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A study into Stille cross-coupling reaction mediated by palladium catalysts deposited over siliceous supports bearing N-donor groups at the surface

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Mesoporous molecular sieve SBA-15 and conventional silica gel were grafted with 3-[2-(diethylamino)ethylamino]propyl groups and used as supports for the preparation of deposited palladium catalysts, which were subsequently evaluated in Stille cross-coupling reaction of aryl bromides. The highest conversions were achieved with the metal-saturated catalyst resulting from the modified SBA-15. Influence of various reaction parameters (solvent, additive, temperature, etc.) on the overall yield and selectivity was studied. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: palladium; supported catalysts; Stille reaction; X-ray diffraction; TEM measurements

Introduction

Palladium-catalyzed cross-coupling reactions (e.g. Suzuki–Miyaura,[1] Heck–Mizoroki[2] and Stille[3] reactions) are frequently employed in the large-scale synthesis of fine chemicals and pharmaceutically active substances.[4] In view of their manifold practical applications, numerous attempts have been made to develop highly active *and* reusable noble metal catalysts for these reactions, typically those based on palladium immobilized over siliceous supports, polymers and other inert materials.[5] Silicate and aluminosilicate supports represented by conventional (amorphous) silica gel, mesoporous molecular sieves and zeolites proved to be particularly attractive for this purpose owing to their high structural variability, relatively easy functional modification as well as thermal and chemical stability.[6]

The deposition of the active metal component is typically performed by means of attached donor groups (i.e. by coordination of various donor groups attached to the support's surface) or without these ligating moieties. The latter approach based on in-synthesis[7] or post-synthesis palladation (and subsequent reduction to Pd(0) if appropriate) affords materials showing typically worse catalytic results than those resulting by the ligand-assisted metal deposition. The other approach requires the presence of donor groups suitable for palladium coordination, which can be introduced either during the synthesis of the support or by post-synthetic modifications of the surface of the parent solid material. The donor-modified supports are subsequently palladated and can be applied in catalysis (directly or after reduction of Pd(II) to Pd(0)).[8] Covalent anchoring of the donor groups is usually achieved via the reaction of the support with appropriate alkoxysilanes, followed by further reactions if required.[9]

In our work, we used N-donor groups mostly because of their stability, easy accessibility and favorable coordination properties. Materials of this type were previously tested in C–C bond-forming and dehalogenation reactions.[10,11] This contribution extends our work toward the palladium-catalyzed Stille reaction, which is, despite the generally high toxicity of organotin compounds, widely used owing to its high functional group tolerance and complementary character to other cross-coupling reactions.

It should be noted that several reports are available in the literature describing the use of Pd catalysts deposited over siliceous supports in model Stille reactions. For instance, Cai and coworkers[12] described the use of Pd catalysts heterogenized on 3-mercaptopropylated MCM-41, and Jin *et al.* reported on Stille coupling mediated by a Pd catalyst deposited on silica gel modified with chelating N,O-donor groups.[13] Carbonylative variant of the Stille reaction was performed with analogous catalysts bearing P, N-donor groups.[14] In our contribution we focus on model reactions, paying particular attention to the influence of various reaction parameters on the reaction outcome.

Results and Discussion

Preparation and Characterization of the Catalysts

Catalysts for this study were prepared using two different supports: the all-siliceous mesoporous molecular sieve SBA-15 (**1** in Scheme 1)[11] and conventional, chromatography-grade silica gel (size fraction 63–200 μm). The surfaces of these supports were first functionalized with 3-chloropropyl groups

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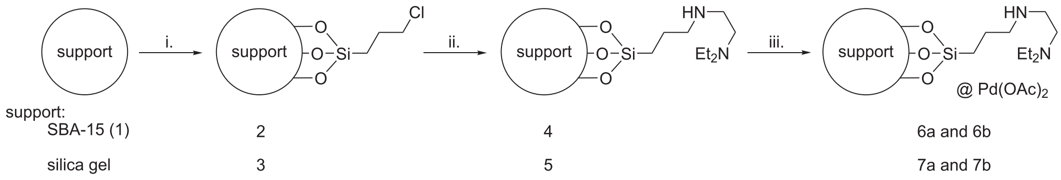


Scheme 1. Preparation of Pd catalysts **6** and **7**. Legend: *i*, (3-chloropropyl)triethoxysilane in toluene, refluxing (repeated twice); *ii*, treatment with $Et_2NCH_2CH_2NH_2$ in toluene and then with ammonia in ethanol–water; *iii*, $Pd(OAc)_2$ in dichloromethane.

via treatment with an excess of (3-chloropropyl)triethoxysilane in refluxing toluene. This procedure was repeated twice to ensure a full coverage of the accessible surface with the modifying groups. The 3-chloropropyl groups were subsequently converted to 3-[2-(diethylamino)ethylamino]propyl ones by alkylation with *N*,*N*-diethyl-1,2-diaminoethane and subsequent neutralization of the intermediate ammonium salt with ammonia in an ethanol–water solution to give materials **4** and **5**.

In the last step, the aminated supports were loaded with palladium using palladium(II) acetate dissolved in dichloromethane. Two catalysts were prepared from each modified support: one containing ~0.09 mmol Pd per gram of the support (**6a** and **7a**) and its metal-saturated counterpart (**6b** and **7b**). Considering that catalysts **6a** and **7a** resulted upon the addition of 0.1 mmol Pd $(OAc)_2$ per gram of the support, the amount of palladium in the final products indicates that virtually all metal component was anchored during the metalation step. Owing to the relatively low metal loading, materials **6a** and **7a** contain an excess of amine groups, the N/Pd ratios being 7.61 for **6a** and 10.20 for **7a**, containing more functional groups. The metal-saturated catalysts differed significantly in the amount of deposited palladium (**6b**: 0.31 mmol Pd g^{-1}; **7b**: 0.45 mmol Pd g^{-1}), which is indeed in accordance with the different amounts of the grafted donor groups. On the other hand, both metal-saturated catalysts exerted similar N/Pd values (1.97 for **6b**, and 1.87 for **7b**), approaching the limiting value of 2 corresponding to one palladium atom per one potentially chelating $Et_2NCH_2CH_2N(CH_2)_3Si\equiv$ donor group.

The prepared materials were characterized by elemental analysis (C, H, N and Cl by conventional combustion method, Pd by optical emission spectroscopy), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), IR spectroscopy and by nitrogen adsorption isotherms. The calculated textural parameters and XRD data are summarized in Table 1.

TEM micrographs of material **6b** (Fig. 1) revealed the well-ordered porous structure of the siliceous support and the absence of nanosized metallic particles, which is in accordance with the powder XRD measurements (Fig. 2). The pattern observed for the parent SBA-15 (material **1**) consisted of three characteristic diffraction lines, typical for hexagonal SBA-15 type material.[15] The most intense diffraction line at $2\theta = 0.87°$ was attributed to diffraction (0 0 1), whereas the relatively weaker ones at 1.47° and 1.64° could be assigned to reflections (1 1 0) and (2 0 0), respectively. The XRD patterns, which remained after modification practically unaffected except for an insignificant shift of the diffraction peaks, further suggested that the stepwise modification of the solid support does not affect internal structure of the crystalline fraction. In addition, the XRD patterns corroborated the absence of nanosized metallic palladium particles in catalysts **6** and **7** by showing no diffraction peaks in the region of palladium (1 1 1) diffraction at $2\theta \approx 40°$.

Adsorption–desorption isotherms of parent SBA-15 and catalyst **6a** are shown in Fig. 3 and the calculated textural parameters are given in Table 1. The isotherms of SBA-15-based materials displayed the characteristic hysteresis loop typical for mesoporous materials with cylindrical pores.[16] The fact that the adsorption and desorption branches did not overlap in the high-pressure region (p/p_0 ~0.8–1) indicates some structural defects and, perhaps, the presence of pores of different size. In the series of SBA-15 type materials, the calculated BET (Brunauer–Emmett–Teller) surfaces decreased along the reaction sequence, particularly during the amination step which, indeed, can reflect a partial decomposition of the support (base hydrolysis). As a result, the surface areas in catalysts **6** as the final products were comparable to those of **7** prepared from amorphous silica. On the other hand, the average pore size determined according to the BJH (Barrett–Joyner–Halenda) method[17] remained practically constant (~ 8 nm) for all SBA-15 type materials.

Catalytic Tests

The initial catalytic experiments aimed at surveying the influence of the reaction conditions were performed for the coupling of phenyltributyltin (**8**) with 4-bromotoluene (**9**) as this reaction allows one to distinguish between the cross-coupling (4-methylbiphenyl; **10**) and homocoupling products (biphenyl **11**; Scheme 2). First, the series of catalysts **6** and **7** at 0.5 mol% palladium loading was evaluated in this reaction performed in *N*,*N*-dimethylformamide (DMF) at 80°C. The results achieved

Table 1. Summary of X-ray diffraction patterns and textural parameters

Material	2θ (°)	BET surface area (m^2 g^{-1})	BJH pore volume (cm^3 g^{-1})	Average pore diameter (nm)
1	0.87, 1.47, 1.64	678	0.97	7.7
2	0.86, 1.46, 1.57	579	0.92	7.7
4	0.82, 1.42, 1.59	297	0.86	8.2
6a	0.82, 1.42, 1.56	311	0.83	7.9
6b	0.84, 1.45, 1.58	295	0.81	8.0
7a	—	347	0.46	4.7
7b	—	312	0.40	4.6

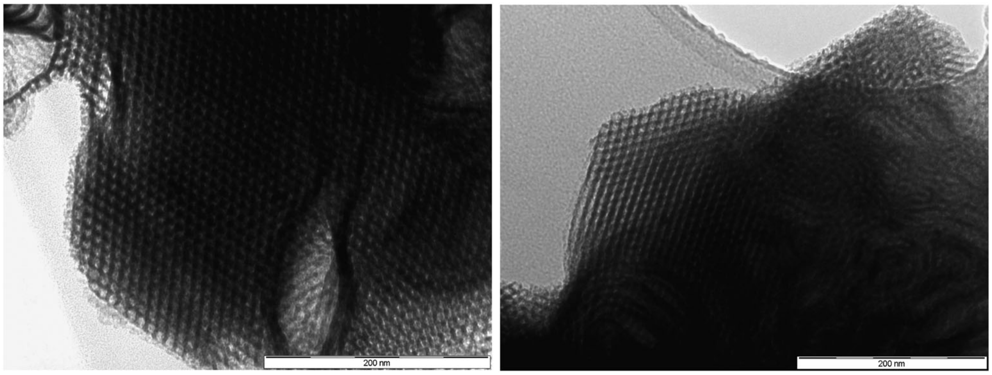


Figure 1. Representative TEM images of catalyst **6b**.

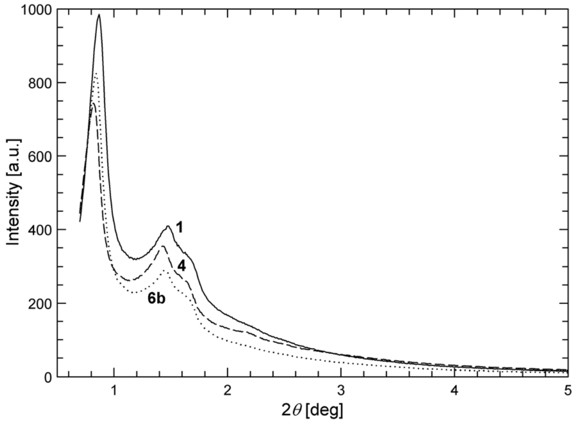


Figure 2. Small-angle X-ray diffraction patterns of materials **1** (solid line) and **4** (dashed line) and catalyst **6b** (dotted line).

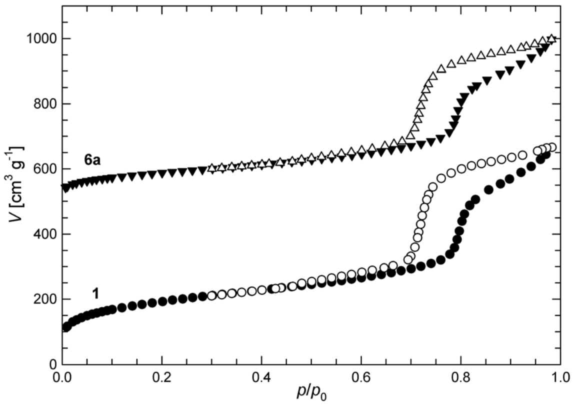
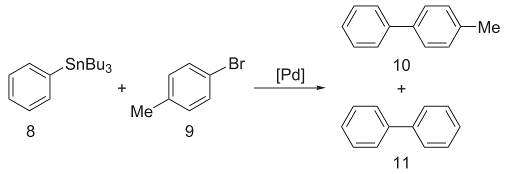


Figure 3. BET adsorption isotherms for the parent SBA-15 (**1**; circles) and material **6a** (triangles). Filled symbols, adsorption; empty symbols, desorption.



Scheme 2. The model Stille coupling of phenyltributyltin (**8**) with 4-bromotoluene (**9**) to give 4-methylbiphenyl (**10**).

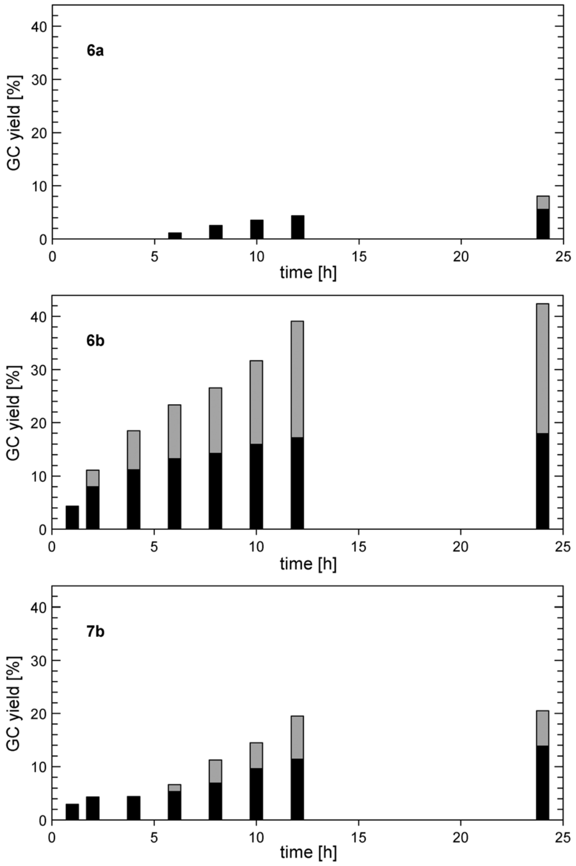


Figure 4. Kinetic profiles for the model Stille coupling mediated by catalysts **6a**, **6b** and **7b**. Material **7a** showed no catalytic activity and was therefore omitted from this figure. Black bars indicate the yield of 4-methylbiphenyl (**10**); gray bars indicate the yield of biphenyl (homocoupling product). The bars are missing in cases where no product was detected.

with catalysts **6a**, **6b** and **7b** are presented graphically in Fig. 4. Note: since biphenyl is formed from two molecules of stannane **8**, the gas chromatographic (GC) yield expressing the content of **11** in the reaction mixture was multiplied by two to represent to the real chemical yield. The data in the figures thus correspond to the relative 'rates' of the two parallel reactions.

The best catalytic results were obtained with the metal-saturated catalyst obtained from SBA-15-type support, material **6b**. This catalyst achieved nearly 20% yield of the coupling product and

~24% yield of biphenyl in 24 h. The related material **6a**, having a lower metal loading, performed considerably worse, affording the coupling product in only 6% yield after 24 h. Unlike its metal-saturated counterpart, this catalyst also showed a significant induction period (~4 h). Catalytic results obtained with **7b** resulting from silica gel were slightly worse than for the analogous material **6b**, which contains less palladium per gram of the support than **7b**. On the other hand, the metal-unsaturated material **7a** showed, rather unexpectedly, no detectable catalytic activity. Considering these results, it appears likely that the catalytic performance is determined mainly by the relative proportion between the anchored palladium and the amount of the N-donor moieties (i.e. by the N/Pd ratio). Whereas the metal-unsaturated catalysts showing high N/Pd ratios exerted relatively low catalytic activity (note: material **7a** proved to be inactive), the best results were achieved with the metal-saturated catalyst 6b, showing a relatively high N/Pd ratio (cf. the N/Pd ratios: **6a**, 7.61; **6b**, 1.97; **7a**, 10.2; and **7b**, 1.87) but a lower number of anchoring groups than in **7b**.

The most reactive catalyst, **6b**, was subsequently tested in different solvents. The reactions performed at 80°C and with 0.5 mol% of palladium in tri-*n*-butylamine (it should be noted that Vedejs *et al.*[18] noted an increase in reactivity upon using an intramolecularly N-coordinated organotin reagent whereas, in our case, the amine *solvent* as an 'external' donor stopped the reaction) and propionitrile did not proceed at all (neither **10** nor biphenyl were detected by GC analysis in the reaction mixtures after 24 h), while those in *n*-butanol, di-*n*-butylether and toluene achieved 2–5% yields of **10** after 24 h. A similar reaction in dioxane gave the coupling product in 7% yield. It is noteworthy that no homocoupling product **11** was detected in the final reaction mixtures obtained in *n*-butanol, dioxane and toluene. Finally, a result comparable to that achieved in DMF was obtained with *N*,*N*-dimethylacetamide (26% GC yield of the coupling product **10** and ~16% yield of **11**).

The Stille reaction is known to be affected by fluoride salts,[19] yet their mode of action has not been fully clarified. One of the hypotheses attributes the better yields achieved in the presence of fluoride reagents to the formation of insoluble organotin fluorides, which helps in shifting the reaction equilibrium toward the side of the products.[20] Another explanation takes into the account a labilization (increased reactivity) of the Sn–C bond upon the formation of pentacoordinate tin centres from the starting stannanes and fluoride ions.[21]

The results obtained after addition of alkali metal fluorides or tetrabutylammonium fluoride trihydrate (TBAF; 2 equiv. with respect to **8** and **9**) to our catalytic system are presented in Fig. 5. In the case of reaction carried out in DMF, the addition of sodium, potassium and cesium fluorides improved the overall catalytic performance, resulting in higher yields of the coupling product **10** and even the undesired biphenyl **11**. A slight decrease in the yields of both products was observed for LiF, while the addition of TBAF, which is fully soluble in the reaction mixture, practically stopped the coupling reaction. A similar situation was seen in *N*,*N*-dimethylacetamide (DMA) except that even LiF improved (albeit slightly) the reaction outcome in terms of the yields. On the other hand, KF afforded the best results in both solvents.

When CuI was employed as an additive (10 mol%; other conditions unchanged) to the reaction system, the reaction became less selective to the desired heterocoupling product **10**, as evidenced by the decrease in the amount of **10** in the reaction mixture (GC yields: ~10% in DMF and 12% in DMA after 24 h) and an increase in the amount of **11** (GC yields: ~32% in DMF and 33% in DMA).

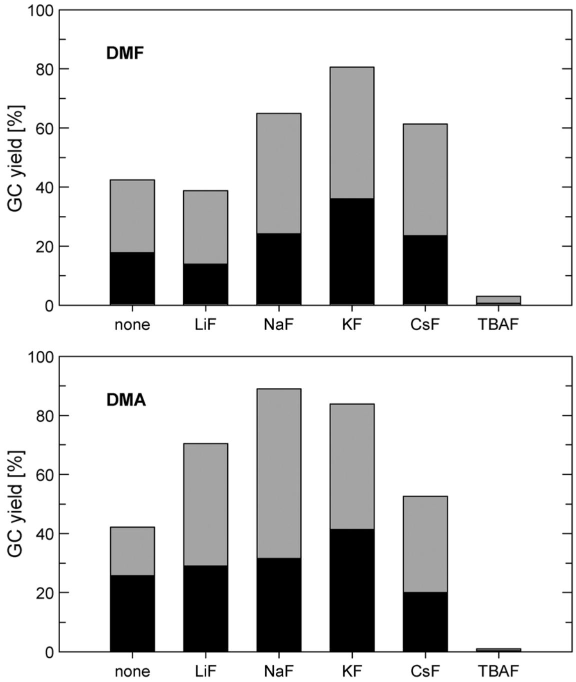


Figure 5. Influence of fluoride additives on the course of the coupling reaction. Black bars represent the yield of the coupling product **10**, gray bars that of biphenyl **11**. Conditions: PhSnBu3 (1.0 mmol), 4-bromotoluene (1.0 mmol), additive (2.0 mmol), mesitylene (1.0 mmol; internal standard) and catalyst **6b** (0.5 mol% Pd), reaction in DMF or DMA (4 ml) at 80°C for 24 h. TBAF, $[Bu_4N]F.3H_2O$.

Influence of the reaction temperature was assessed next for the model coupling reaction performed in the presence of KF, which afforded the highest conversions and selectivity among the additives tested. The results summarized in Fig. 6 indicate that the best yields of the coupling product **10** are obtained at 80°C, while the selectivity (i.e. the **10**/[**10** + **11**] ratio) increases with increasing reaction temperature owing to a diminished formation of the homocoupling product **11** in both DMF and DMA.

The selectivity of the reaction did not change upon changing the amount of catalyst **6b** in the reaction mixture. Upon increasing the amount of Pd in the reaction mixture from 0.1% to 0.2%, the yield of the coupling product **10** increased from ~ 20% to 28% (after 1 h at 80°C). Surprisingly, a further increase in the amount of the catalyst up to 1.0% increased the yield of **10** only slightly (Fig. 7). This in turn results in a pronounced change in the overall turnover number (TON = mmol **10**/mmol Pd), which decreases with increasing metal loading (Fig. 7).

In an attempt at increasing the amount of the desired heterocoupling product, the reaction was also performed with an excess of phenyltributyltin (2 equiv. with respect to **9**; KF additive) under otherwise identical conditions in DMF. Indeed, the addition of phenyltributyltin led to an increase in the amount in **10** in the reaction mixture (42% after 1 h, 48% after 6 h). When the same amount of $PhSnBu_3$ was added sequentially in two portions (i.e. one equivalent to the initial reaction mixture followed by another equivalent after heating for 6 h), the reaction outcome practically did not change (cf. 35% yield of **10** after 12 h). This observation suggesting that the catalyst loses its activity dramatically during the course of the catalytic run and also the large amount of side products present in the solid phase (harmful

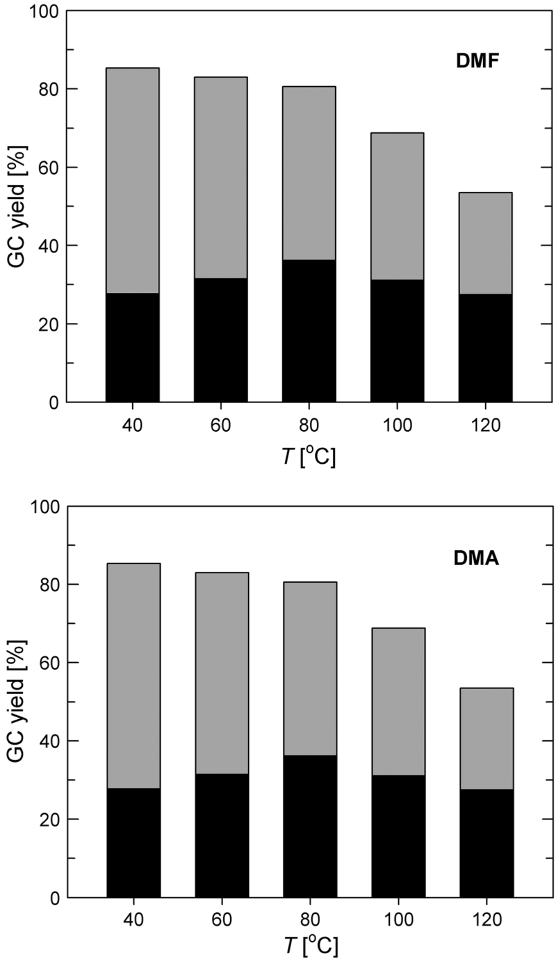


Figure 6. Influence of the reaction temperature on the yield of the coupling reaction. Black bars represent the yield of the coupling product **10**, gray bars that of biphenyl **11**. Conditions: $PhSnBu_3$ (1.0 mmol), 4-bromotoluene (1.0 mmol), KF (2.0 mmol), mesitylene (1.0 mmol) and catalyst **6b** (0.5 mol% Pd), reaction in DMF or DMA (4 ml) at 80°C for 24 h.

organotin compounds, base and other additives) led us to abandon any recyclation tests.

In order to determine the nature of the catalyst (note that a number of approaches toward establishing the nature of heterogenized catalysts have been devised; in the current work, we restricted ourselves (also in view of the catalyst stability) to the 'hot filtration' and mercury poisoning tests; see selected references)[22] simple hot filtration and mercury poisoning tests were carried out with the representative catalyst **6b**. Both these tests suggested the heterogeneous nature of the catalyzed process. In the first case, the reaction was allowed to proceed under the usual conditions for 1 h before the reaction mixture was centrifuged at 4000 rpm for 5 min and the liquid phase was filtered while hot through a 0.45 μm PTFE syringe filter. The filtrate was warmed again and its composition was monitored by GC analysis. The results are presented in Fig. 8. Whereas the non-filtered reaction mixture showed the expected kinetic profile, the removal of the solid phase resulted in marked decrease in the catalytic activity. In the second case, mercury (~0.2 ml) was added to the reaction mixture prepared as described in the Experimental section (see also caption to Fig. 8). GC analysis performed after reacting at 80°C for 6 h revealed only ~3% yield of **10** and 1% yield of **11**. Theses values are at the limit of reliable quantification and may well reflect the fact that the mercury (catalytic poison) was added as the last component to the pre-heated reaction mixture.

In addition, the catalyst recovered after a catalytic run was subjected to powder XRD and TEM analysis. The TEM images indicated loss of the periodical internal structure of the mesoporous support. In addition, the micrographs showed dark oval spots attributable to metallic particles that are presumably formed via aggregation of fine metallic particles resulting primarily via reduction of the deposited Pd(II) precursor. Similarly, the X-ray diffraction patterns of the recovered material lack the characteristic peaks due to SBA-15 support at low diffraction angles. Instead, a strong sharp peak is seen at $2\theta = 6.77°$ accompanied by a weaker peak at $2\theta = 9.46°$. A search in the Powder Data File database showed good agreement of these values with those reported for ITQ-14 (card no. 01-070-7350) and VPI-8 (card no. 00-056-0626). These data clearly suggest a massive structural change of the support to afford other (perhaps largely amorphous) siliceous phases, very likely due to an action of KF additive on the parent mesoporous sieve (Fig. 9).

Finally, catalyst **6b** was utilized in reactions of different substrates under optimized conditions. The results summarized in Table 2 indicate that the catalyst promotes the reaction of **8** with

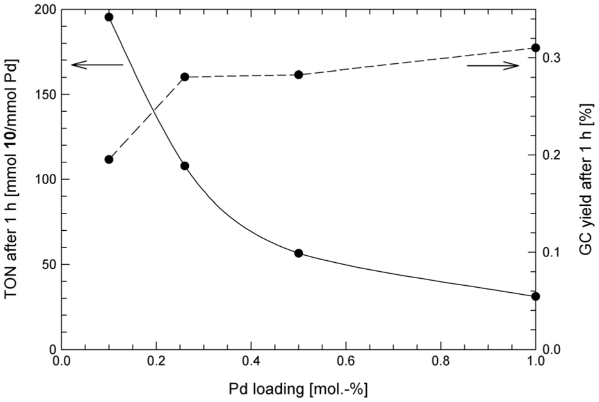


Figure 7. Dependence of the yield of the coupling product **10** and TON on the loading of catalyst **6b** after 1 h of reaction. Conditions: $PhSnBu_3$ (1.0 mmol), 4-bromotoluene (1.0 mmol), KF (2.0 mmol), mesitylene (1.0 mmol) and catalyst **6b**, reaction in DMF (4 ml) at 80°C for 1 h.

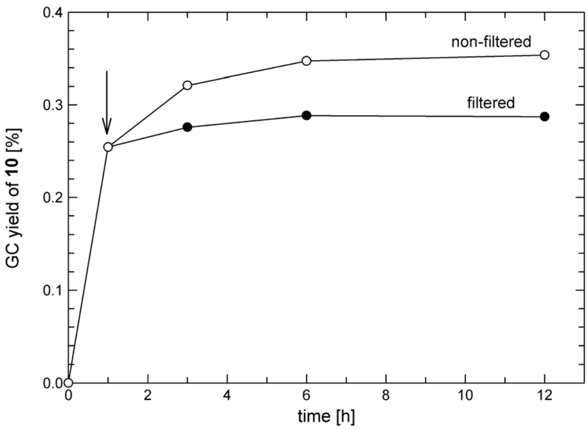


Figure 8. Results of the filtration test with catalyst **6b**. Conditions: $PhSnBu_3$ (1.0 mmol), 4-bromotoluene (1.0 mmol), KF (2.0 mmol), mesitylene (1.0 mmol) and catalyst **6b** (0.5 mol% Pd), reaction in DMF (4 ml) at 80°C.

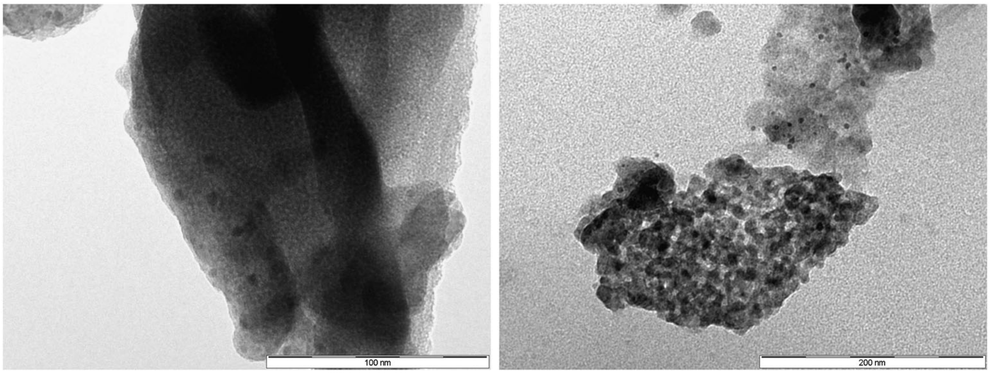


Figure 9. TEM images of catalyst **6b** recovered from a catalytic experiment in the presence of KF.

Table 2. Results of the coupling reactions with other substrates[a]

Entry	Halide	Stannane	Product	NMR yield (%)
1	4-Bromotoluene	Bu_3SnPh	**10**	32
2	4-Bromanisole	Bu_3SnPh	4-Methoxybiphenyl	42
3	4-Chlorotoluene	Bu_3SnPh	**10**	0
4	4-Iodotoluene	Bu_3SnPh	**10**	61
5	4-Bromotoluene	$SnPh_4$	**10**	14
6	Benzylbromide	Bu_3SnPh	Diphenylmethane	63
7	4-Bromanisole	$Bu_3SnCH=CH_2$	4-Vinylanisole	0
8	4-Bromanisole	$Bu_3SnCH_2CH=CH_2$	4-Allylanisole	0

[a]Conditions: stannane (1.0 mmol), halide (1.0 mmol), KF (2.0 mmol), mesitylene (1.0 mmol) and catalyst **6b** (0.5 mol.% Pd), reaction in DMF (4 ml) at 80°C for 6 h.

4-bromotoluene and 4-bromoanisole (deactivated substrates) to a similar extent (entries 1 and 2). Replacing 4-bromotoluene with the corresponding iodide expectedly resulted in a higher yield of the coupling product, while no appreciable reaction was observed for 4-chlorotoluene (entries 3 and 4). Replacement of **8** with tetraphenyltin (entry 5) in the model reaction also resulted in a lower conversion. Good results were achieved in the reaction of **8** with benzylbromide, which provided diphenylmethane in a 63% yield after 6 h (entry 6). On the other hand, catalyst was not able to promote the coupling of vinyl- and allyl-stannanes (entries 7 and 8).

Conclusions

The results presented in this paper indicate that palladium catalysts deposited over siliceous supports bearing N-donor groups at the surface can be employed in the Stille coupling of aryl bromides with phenyltributyltin. However, careful attention has to be paid to both optimization of the catalyst design and catalytic conditions as the catalyst performance varies greatly with the amount of N-donor groups and the N/Pd ratio as well as with the reaction conditions (temperature, solvent, possible additives, etc.). The catalysts are heterogeneous in nature and probably serve as reservoirs of active metal for the reaction proceeding in the liquid phase. The observed reaction profiles, which typically level off during the course of the reaction, suggest that the catalysts lose their activity during the catalytic run, probably due to aggregation of the metal particles or blocking of the support surface.

Experimental

Materials and Methods

Toluene and dichloromethane (Lachner) were dried by standing over sodium metal and anhydrous potassium carbonate, respectively, and were freshly distilled under argon prior to use. Other chemicals and solvents (DMF) were used as received from commercial suppliers (Lachner, Sigma-Aldrich, Fluka).

Powder XRD patterns were recorded with a Bruker D8 diffractometer using graphite monochromated Cu Kα radiation (1.5412 Å) and a position-sensitive detector Våntec-1 in Bragg–Brentano arrangement. Nitrogen adsorption isotherms were determined with a Micromeritics 2020 instrument at −196°C. The samples were degassed by heating to 130°C and then evacuated until a pressure of 1 mPa was attained (at least for 24 h) prior to measurement. ^1H NMR spectra were measured for solutions in $CDCl_3$ on a Varian VNMRS 300 spectrometer operating at 299.94 MHz. The conversion was determined by a comparison of integral intensities of the signals due to the product (methoxy or benzylic CH_2 protons) and the signal of C_6Me_6 used as an internal standard.

The content of palladium was determined by optical emission spectroscopy with inductively coupled plasma (ICP-OES) on an IRIS Interpid II instrument (Thermo Electron) using axial plasma and an ultrasonic nebulizer CETAC U-5000AT+ (wavelength used for spectrophotometric analysis: 324.270 nm). The samples were dissolved in a mixture of concentrated HNO_3 and HF (2:3; both Suprapure, Merck; 50°C/15 min) and the solutions were diluted with redistilled water. The content of C, H, N and Cl were determined by conventional combustion analysis.

TEM images were obtained with a JEOL 2010 transmission electron microscope (point resolution 0.19 nm, acceleration voltage 160 kV). The samples were dispersed in ethanol and ultrasonicated for 2 min. The resulting suspensions were applied to a copper grid covered with holey carbon membrane and allowed to dry in the air.

Catalyst Preparation

Mesoporous molecular sieve SBA-15 (**1**) was prepared in analogy to the literature procedure[23] as follows. A polyethylene vessel was charged successively with triblock copolymer Pluronic P123 ((ethylene oxide)$_{20}$(propylene oxide)$_{70}$(ethylene oxide)$_{20}$ from Sigma-Aldrich; 10 g), $Na_2SiO_3.9H_2O$ (29.7 g, 0.10 mmol) and deionized water (256 ml). The resulting mixture was stirred until the solid reagents completely dissolved (4 days) and then warmed to 45°C in a water bath. Concentrated aqueous HCl (65 ml 35%, ~0.75 mol) was introduced and the resulting mixture was stirred at 45°C for another 90 min. It was then reacted at 90°C without stirring and under autogenous pressure for 7 days. The separated solid was filtered off, washed with deionized water until the washings were neutral and twice with ethanol, and dried in air. The resultant solid was extracted with ethanol in Soxhlet apparatus in order to remove the polymeric template and dried in air once again (2 days). Prior to the subsequent functionalization, the solid mesoporous sieve was calcined at 550°C for 6 h (the temperature was raised from room temperature to 550°C with an increase of 1°C per minute and then maintained at 550 °C for 6 h).

*Characterization data for **1***

Powder XRD, 2θ (deg.): 0.87 (s), 1.47 (m), 1.64 (sh). BET surface area: 678 m^2 g^{-1}. FT-IR, ν_{max} (cm^{-1}): 3745 (vs), 3330 (br w), 1976 (vw), 1866 (vw), 1634 (w), 1164(sh), 1066 (s), 962 (m), 804 (m), 572 (w), 460 (m).

Neat (3-chloropropyl)triethoxysilane (13.5 g) was added to a suspension of calcined SBA-15 (**1**) in dry toluene (16.2 g in 400 ml of the solvent). After the resulting mixture was heated at reflux under argon for 16 h, the solid was filtered off and washed successively with toluene (2 × ~50 ml), acetone and pentane (~50 ml each). The resulting material was dried first in the air and then at 120°C under vacuum (~10 torr) for 3 h. The silylation procedure was repeated once again (13.5 g (3-chloropropyl)triethoxysilane in 300 ml toluene; isolation as above) to afford material **2**.

*Characterization data for **2***

Elemental analysis (mmol g^{-1}): C 2.56, H 11.6, Cl 0.30. Powder XRD, 2θ (deg.): 0.85 (s), 1.46 (m), 1.63 (sh). FT-IR, ν_{max} (cm^{-1}): 3745 (w), 3308 (br w), 1964 (vw), 1866 (vw), 1632 (w), 1184 (sh), 1074 (s), 958 (m), 808 (w), 460 (m).

Material **3** was obtained similarly from chromatographic silica gel (63–200 μm, Fluka). The support was first calcined and then twice silylated as specified above (26.1 g dried silica gel; 22.1 g (3-chloropropyl)triethoxysilane in 1000 and 200 ml dry toluene for the first and second silylation steps, respectively).

*Characterization data for **3***

Elemental analysis (mmol g^{-1}): C 4.47, H 7.29, Cl 0.55.

In the next step, the chloropropylated supports were aminated with *N,N*-diethyl-1,2-diaminoethane. A mixture of material **2**, $Et_2NCH_2CH_2NH_2$ (17.4 g) and toluene (200 ml) was stirred under argon at 100°C for 39 h. The solid product was filtered off, washed with toluene (100 ml) and ethanol (400 ml in several portions) and left to dry in the air (1 day). The solid converted to free amine form by stirring with a mixture of ethanol and 25% aqueous ammonia (3:1, 150 mmol) for 2 h, filtered, washed with ethanol until the washings were neutral and dried in the air to give material **4**. Material **5** was prepared similarly from chloropropylated silica **3**.

*Characterization data for **4***

Elemental analysis (mmol g^{-1}): C 3.73, H 15.9, N 0.68, Cl below ~0.05. Powder XRD, 2θ (deg.): 0.83 (s), 1.42 (m), 1.52 (sh). FT-IR, ν_{max} (cm^{-1}): 3330 (br w), 1633 (w), 1473 (vw), 1175 (sh), 1078 (s), 962 (w), 802 (w), 558 (sh), 463 (s).

*Characterization data for **5***

Elemental analysis (mmol g^{-1}): C 5.23, H 11.0, N 0.93, Cl below ~0.09. FT-IR, ν_{max} (cm^{-1}): 3200 (br m), 2980 (w), 2942 (w), 2885 (vw), 2828 (vw), 1986 (w), 1866 (w), 1638 (w), 1457 (w), 1179 (sh), 1077 (s), 963 (sh), 796 (m), 555 (sh), 457 (s).

For the preparation of the metal-unsaturated catalysts **6a** and **7a**, a solution of palladium(II) acetate (0.112 g, 0.1 mmol per g of the support) in dry dichloromethane (20 ml; the solution was filtered through a 0.45 μm syringe filter prior to the addition) was added to the respective aminated support (5.0 g of **3** or **4**). The mixture was diluted with dichloromethane (100 ml) and stirred under argon for 2 h. The solid was filtered off, washed carefully with dichloromethane and, finally, dried in air.

*Characterization data for **6a***

Elemental analysis (mmol g^{-1}): C 3.74, H 15.1, N 0.67, Cl 0.17; Pd 0.088. Powder XRD, 2θ (deg.): 0.82 (s), 1.42 (m), 1.59 (sh). BET surface area: 311 m^2 g^{-1}. FT-IR, ν_{max} (cm^{-1}): 3340 (br w), 1632 (w), 1552 (w), 1410 (w), 1172 (sh), 1084 (s), 964 (w), 802 (w), 560 (sh), 456 (s).

*Characterization data for **7a***

Elemental analysis (mmol g^{-1}): C 5.20, H 11.6, N 0.89, Cl 0.25; Pd 0.087. BET surface area: 347 m^2 g^{-1}. FT-IR, ν_{max} (cm^{-1}): 3250 (br w), 2974 (w), 2946 (w), 2886 (w), 2825 (vw), 1996 (vw), 1860 (w), 1632 (w), 1568 (w), 1464 (w), 1400 (w), 1179 (sh), 1074 (s), 997 (sh), 796 (w), 562 (sh), 457 (s).

The corresponding metal-saturated catalysts **6b** and **7b** were prepared similarly using an excess of palladium(II) acetate to ensure saturation of the support with the metal component (0.561 g (2.5 mmol) $Pd(OAc)_2$ per 5.0 g **3**, and 0.898 g (4 mmol) $Pd(OAc)_2$ per 5.0 g **4**). Unanchored palladium(II) acetate was removed by washing with a copious amount of dichloromethane (1 l in several portions).

*Characterization data for **6b***

Elemental analysis (mmol g^{-1}): C 4.45, H 14.2, N 0.61, Cl 0.16; Pd 0.31. Powder XRD, 2θ (deg.): 0.84 (s), 1.44 (m), 1.58 (sh). BET surface area: 295 m^2 g^{-1}. FT-IR, ν_{max} (cm^{-1}): 3253 (br w), 1634 (vw), 1557 (w), 1428 (w), 1166 (sh), 1085 (s), 961 (w), 800 (w), 558 (w), 460 (s).

*Characterization data for **7b***

Elemental analysis (mmol g^{-1}): C 6.35, H 14.53, N 0.84, Cl 0.14; Pd 0.45. BET surface area: 312 m^2 g^{-1}. FT-IR, ν_{max} (cm^{-1}): 3200 (br w), 2978 (w), 2940 (w), 2882 (w), 1996 (w), 1866 (w), 1574 (m), 1413 (w), 1352 (w), 1179 (sh), 1081 (s), 966 (sh), 803 (m), 690 (w), 562 (w), 450 (s).

Catalytic Tests

Initial kinetic experiments were performed with a parallel batch reactor (Heidolph Synthesis I). The progress of the reactions was monitored by GC using an Agilent 6850 chromatograph equipped with a DB-5 column (internal diameter 0.18 mm, film thickness 0.18 μm, length 20 m). The reaction mixtures prepared by mixing the appropriate Pd catalyst (0.5 mol% Pd), halide (1.0 mmol), organotin reagent ($PhSnBu_3$, 1.0 mmol), mesitylene (1.0 mmol) and solvent (4 ml) were heated (usually for 80°C) and continuously stirred. Aliquots were withdrawn at regular intervals and centrifuged at 4000 rpm for 5 min prior to GC analysis. For the filtrate test, the amount of reactants was doubled and the reaction mixture was centrifuged and its half was filtered through a 0.45 μm PTFE syringe filter while hot to avoid readsorption of the metal catalyst on to the solid phase.

In the case of preparative batch reactions performed with catalyst **6b**, the reaction mixture contained the substrate (1.0 mmol 4-bromoanisole or benzyl bromide), organotin reagent (1.1 mmol), the catalyst (16.2 mg 6b, 0.5 mol% Pd), hexamethylbenzene (internal standard, 1/6 mmol), KF (2.0 mmol) and dry DMF (4 ml). The reaction was allowed to proceed at 80°C for 6 h with continuous stirring and, after cooling to room temperature, was terminated by addition of 1 M aqueous KF (10 ml). The products were extracted with pentane (10 ml). The organic layer was dried over magnesium sulfate, filtered and evaporated, leaving a residue, which was analyzed by ^1H NMR spectroscopy.

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