A simple procedure for the covalent grafting of triphenylphosphine ligands on silica: application in the palladium catalyzed Suzuki reaction†

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An organic–inorganic hybrid material derived from covalently grafting a palladium complex of the type $(L)_2PdCl_2$ ($L = Si(OMe)_3$ functionalized PPh_3) on silica was synthesized, characterized and sucessfully applied as a catalyst for the Suzuki reaction.

Introduction

The palladium catalyzed Suzuki cross-coupling of aryl halides with arylboronic acids to form biaryls has emerged as an extremely powerful tool in organic synthesis.[1] However, in homogeneous catalysis separation and recovery of the catalyst are difficult, which is of special disadvantage for large-scale preparations. Therefore, a large number of heterogeneous palladium containing catalysts have been developed during the last years. These solids can simply be recovered from the reaction mixture by filtration and reused.[2] Organic polymers and inorganic oxides (*e.g.*, silica gel) are commonly used as supports for the synthesis of such catalysts.[2,3] Different palladium complexes, bearing ligands such as carbenes, amines or thiols, have been immobilized on silica supports.[4] In a detailed study, Clark and Paul investigated the relationship between chemical structure and catalytic activity in the Suzuki coupling reaction for a wide variety of bidentate ligands grafted on silica including *N*,*N*-, *N*,*S*- and *N*,*O*-donating systems.[5] They found that lowering the bond energy between the palladium centre and the ligand results in an increase in reactivity. Grudden *et al.* reported that thiol modified mesoporous materials are remarkable scavengers for palladium, and the resulting palladium encapsulated materials catalyze Suzuki type coupling reactions with virtually no leaching of palladium.[6] Corma *et al.* immobilized an oxime-carbapalladacycle complex on mercaptopropyl modified silica. This solid is an active and stable heterogeneous catalyst for the Suzuki coupling reaction of aryl bromides and chlorides in water.[7]

Although significant efforts have been achieved to develop heterogenized palladium containing catalysts, such systems still suffer from high catalyst loadings and a lower efficiency compared to their analogues in the homogeneous phase. Moreover, the catalytic activity of heterogeneous palladium catalysts sometimes happens to decrease or even disappear after use.[8]

Palladium triphenylphosphine complexes have often been used for Heck and Suzuki couplings, mainly due to the simple handling of these complexes and the cheap phosphine donor ligand. Depending on the substrate they show good activity and selectivity. Additionally, some heterogeneous catalysts require the addition of phosphine ligands such as PPh_3 to obtain reasonable activity.[9] It therefore is not surprising that the heterogenization of phosphine ligands on solid supports was taken as a tool for the heterogenization of palladium. In an early report Trost *et al.* described polymer-supported palladium catalysts based on diphenylphosphanyl functionalized polystyrene.[10] In the following years a variety polymer-supported palladiumphosphine complexes were synthesized and used for coupling reactions.[11] However, to the best of our knowledge no procedure for the covalent heterogenization of palladiumphosphine complexes on porous silica as the support has been reported.

In the present work, we describe the synthesis of a novel heterogeneous cross-coupling catalyst by immobilization of a functionalized palladium triphenyphosphine complex on the surface of silica gel. The material was characterized by solid state ^{29}Si, ^{13}C and ^{29}P CP-MAS NMR spectroscopy, SEM and EDX, surface area BET measurements, IR and elemental analysis. Furthermore, the catalytic properties of the palladium containing material was studied exemplarily for the Suzuki cross-coupling between aryl halides and arylboronic acid.

Results and discussion

Synthesis and characterization of the palladium catalysts

It should be mentioned at this point that the usage of diarylalkyl phosphines like $Ph_2P(CH_2)_3Si(OEt)_3$ has already been reported for the synthesis of phosphine functionalized silica materials.[12] However, these ligands are much more sensitive towards oxidation than triarylphosphines.[13] Additionally, the steric demand of the alkyl chain is moderate and the linker between the phosphorus donor and the silicon based anchoring group is short, which might favour additional interactions between the framework walls and the active site. We therefore focused on immobilizing a triphenylphosphine based system onto silica *via* an alkyl chain linker attached to one of the aryl rings of the phosphine ligand.

In general, there are two ways to immobilize a catalytically active complex covalently on the surface of a solid support: on one hand,

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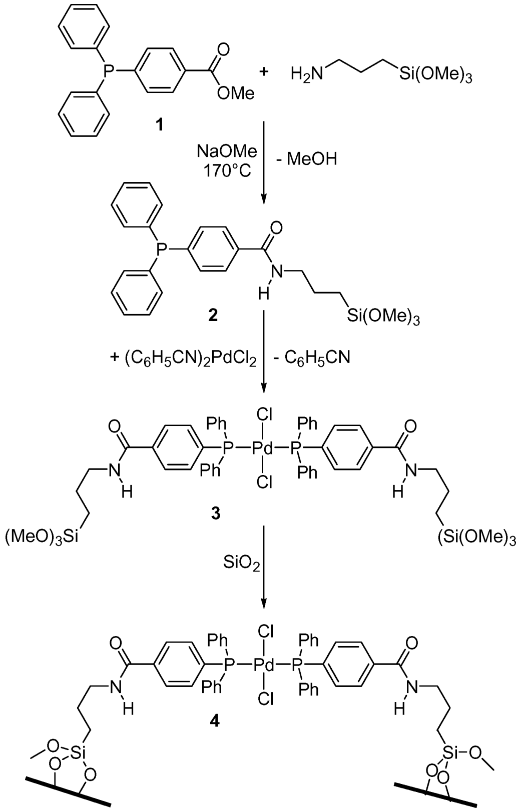
the active complex can be prepared prior to the grafting procedure, on the other hand, the ligand system can be grafted first followed by treatment of this hybrid material with an appropriate source of the active metal centre. For our palladium system we chose the first route, since it determines the molar ratio of palladium and phosphine to 1 : 2, the palladium complex can be purified and spectroscopically characterized before starting the anchoring procedure and the two phosphines will be anchored in an ideal position for coordination to one palladium site on the surface. This prevents the generation of palladium centres coordinated to one or three phosphine molecules.

Starting from 4-diphenylphosphinylbenzenecarboxylicacid methylester (**1**)[14] the $Si(OR)_3$ function required for the grafting was introduced by a solvent free NaOMe catalyzed thermal aminolysis with 3-trimethoxysilylpropylamine (Scheme 1). The oily product **2** was characterized by NMR spectroscopy: three sets of signals at high field in the ^1H NMR spectrum (3.46, 1.76, 0.73 ppm), which are typical for the silicon functionalized propylene chain, a sharp singlet (3.58 ppm) for the $Si(OMe)_3$ group, one broad singlet at 6.53 ppm for the NH group and a quite complex pattern of resonances between 7.3 and 7.7 ppm for the five magnetically inequivalent protons of the aryl rings, which are all coupling with the phosphorus atom. The $^{31}P\{^1H\}$ NMR spectrum shows one sharp resonance at –4.10 ppm, typical for a triaryl substituted phosphorus atom. For the synthesis of the palladium(II) complex **3**, ligand **2** was dissolved in CH_2Cl_2 and treated with half an equivalent of di(benzonitrile)dichloropalladium(II), giving the desired product in almost quantitative yields. The resonance of the phosphorus atom is shifted to 24.4 ppm due to the formation of the complex.[15] In the last step of the synthesis, the complex was covalently anchored on a commercially available mesoporous but not ordered silica gel (Aldrich, TLC standard grade).



Scheme 1 Synthesis of the hetrogenized palladium catalyst **4**.

After grafting of the palladium(II) complex **3**, the palladium content in the solid material **4** was determined by elemental analysis. Additionally, to these data Table 1 shows the results of the BET measurements for the parent silica and palladium functionalized silica **4**. Although 0.4 mmol of **3** per gramme of SiO_2 were applied in the grafting procedure, elemental analysis shows that only 0.18 mmol g^{-1} of palladium complex **3** were finally immobilized on the silica surface. For solid **4**, the expected reduction of the specific surface area, the pore volume and pore diameter with respect to the parent support could be quantified. This indicates that the surface modification indeed takes place inside the primary mesopores of the silica gel.

The presence of palladium in the compound **4** was confirmed by EDX analysis (see ESI).† As revealed by SEM done at a resolution of 50 nm no larger palladium particles ($d \geq 50$ nm) are present on the surface of the support (Fig. 1). This does not change after a fourfold reuse of the catalyst (see ESI).† Both observations confirm a uniform dispersion of the active sites.

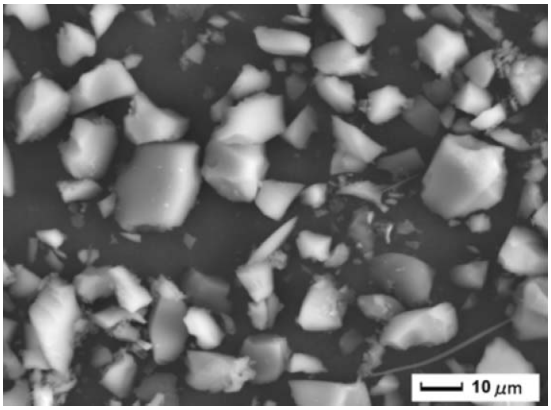


Fig. 1 SEM image of the freshly prepared catalyst **4**.

Table 1 Characterization of the parent silica gel and the hybrid material **4**

Material	$S_{BET}/m^2\ g^{-1}$	Pore volume/$cm^3\ g^{-1}$	BJH pore diameter/nm	Chem. composition (wt%) C	H	N	Immobilized Pd[a]/mmol g^{-1}
Neat silica	500	0.75	6.0	—	—	—	—
4	247	0.43	5.5	10.1	1.4	0.5	0.18

[a] Calculated according to the nitrogen content the elemental analysis.

The analysis of the nitrogen adsorption and desorption data exhibited a type IV isotherm (definition by IUPAC) with a hysteresis characteristic for mesoporous materials possessing pore diameters between 2 and 50 nm (Fig. 2).[16] This indicates that the overall mesoporosity is maintained after the introduction of palladium complex.

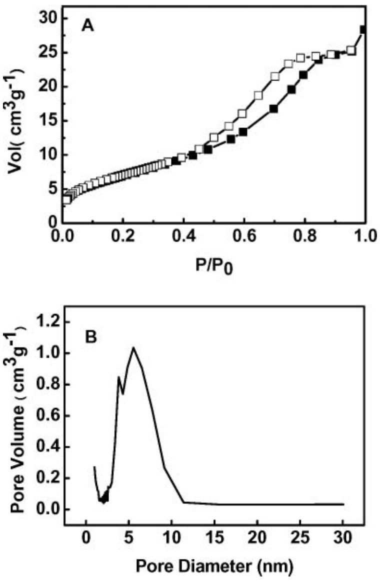


Fig. 2 (A) N_2 adsorption/desorption isotherms at 77 K and (B) pore size distribution of **4**; adsorption points are marked by solid squares and desorption points by empty squares.

The ^{29}Si CP-MAS NMR spectrum (Fig. 3) of the hybrid material **4** provides direct evidence for the covalent incorporation of the phosphinepalladium(II) complex **3**. According to the literature, the signals at –110, –101, and –92 ppm correspond to the $Si(OSi)_4$ (Q^4), $HOSi(OSi)_3$ (Q^3), and $(HO)_2Si(OSi)_2$ (Q^2) sites of the inorganic silica framework.[17] Covalent grafting of **3** on the silica surface makes the Q^2 signal of the neat silica almost disappear, which is due to the consumption of highly reactive geminal Si–OH groups during the condensation reaction.[18] For the modified material **4**, three additional broad and overlapping signals appear at –49, –58, and –67 ppm, which can be assigned to $R–Si(RO)_2(OSi)$ (T^1), $R-Si(RO)(OSi)_2$ (T^2), and $R-Si(OSi)_3$ (T^3) organosiloxane sites. Since the T^1 resonance is dominant over T^2 and T^3, the covalent grafting of the silylated phosphine is mainly due to $R–Si(RO)_2(OSi)$ sites.

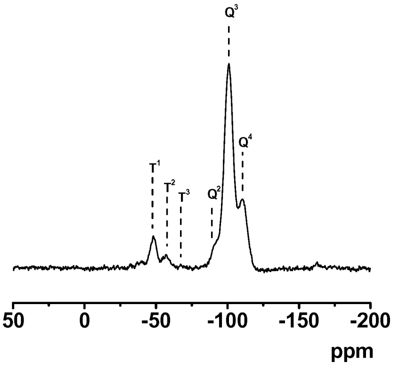


Fig. 3 ^{13}Si CP-MAS NMR spectrum of the hybrid material **4**.

The ^{13}C CP-MAS NMR spectrum of **4** (Fig. 4) shows signals for the aryl groups in the range from 145.1 to 120.1 ppm. Three resonances at 42.8, 22.6, 9.0 ppm can be correlated with the resonances of the propylene linker in the precursor **3** (42.4, 22.7 and 6.6 ppm). A signal at 168.0 ppm can be assigned to C=O group of the linker. It is found at an almost similar chemical shift as for **3**, which indicates, that the interaction between the amide group of the linker and the silica framework is only weak.[19] The dominant resonance at 48.9 ppm can be assigned to organosilica $C-SiOCH_3$ groups, implying that the hydrolysis/condensation of **3** is not fully completed[18] as already mentioned in the discussion of the ^{29}Si CP-MAS NMR spectrum.

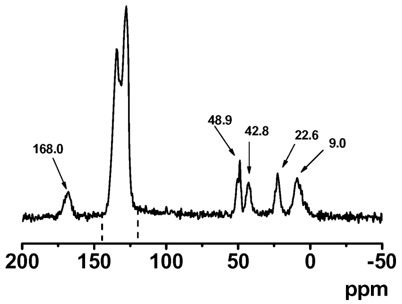


Fig. 4 ^{13}C CP-MAS NMR spectrum of the hybrid material **4**.

The structural retention of the palladium(II) complex during the immobilization process is further proved by the ^{31}P CP-MAS NMR of **4**. As shown in Fig. 5, the ^{31}P-NMR signal of **4** in the solid state (23.6 ppm) corresponds well with the chemical shift of the palladium complex in solution (24.4 ppm). There is no signal of uncoordinated phosphine and phosphineoxide. The unsymmetrical phosphorus resonance is due to differences in the chemical environment of the phosphine and the palladium sites which are located in close proximity to the surface.

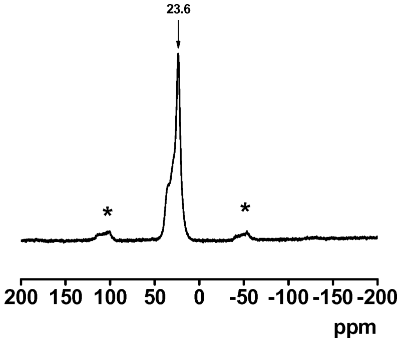
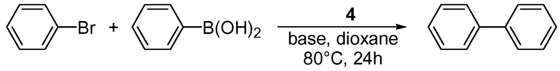


Fig. 5 ^{31}P CP-MAS NMR spectrum of the hybrid material **4**; the asterisks denote rotational side bands.

The presence of the palladium complex on the silica surface is indicated in the IR spectrum by a weak amide band at 1539 cm^{-1}, which is found at the same wavenumber as for the precursor **3** (see supporting information). A second amide band at 1645 cm^{-1}, which is observed for **3**, is overlapped by an absorption of the support at 1636 cm^{-1}.

Application for the Suzuki reaction

To evaluate the general activity of catalyst **4**, the Suzuki reaction of phenylboronic acid with an aryl halide (benzene bromide) was examined (Scheme 2 and Table 2). Initially, an optimization of the base was performed using Cs_2CO_3, K_3PO_4, K_2CO_3 and KF under identical conditions. These bases have frequently been applied for homogeneous and heterogeneous catalyzed Suzuki coupling reactions.[20] Cs_2CO_3 and K_3PO_4 turned out to be highly efficient under the given conditions.



Scheme 2 Suzuki coupling of aryl bromide and phenylboronic acid.

Table 2 Suzuki reaction of bromobenzene and phenylboronic acid with different bases[a]

Base	Cs_2CO_3	K_3PO_4	K_2CO_3	KF
Yield (%)[b]	90	92	76	71

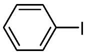
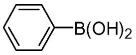
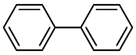
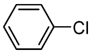
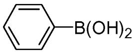
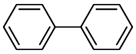
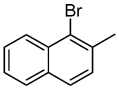
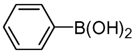
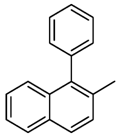
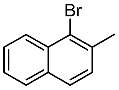
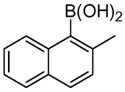
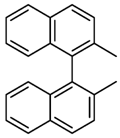
[a] Reaction conditions: PhBr (1 mmol); $PhB(OH)_2$ (1.5 mmol); base (1.2 mmol); Pd (1 mol% relative to aryl halide); dioxane (5 mL), 80 °C. [b] Determined by GC-MS with *n*-decane as the internal standard.

The activity of the heterogenized catalyst system is in general comparable to that of $(PPh_3)_2PdCl_2$ and of a related system where $PdCl_2$ was heterogenized using a polymer (PS-DEAM resin) bound phosphine ligand of the type Ph_2PPh-CONHR.[21]

Based upon these results, a series of different substrates were tested in the presence of catalyst **4** (Table 3). The coupling of iodobenzene and arylboronic acid afforded the expected biaryl in very good yield (entry 1). However, for the less reactive chlorobenzene, a pronounced reduction in activity was observed (entry 2). Rising the reaction temperature up to 120 °C did not increase the conversion but resulted in a yield of only 8% after 24 h, probably due to rapid catalyst deactivation. Additionally sterically hindered substrates were investigated: the coupling of 1-bromo-2-methylnaphthalene and boronic acid almost reached completion. In contrast, the reaction between 1-bromo-2-methylnaphthalene and 2-methylnaphthylboronic acid, which would be interesting for the synthesis of 1,1′-dimethyl-2,2′-binaphthyl, afforded only traces of the product, probably due to inherent difficulties in coupling two sterically hindered arenes.

Reusability is an important feature that determines the applicability of a heterogeneous catalysts. We examined the reusability of **4** with Cs_2CO_3 as the external base. After the first use of the catalyst in the Suzuki reaction, the reaction mixture was treated as described in the experimental part. The recovered catalyst was used successfully for four subsequent reactions and exhibited consistent catalytic activity, indicating the excellent reusability of this heterogeneous catalyst (Table 4).

Table 3 Suzuki reactions between aryl halides and aryboronic acids[a]

Halide	Arylboronic acids	Product	Yield (%)[b]
			99
			24
			98[c]
			Traces

[a] Reaction conditions: aryl halide (1 mmol); arylboronic acid (1.5 mmol); K_3PO_4 (1.2 mmol); Pd (1 mol% relative to aryl halide); dioxane (5 mL), 80 °C. [b] Determined by GC-MS with *n*-decane as the internal standard. [c] GC-MS and ^1H NMR.

Table 4 Study on the reusability of **4** in the Suzuki reaction[a]

	Yield (%)[b]			
Base	1st run	2nd run	3rd run	4th run
Cs_2CO_3	90	88	89	82

[a] Reaction conditions: PhBr (1 mmol); $PhB(OH)_2$ (1.5 mmol); base (1.2 mmol); Pd (1 mol% relative to aryl halide); dioxane (5 mL), 80 °C. [b] Determined by GC-MS with *n*-decane as the internal standard.

It should also be pointed out here that the initially yellow coloured catalyst turned to grey after the first run, and the colour darkened gradually with further recycling. This is possible by the formation of metallic nanoparticles during the catalytic transformation. A similar observation was reported by Trilla *et al.*[22] However, by microscopic investigations no palladium particles with a diameter larger than 50 nm could be detected (see ESI).† We suppose that both the silica matrix and the organic ligand contribute to a stabilization of small palladium nanoparticles. To clarify the role of the phosphine ligand, we set up a control experiment, with a catalyst prepared by directly loading $PdCl_2(PhCN)_2$ on silica. The overall palladium loading was similar to that of **4**. Running a Suzuki reaction between phenylboronic acid and bromobenzene with this catalyst under identical reaction conditions as before gave less than 50% of conversion after 24 h in the first run. The activity of this catalyst was completely lost after the first run. This suggests that the grafted phosphine ligand plays an important role for the activity and stability of catalyst.

A further objective of our studies was to determine whether **4** acts as a truly heterogeneous catalyst. To test this, the coupling reaction was carried out for 1 h until a conversion of about 30% was reached. Then the catalyst was removed by filtration at the reaction temperature. The filtrate was treated with another 1.2 equiv. of Cs_2CO_3 and heated for additional 23 h at 80 °C. The reaction continued although the conversion did not reach the level obtained with **4**, which means that at least a part of the catalytic activity of **4** must be assigned to a homogeneous reaction. To determine the degree of leaching of the metal from the heterogeneous catalyst, the catalyst was removed by filtration at 80 °C after the reaction was completed (24 h) and the palladium content of the filtrate was determined by atomic absorption spectrometry (AAS). We found a palladium contamination of about 0.4% relative to the original Pd loading of **4**, which implies that leaching is not a serious problem for this catalyst. This is also confirmed by the excellent reusability of this catalytically active material.

Experimental

Materials

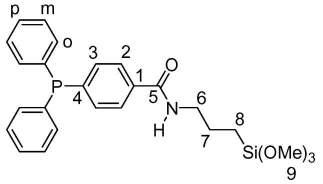
The silica gel used for the heterogenization was obtained from Aldrich (TLC standard grade, without binder, catalogue no. 28 850-0), all other chemicals were supplied by Acros. The solvents used for the preparations were dried by standard methods. All reactions were performed under inert gas conditions (N_2).

Characterization

Elemental analyses were carried out at the Department of Chemistry (TU Kaiserslautern). Infrared spectra were recorded with a Perkin-Elmer FT-IR 1000 spectrometer. NMR spectra were recorded with a Bruker Avance 400 or 600 spectrometer. The infrared spectra (KBr) were recorded using a Jasco FT/IR-6100 spectrometer in a frequency range between 4000–400 cm^{-1}. Nitrogen adsorption/desorption isotherms were measured at the liquid nitrogen temperature, using a Quantachrome Autosorb 1 sorption analyzer. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) equation at a relative pressure of 0.9 (P/P_0), and the pore size distribution curves were analyzed with the desorption branch by the BJH method. ^{13}C CP-MAS, ^{31}P CP-MAS and ^{29}Si CP-MAS NMR spectra were obtained on a Bruker DSX Avance spectrometer at resonance frequencies of 100.6, 162.0 and 79.5 MHz, respectively. The analyses of catalysts surfaces before or after the reaction were done by scanning electron microscopy (SEM) with JSM-6490LA and energy dispersive X-ray analysis (EDX). The atomic adsorption spectrum was measured by a Perkin Elmer AAnalyst 300.

Catalyst synthesis

4-Diphenylphosphinylbenzenecarboxylicacid-4*N*-(3-trimethoxysilypropyl)amide (2). 1.27 g (3.97 mmol) of **1** and 0.021 g (0.397 mmol) of NaOMe were mixed with 0.71 g (3.97 mmol) of 3-trimethoxysilylpropylamine and heated to 170 °C for 4 h. After cooling to room temperature, all volatiles were removed *in vacuo*, the residue was dissolved in CH_2Cl_2, filtered over a Whatman® filter to remove NaOMe. After removing the solvent, 1.67 g (90%) of **2** were obtained as a yellow oily residue. The numbering scheme for the NMR assignment is given in Scheme 3. ^{1}H NMR (400.13 MHz, 25 °C, $CDCl_3$): δ 7.72, 7.74 (2 × s, 2H, ratio 1 : 1, 2×H^2), 7.30–7.38 (m, 12H, H_{ar}), 6.53 (br, NH), 3.58 (s, 9H, H^9), 3.45–3.49 (m, 2H, H^6), 1.78–1.74 (m, 2H, H^7), 0.71–0.75 (m, 2H, H^8). ^{13}C{1H} NMR (150.92 MHz, 25 °C, $CDCl_3$) δ 167.1 (s, C=O), 141.8 (d, $^{1}J_{PC}$ = 13.9 Hz, C^4), 136.5 (d, $^{1}J_{PC}$ = 11.1 Hz, C^i), 134.9 (s, C^1), 133.9 (d, $^{2}J_{PC}$ = 20.3 Hz, C^0), 133.5 (d, $^{2}J_{PC}$ = 18.5, C^3), 129.0 (s, C^p), 128.6 (d, $^{3}J_{PC}$ = 6.5 Hz, C^m), 126.8 (d, $^{3}J_{PC}$ = 6.5 Hz, C^2), 50.3 (s, C^9), 42.4 (s, C^6), 22.7 (s, C^7), 6.7 (s, C^8). ^{31}P {1H} NMR (161.98 MHz, 25 °C, $CDCl_3$) δ –4.10. IR (KBr, cm^{-1}) 3315 m, 3052 w, 2939 m, 2838 m, 1636 s, 1597 m, 1541 s, 1481 m, 1434 m, 1390 w, 1305 m, 1191 m, 1087 s, 1018 w, 815 s, 745 s, 697 s, 505 w.



Scheme 3 Assignment of the NMR spectra for **2** and **3**.

Dichloridobis[(4-diphenylphosphinylbenzenecarboxylicacid-4*N*-(3-trimethoxysilypropyl)amide]palladium(II) (3). 178 mg (0.46 mmol) of di(benzonitrile)dichloropalladium(II) were dissolved in 30 mL of dry CH_2Cl_2. This solution was added to a solution of 430 mg (0.92 mmol) of **2** in 10 mL of CH_2Cl_2. The reaction mixture was stirred for 4 h at room temperature, then filtrated through a Whatman® filter and the filtrate was evaporated to dryness under reduced pressure. The residue was washed with ether (3 × 10 mL) to give a pale yellow solid. Yield: 511 mg (99%). Anal. calcd for $C_{50}H_{60}N_2Cl_2O_8P_2PdSi_2$ (1112.5) C 53.96, H 5.40, N 2.52, found (%) C 53.26, H 5.38, N 2.53. ^{1}H NMR (400.13 MHz, 25 °C, $CDCl_3$): δ 7.73–7.34 (m, 14H, H_{ar}), 6.87 (br, NH), 3.52 (s, 9H, H^9), 3.35–3.34 (m, 2H, H^6), 1.69–1.66 (m, 2H, H^7), 0.65 (t, J_{HH}= 8.3 Hz, 2H, H^8). ^{13}C{1H} NMR (150.92 MHz, 25 °C, CDC_{13}) δ 166.7 (s, C=O), 136.7 (s, C^i), 135.0 (m, C^0), 134.8 (m, C^3), 133.3 (m, C^4), 131.5 (s, C^p), 129.0 (m, C^1), 128.3 (m, C^m), 126.5 (m, C^2). 50.5 (s, C^9), 42.4 (s, C^6), 22.7 (s, C^7), 6.6 (s, C^8). ^{31}P{1H} NMR (161.98 MHz, 25 °C, $CDCl_3$) δ 24.43. IR (KBr, cm^{-1}) 3383 m, 3054 w, 2939 m, 2838 w, 1644 m, 1538 m, 1483 w, 1435 m, 1304 w, 1190 m, 1093 s, 813 w, 747 w, 693 m, 514 m.

Hybrid catalyst 4. **3** was immobilized on SiO_2 according to a standard procedure: 150 mg (0.13 mmol) of **3** dissolved in 4 mL of dry CH_2Cl_2 was added to a suspension of 340 mg of silica in 40 mL of dry toluene. The mixture was stirred for 12 h at 100 °C. The solid was filtered off and extracted with CH_2Cl_2 in a Soxhlet apparatus for 24 h. Finally, the solid was dried *in vacuo* at 50 °C to obtain **4**.

Catalytic Suzuki coupling. A dried Schlenk tube equipped with a magnetic stirring bar was charged under an inert gas atmosphere of nitrogen with the aryl halide (1.0 mmol), the arylboronic acid (1.5 mmol), Cs_2CO_3 (1.2 mmol), **4** (60 mg, 0.01 mmol Pd) and 5 mL of dioxane. The mixture was heated at 80 °C for 24 h. After cooling to room temperature, the mixture was diluted with Et_2O and filtered. The solid residual catalyst was washed with water (3 × 10 mL) and Et_2O (3 × 10 mL) and then dried at 50 °C. After this, it could be used for the next run. The organic phase was separated and dried over $MgSO_4$ and the GC yield was determined using decane as an internal standard.

Conclusion

We synthesized a heterogeneous material by covalently anchoring the triphenylphosphine palladium complex on the surface of a silica gel. This material performed excellent activity and reusability in the Suzuki coupling reaction. Further studies of other reactions with this material as well as further development of the catalyst system are currently in progress.

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