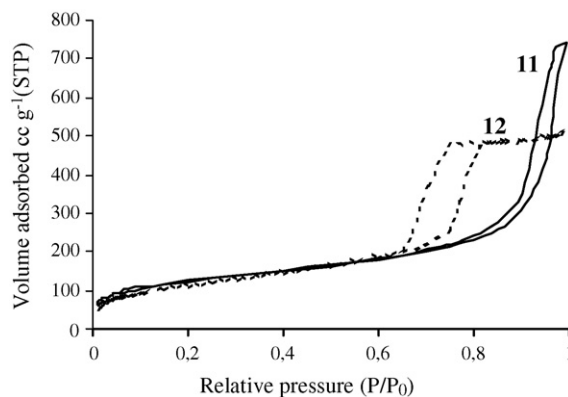
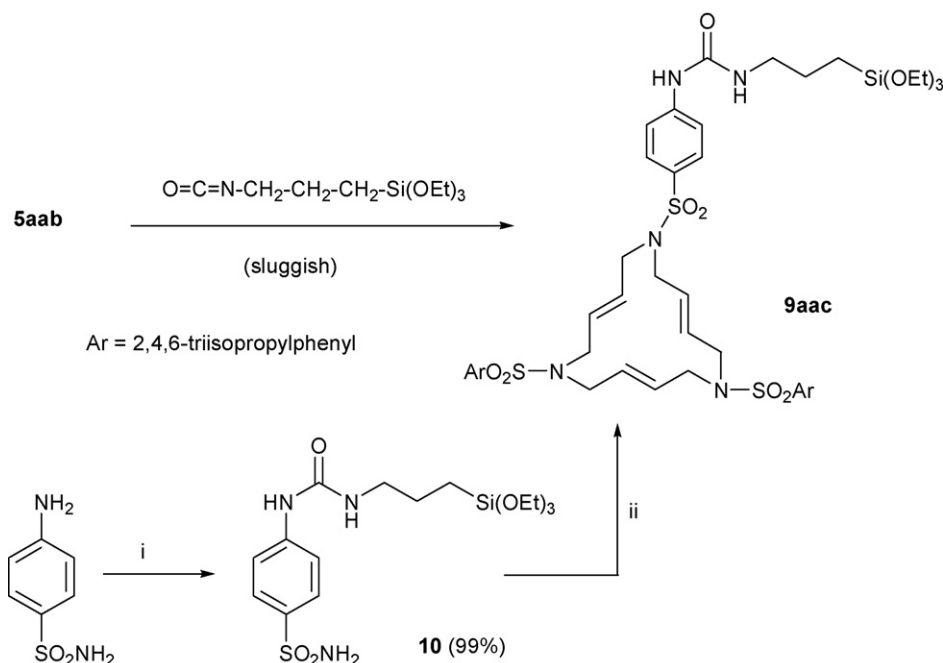


Fig. 4. Nitrogen adsorption isotherms for **11** and **12**.

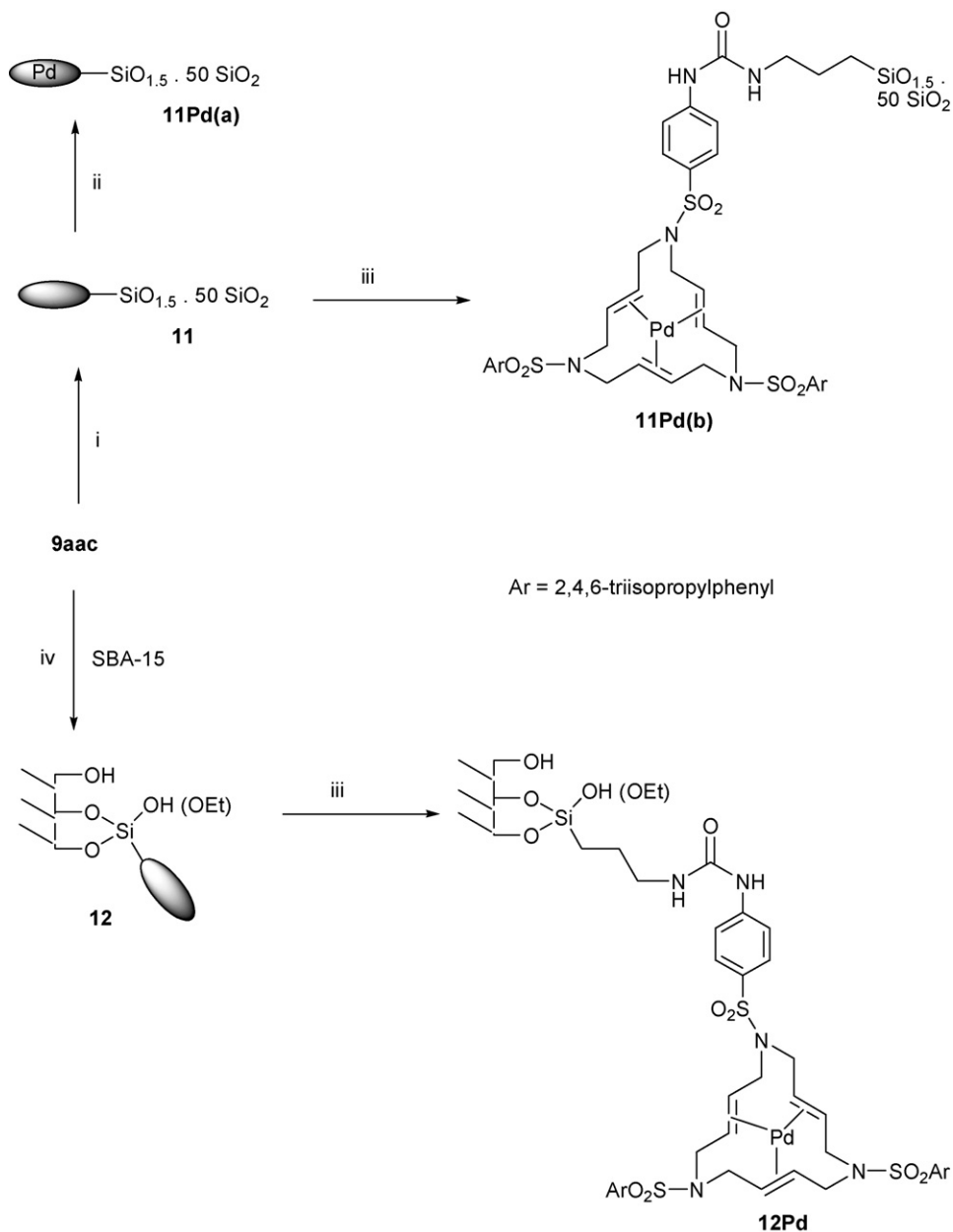
^1H NMR spectrum and found to be 72%. We have to mention that an excess of **4aa** does not constitute a problem, because the dibrominated compound **4aa** does not participate to the formation of the subsequent materials by sol-gel process. Compound **4aa** was eliminated from the hybrid materials by repeated washings.

Two types of organic–inorganic hybrid materials were prepared from the monomer **9aac** (Scheme 3). Material **11** was obtained by co-gelification of **9aac** with 50 equiv. of TEOS in ethanol as solvent (see Section 2). The results of elemental analyses of the material **11** revealed a Si/N ratio of 13.5 (0.21 mmol macrocycle/g). The N_2 adsorption–desorption isotherm of **11** was characteristic of a macroporous material (Fig. 4); the BET surface area was found to be $436 \text{ m}^2/\text{g}$ (Table 1).

In order to incorporate the palladium(0) into the macrocycle, the material **11** was first treated with a dioxane solution of bis(dibenzylideneacetone)palladium(0) ($\text{Pd}(\text{dba})_2$) heated



Scheme 2. Preparation of monomer **9aac**. Reagents and conditions: (i) 3-(triethoxysilyl)propyl isocyanate, anh. THF, r.t., Ar atmosphere; (ii) **4aa** (1.5 equiv.), K_2CO_3 , anh. CH_3CN , reflux, Ar atmosphere.



Scheme 3. Preparation of hybrid palladium(0)-containing materials **11Pd(a)**, **11Pd(b)**, **12Pd** from **9aac**. Reagents and conditions: (i) 50 TEOS, H₂O, tetrabutylammonium fluoride, EtOH, r.t.; (ii) Pd(dba)₂, refluxing dioxane; (iii) Pd(dba)₂, CH₂Cl₂, r.t.; (iv) refluxing toluene, 24 h.

under reflux for 16 h. The percentage of palladium in the resulting solid **11Pd(a)** was determined by ICP and found to be 2.25%, whereas the theoretical value was 2.13%. This result suggested that some metal was adsorbed on the surface of the silica. Therefore, milder conditions were tested to achieve the macrocycle complexation. Treatment of **11** with Pd(dba)₂ in dichloromethane at room temperature for 6 h gave rise to a white solid **11Pd(b)** containing 0.74% of Pd (0.07 mmol/g) (ICP).

On the other hand, grafting of **9aac** to a mesostructured SBA-15 silica was accomplished in toluene heated under reflux for 24 h to afford **12** (Scheme 3). The Si/N ratio was inferred from the results of elemental analyses of **12** and found to be 11.3, indicating that the extent of macrocycle incorporated in the

mesoporous silica was 0.28 mmol of macrocycle/g. The relevant physicochemical data for **12** are reported in Table 1. The N₂ adsorption–desorption isotherm of **12** is shown in Fig. 4. It is worth noting that the BET surface area decreased with respect to SBA-15 as well as the pore volume and pore diameter as expected after grafting. The powder X-ray diffraction pattern of **12** was very similar to this of SBA-15.

Treatment of **12** with Pd(dba)₂ was performed in dichloromethane at room temperature for 6 h, giving rise to **12Pd** which contains 2.33% of Pd (0.22 mmol Pd/g) (Table 2). It is worth noting that treatment of SBA-15 with Pd(dba)₂ under the same mild conditions did not give physisorption of metal on silica. Amino and urea groups do not compete with the triolefinic macrocycle for metal coordination if a palladium(0)

Table 2
Content in palladium(0) within different materials

Sample	%wt Pd ^a	Pd mmol g ⁻¹
8	1.55	0.145
11Pd(b)	0.74	0.07
12Pd	2.33	0.22

^a Determinated by ICP and from the elemental analysis.

Table 3
Results of Csp³–Csp² Suzuki cross-coupling giving rise to **15**^a

Run	8		11Pd(b)		12Pd	
	<i>t</i> (h)	Yield (%) ^b	<i>t</i> (h)	Yield (%) ^b	<i>t</i> (h)	Yield (%) ^b
1	1.5	86	0.5	76	0.5	95
2	1.5	78	0.5	78	1.0	95 ^c
3	1.5	78	1.0	89 ^c	2.0	98 ^c
4	2.5	61	1.0	95	1.0	94
5	2.5	97	1.0	93	1.0	98 ^c

^a **13/14**/base = 1/1.08–1.2/7.7–9.2.

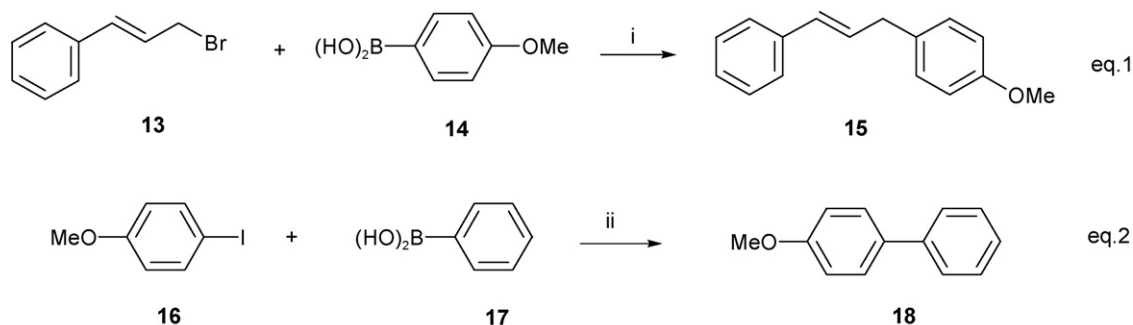
^b Isolated yield (conversion 100%).

^c Conversion by ¹H NMR.

source is used (unpublished results with a silylated soluble urea monomer).

3.3. Activity and recyclability of the hybrid materials as catalysts in Suzuki cross-couplings

The activity of the palladium(0) containing materials **8**, **11Pd(b)** and **12Pd** were tested as catalysts in the Suzuki [15] sp³–sp² and sp²–sp² cross-coupling reactions (Scheme 4, Eqs. (1) and (2)) of arylboronic acids with cinnamyl bromide and *p*-methoxyphenyl iodide (Tables 3 and 4). To the best of our knowledge, while there are some reports about the use of silica anchored palladium(II) species [16a–p] in Suzuki cross-coupling reactions, there is no example of palladium(0) complexes covalently attached to the silica matrix as catalyst for this type of reaction, apart from our mentioned studies [8,9] and recent papers about a PEG-coated mesoporous silica-nanoparticles supported palladium(0) complex [16q] and palladium(0) nanoparticles supported on covalently modified silicas [16r].



Scheme 4. Suzuki cross-couplings tested with hybrid silica catalysts. Reagents and conditions: (i) 2.8–3.3% Pd, K₂CO₃, anhydrous toluene, 95 °C, inert atmosphere [13] = 0.04–0.05 M; (ii) 2.6–3.0% Pd, Cs₂CO₃, degassed dioxane, 100 °C, inert atmosphere [16] = 0.15–0.23.

Table 4
Results of Csp²–Csp² Suzuki cross-coupling giving rise to **18**^a

Run	8		11Pd(b)		12Pd	
	<i>t</i> (h)	Conv. (%) ^b	<i>t</i> (h)	Conv. (%) ^b	<i>t</i> (h)	Conv. (%) ^b
1	5	95	18	86	8	98
2	5	74	24	84	8	97
3	5	93	24	87	8	54
4	5	40	24	–	8	52
5	5	48	24	68	8	58

^a **16/17**/base = 1/1.6/4.

^b Conversion by ¹H NMR.

Degassing of the solvent was necessary to prevent the formation of minor amounts of side products. Under these conditions, the crude mixtures contained only the final coupling products, **15** or **18** (Scheme 4) respectively, and the organic halide not consumed (100% selectivity).

The palladium-catalysed reaction between cinnamyl bromide **13** and *p*-methoxyphenylboronic acid **14** was achieved in anhydrous toluene at 95 °C, in the presence of potassium carbonate as base [14], to afford **15** within 0.5–3.0 h as reaction times, depending on the catalyst used (Eq. (1), Scheme 4 and Table 3). The order of efficiency observed in the first cycle (reaction time required for 100% conversion) was: **12Pd**, **11Pd(b)** > **8**. The leaching of palladium determined by ICP in the first cycle was not very high (0.4% for **12Pd**, 0.7% for **8**, 3.5% for **11Pd(b)**). The catalysts were separated by filtration and reused up to five runs. As noted in Table 3, it was necessary to increase the reactions times in order to obtain complete disappearance of substrate in the third or fourth cycle, but fair to good yields in final product were obtained in all runs.

The palladium-catalysed cross-coupling reaction between the deactivated aryl iodide, *p*-iodoanisole **16**, and the phenylboronic acid **17** affording 4-methoxybiphenyl **18** was performed in dioxane at 100 °C, in the presence of cesium carbonate (Eq. (2), Scheme 4 and Table 4). It is worth noting that the experimental conditions were adopted after a screening of different bases, solvents and reaction temperatures by using a non-anchored macrocyclic complex. The concomitant use of insoluble catalyst and base did not constitute a trouble for the reaction to proceed. Furthermore, we observed that an organic base (Et₃N) in an organic solvent was not a good choice and that aqueous conditions have to be avoided for this type of catalysts.

Table 5
Results of Csp^3-Csp^2 and Csp^2-Csp^2 Suzuki cross-couplings giving rise to **15** and **18** (Scheme 4) tested with recoverable polystyrene-supported triolefinic macrocyclic palladium(0) catalyst [4a]

Run	15		18	
	<i>t</i> (h)	Yield (%) ^a	<i>t</i> (h)	Conv. (%) ^b
1	2.5	82	8	99
2	2.5	89	8	87
3	3.0	87	8	95
4	3.5	97	8	24
5	2.5	89	8	7

^a Isolated yield.

^b Conversion by ¹H NMR.

As expected, longer reaction times (5–24 h) were required for this more challenging cross-coupling reaction [8,9] The decreasing activity order of the materials tested as catalyst in this reaction was: **8** > **12Pd** > **11Pd(b)**. The catalysts prepared from the complex **6aab** (**8**) and the macrocycle **9aac** (**11Pd(b)**, **12Pd**) could be used five times but with conversions decreasing after recycling. The percentage of palladium leaching determined in the first cycle was 2.0% for **11Pd(b)**, 3.7% for **12Pd**, 7.9% for **8**.

Indeed, **12Pd** prepared by grafting of **9aac** is a better catalyst than **11Pd(b)** prepared by co-gelification of TEOS and **9aac**.

Some of the hybrid macrocycle-containing palladium(0) catalysts presented in this paper (**11Pd(b)**, **12Pd**) have better activity and recyclability in the Csp^3-Csp^2 cross-coupling (Eq. (1), Scheme 4) than other silica-anchored macrocyclic versions reported previously by us [8,9]. That is also true for **8**, **11Pd(b)**, **12Pd** in the Csp^2-Csp^2 coupling reaction (Eq. (2), Scheme 4) [8,9]. The cross-linked polystyrene-supported version of our macrocyclic palladium(0) complex previously described by some of us [4a] has been tested for comparison with the same substrates and the same reaction conditions as those described in Scheme 4 (Table 5). Hybrid catalysts **8**, **11Pd(b)** and **12Pd** offered better results than the polystyrenic catalyst for the Csp^3-Csp^2 cross-coupling (Eq. (1), Scheme 4). For the Csp^2-Csp^2 coupling reaction (Eq. (2), Scheme 4), the catalysts **8** and **12Pd** are clearly superior to the polystyrene-supported version, which involves a very significant decrease in the fourth cycle conversion.

These types of macrocyclic triolefinic palladium(0) catalysts have also been heterogenized by electrochemical polymerization of pyrrole-containing monomers [17]. Although the catalyst immobilization onto the electrode surface allows an easy recycling by removing the electrode from the solution vessel and washing it before a new reuse, the Suzuki cross-couplings reported [17] refer only to the formation of 1,3-diphenylpropene and to the couplings between benzenboronic acids with activated or nonactivated aryl iodides (iodobenzene, *p*-nitroiodobenzene), the deactivated *p*-iodoanisole being not tested under these conditions. The results obtained are inferior to ours.

Better results were obtained in the literature with organosilicas derived from a disilylated carbapalladacycle [16m] and di(2-pyridyl)methylamine-palladium dichloride complex [16p]

and from mercaptopropyl-modified mesoporous silica [16n]. That should be due to the nature of the palladium complex precursor. However, in the case of SBA-15-SH-modified materials [16n], care must be taken in order to prevent easy oxidation of the catalyst. In contrast, our supported catalysts are stable under air atmosphere.

The formation on palladium nanoparticles during our reactions is discarded because the white insoluble catalysts did not become dark after recycling [16p]. Our triolefinic macrocycles form discrete white palladium(0) complexes [5] except when fluorinated or polyethoxylenated chains are present in the structure. In those cases black residues are obtained containing nanoparticles [18].

4. Conclusions

In summary, we describe the preparation of organic-inorganic hybrid materials containing 15-membered azamacrocyclic triolefinic palladium(0) complexes using several approaches: anchoring of a macrocyclic palladium(0) complex to a mesostructured silica functionalised by an appropriate group, grafting of monosilylated monomer on mesostructured silica SBA-15, cogelification of monosilylated monomer with TEOS. The prepared palladium(0)-containing materials were tested as reusable catalysts in Suzuki cross-coupling reactions with cinnamyl bromide and *p*-iodoanisole as substrates. Activity and recyclability of the materials were found to be depending on their mode of preparation showing thus how versatile is the sol-gel approach. Some of the palladium-containing materials are superior as catalyst in these reactions to other organosilicas featuring macrocyclic complexes prepared previously by us and to polystyrene supported version of the catalyst.

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