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Tetrahedron Letters 45 (2004) 8789–8791

Tetrahedron Letters

A macrocyclic triolefinic palladium(0) complex covalently anchored to a mesostructured silica as active and reusable catalyst for Suzuki cross-coupling reactions

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Received 16 July 2004; revised 29 September 2004; accepted 4 October 2004

Abstract—A mesoporous hybrid material containing a 15-membered triazamacrocyclic triolefinic palladium(0) complex was prepared and successfully tested as a reusable heterogeneous catalyst for Suzuki cross-couplings in organic solvents.

The heterogenization of homogeneous catalysts by their immobilization on polymeric organic[1] or inorganic[2,3] supports is an expanding research area offering the advantage of easy product separation and catalyst recovery. Some of us discovered[4] air and moisture stable phosphine-free macrocyclic triolefinic palladium(0) complexes, which were found to be active and recoverable catalysts.[5–8] The macrocycle-containing cross-linked polystyrene catalyst was first prepared and tested[5] in Suzuki cross-couplings of activated substrates in aqueous–organic medium. Phosphines are readily oxidized to their corresponding phosphine oxides, which can prevent the easy recovery and recycling of the catalyst. Thus, phosphine-free palladium catalysts offer the advantage of superior stability.

Then, we turned to mesoporous hybrid organic–inorganic materials, which are a very attractive class of materials. Indeed, they are characterized by their ordered pores distribution with tuneable sizes, high specific surface area, and pore volume. Furthermore, various organic groups can be incorporated and regularly distributed within the surface of channel pores.[9,10]

Herein, we report the covalent anchoring of 15-membered azamacrocyclic triolefinic palladium(0) complex onto mesoporous organosilica SBA-15 type and the activity of this immobilized complex for the Suzuki cross-couplings. Our approach is summarized in Scheme 1.

The mesostructured hybrid organic–inorganic material **1** containing 3-chloropropyl groups was prepared by a direct synthesis method, from tetraethoxysilane (TEOS) and 3-chloropropyltriethoxysilane in a 30:1 ratio in the presence of nonionic surfactant Pluronic P123 following a method previously described.[11] On the other hand, fluorinated macrocycle **2** was prepared from 4-fluorobenzenesulfonamide according to a methodology previously reported[12] for other compounds. Treatment of **2** with an excess of 1,2-ethylenediamine at 100 °C gave compound **3**[13] in 91% yield (Scheme 2).

Nucleophilic displacement of chloride by **3** was subsequently achieved by treating the material **1** with an acetone solution containing **3** and sodium iodide heated under reflux for 24 h in the presence of a large excess of triethylamine (Scheme 1).

The extent of macrocycle **3** incorporated in the mesoporous material was inferred from the results of elemental analyses of Si, Cl, and N. It was found that 25% of chlorine atoms were substituted. This low ratio of

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Keywords: Macrocyclic triolefinic complex; Recoverable palladium catalyst; Mesostructured silica; Hybrid material; Suzuki cross-coupling.

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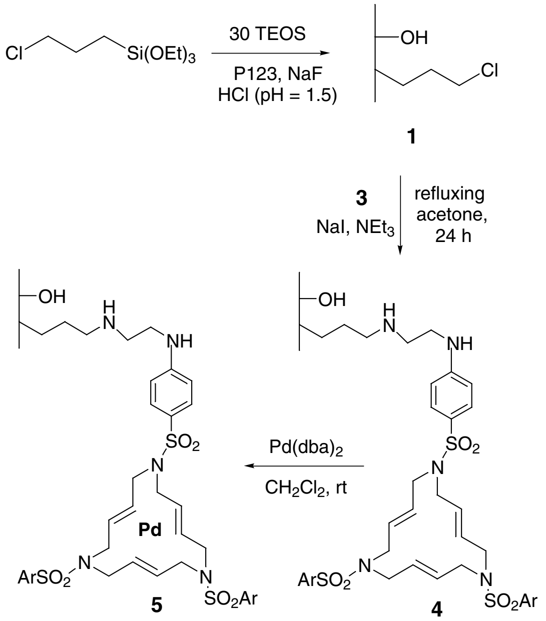
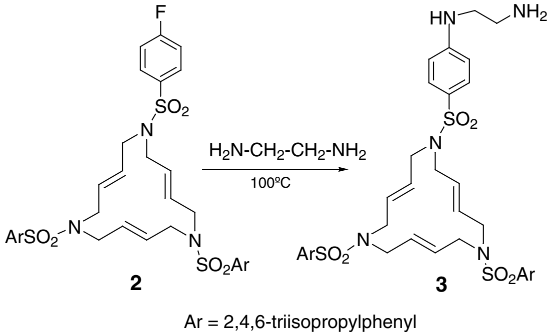
doi:10.1016/j.tetlet.2004.10.007



Scheme 1. Preparation of covalently anchored macrocyclic triolefinic palladium(0) complex onto mesostructured silica.



Scheme 2. Preparation of macrocycle **3**.

anchoring was probably due to steric constraints of **3**. The mesoporous material **4** was treated with bis(dibenzylideneacetone)palladium(0) in dichloromethane at room temperature under stirring for 6h to afford the catalyst **5** as a white solid (Scheme 1). The molar ratio of Pd per macrocycle was found to be about 0.75:1 from the elemental analyses (the catalyst batches of Eqs. 1 and 2 contained 0.44% Pd and 0.65% Pd respectively). In our hands the treatment of SBA-15[14] with Pd(dba)$_2$ under the same mild conditions did not give physisorption of metal on the surface.

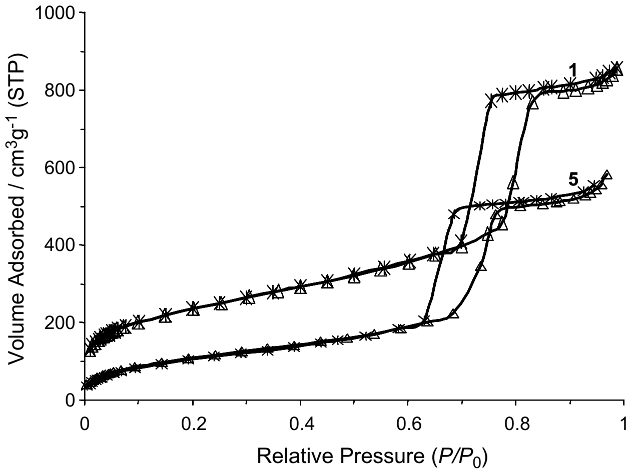
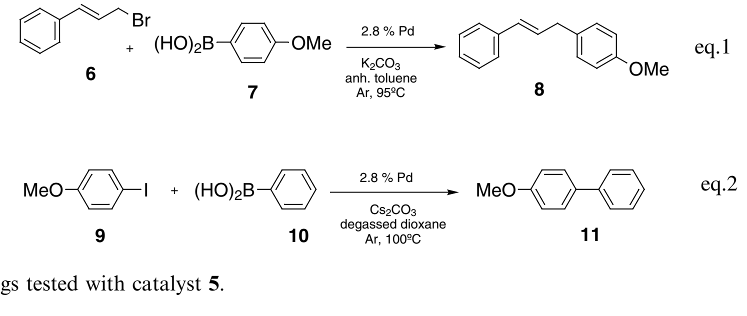


Figure 1. Nitrogen adsorption–desorption isotherms of **1** and **5**.

The XRD results clearly demonstrated that the mesoporous structure was preserved during the anchoring of **3**. The BET measurements showed that the surface area and pore volume decreased as expected (Fig. 1) during the anchoring step (S_{BET} 826 m^2 g^{-1}, V_t 1.36 cm^3 g^{-1} for **1** and S_{BET} 565 m^2 g^{-1}, V_t 0.98 cm^3 g^{-1} for **5**). Nevertheless, the pore diameter did not change (63 Å).

The activity of heterogeneous palladium(0) catalyst **5** was tested in the Suzuki[15] sp^3–sp^2 and sp^2–sp^2 cross-coupling reactions (Scheme 3 and Table 1).

It is worth noting that to the best of our knowledge there are only few reports[16–20] about the use of silica anchored palladium(II) species in Suzuki couplings, but not of covalently attached palladium(0) complexes in this type of cross-coupling. The palladium-catalyzed reaction between cinnamyl bromide **6** and *p*-methoxyboronic acid **7** was achieved in toluene at 95 °C in the presence of potassium carbonate as base,[21] to afford complete conversion to **8** within 2 h. The cross-coupling of a nonactivated aryl iodide, *p*-iodoanisole **9**, with phenylboronic acid **10** was performed in dioxane at 100 °C, in the presence of cesium carbonate, to give good conversions to *p*-methoxybiphenyl **11** in one day. 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, **8** and **11**, respectively, and the organic halide not consumed (100% selectivity; conversion can be taken as the yield). It is worth mentioning that the conditions were adopted after a screening of some bases and



Scheme 3. Suzuki cross-couplings tested with catalyst **5**.

Table 1. Results of Csp^3–Csp^2 and Csp^2–Csp^2 Suzuki cross-couplings giving rise to **8** and **11** (see Scheme 3) tested with recoverable catalyst **5**

Run	**6** to **8**		**9** to **11**	
	t (h)	Conversion (%)	*t* (h)	Conversion (%)
1	2	98[a]	72	81[a]
2	2	80[b]	24	71[a]
3	2	85[b]	24	100[a], 69[b]
4	2.5	70[b]	24	42[a]
5	4	60[b]	24	95[a]

[a] Conversion by ^{1}H NMR.

[b] Isolated yield.

solvents made with the nonanchored macrocyclic complex. In both heterogeneous reactions, the solid catalyst recovered by filtration was washed successively with water, ethanol, and diethyl ether before being recycled up to five times. The percentage of metal leaching was determined in the crude product after the first cycle and was found to be low (0.07% for **8** and 0.7% for **11**).

Some authors have pointed out[22] that released Pd under reaction conditions acts as the true catalyst in immobilized palladium systems and redeposition of the metal after completion of the reaction is claimed. We wanted to find out if there was a contribution of a homogeneous pathway in our case. No significant further conversion to **11** was found when the catalyst **5** was filtered after 5 h of reaction from the cooled down reaction mixture and the liquid phase was allowed to react for 21 h under the same conditions in the presence of new added base. Then, we repeated the experiment (different batch of catalyst **5**) filtering off the solid from the hot reaction mixture after 3 h of reaction (32% conversion). When the remaining liquid phase was made to react for 18 h in the presence of new added base, the conversion raised very significantly. Thus, a homogeneous pathway due to metal releasing in the reaction conditions is, at least in part, responsible for the catalysis.

In summary, a mesostructured hybrid material with covalently attached macrocyclic triolefinic palladium(0) complex was prepared and found to be an active and reusable catalyst in Suzuki cross-couplings.

Acknowledgements

Financial support from MCyT (Project BQU2002-04002-C02) and Generalitat de Catalunya (Project SGR2001-00181) is gratefully acknowledged. B.B. thanks Universitat Autònoma de Barcelona for a predoctoral scholarship. We are indebted to A. Serra for technical assistance.

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13. Compound **2**: mp 166–67 °C; IR (KBr): 2958, 2929, 1599, 1494, 1459, 1363, 1313, 1256, 1150, 1094 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz): δ 1.22 (m, 36H), 2.88 (septet, $J = 7.0$ Hz, 2H), 3.75 (m, 12H), 4.06 (septet, $J = 6.8$ Hz, 4H), 5.73 (m, 6H), 7.18 (m, 6H), 7.80 (dd, $J = 7.8$ and 5.2 Hz, 2H); MALDI-TOF-MS (*m/z*): 920.5 ([M + Na]$^+$), 936.5 ([M + K]$^+$). Anal. Calcd (%) for $C_{48}H_{68}FN_3O_6S_3$: C 64.18, H 7.63, N 4.68, S 10.71; found: C 63.58, H 7.98, N 4.69, S 10.62. Compound **3**: mp 88–90 °C; IR (KBr): 3390 (broad), 2958, 2928, 1600, 1461, 1363, 1317, 1151, 1092 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz): δ 1.22 (m, 36H), 1.47 (broad s, 2H), 2.87 (septet, $J = 6.7$ Hz, 2H), 2.97 (td, $J = 6.4$ and 1.6 Hz, 2H), 3.20 (td, $J = 6.5$ and 5.8 Hz, 2H), 3.70–3.77 (m, 12H), 4.06 (septet, $J = 6.7$ Hz, 4H), 4.67 (t, $J = 5.6$ Hz, 1H), 5.7 (m, 6H), 6.59 (d, $J = 8.9$ Hz, 2H), 7.13 (s, 4H), 7.54 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (62.5 MHz, CDCl$_3$): 23.3, 24.5, 29.0, 33.9, 40.5, 45.2, 48.5, 50.9, 111.7, 123.7, 125.5, 128.8, 129.0, 129.7, 130.7, 151.3, 151.5, 152.9, 158.6. MALDI-TOF-MS (*m/z*): 938.3 ([M + H]$^+$), 960.2 ([M + Na]$^+$), 976.2 ([M + K]$^+$). Anal. Calcd (%) for $C_{50}H_{75}N_5O_6S_3 \cdot H_2O$: C 62.79, H 8.11, N 7.32, S 10.06; found: C 62.83, H 8.16, N 6.85, S 9.47.
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