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# Palladium(II)-Phosphine Complexes Supported on Magnetic Nanoparticles: Filtration-Free, Recyclable Catalysts for Suzuki–Miyaura Cross-Coupling Reactions

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**Abstract:** An organic-inorganic hybrid heterogeneous nanocatalyst system was synthesized by covalent grafting a palladium dichloride complex of the type $(L)_2PdCl_2$ (L = trimethoxysilyl-functionalized triphenylphosphine) on silica-coated magnetic nanoparticles. It is a highly active and recyclable catalyst for the Suzuki–Miyaura cross-coupling reaction. The new catalyst can easily be separated from the reaction mixture by applying an external magnetic field and can be recycled many times without any loss of activity.

**Keywords:** coupling reactions; heterogenization; magnetic nanoparticles; palladium; phosphine ligands

## Introduction

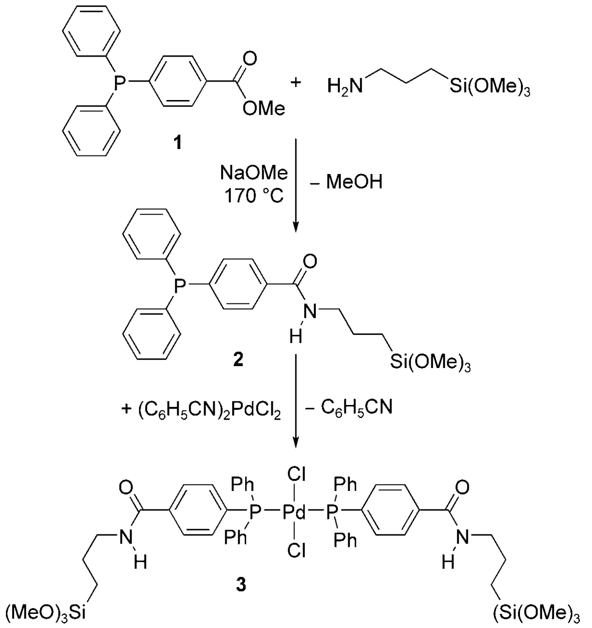
Palladium-catalyzed Suzuki–Miyaura cross couplings of aryl halides and arylboronic acids open up an access to biaryl structures which have found applications in fine chemical and pharmaceuticals synthesis.[1] A phlethora of palladium-derived catalysts were reported for this transformation, however, most of them are homogenous systems possessing the intrinsic advantages of homogeneous catalysts (single-site reactivity, high activity and selectivity, etc.).[2] On the other hand, the difficulty to separate a soluble catalyst from the reaction mixture gives rise to metal contamination in the products and hampers reuse of the expensive noble metal. Thus, a facile and efficient separation of expensive catalysts and their consecutive reuse remains a scientific challenge in terms of economic and environmental considerations.

The recovery of an expensive catalyst, often synthesized by multi-step procedures, can be realized by immobilization on solid supports. During the past years palladium catalysts heterogenized on organic polymers or inorganic solid supports such as zeolites and mesoporous materials were systematically investigated. However, a substantial decrease of the reaction rates, compared to homogeneous systems, had frequently to be considered due to limitations related to the diffusion of the substrates and products through the pores of the support. Often the activity of heterogenized catalysts was found to be poorer than that of their homogenous analogues.[3] Alternatively, ligand-free palladium catalysts were deveopled by simply supporting Pd(0) or $Pd^{2+}$ on porous solids.[4] However, such systems often suffer from palladium leaching.

Notably, the nature of the ligand coordinated to the active palladium sites had a profound influence on the catalytic activity and stability of the catalyst. Phosphines,[5] amines,[6] carbenes,[7] thiols,[8] pincer ligands,[9] or palladacycles[10] were verified in detail for the Suzuki–Miyaura cross-coupling. In particular, triphenylphosphine-palladium complexes were widely used for coupling reactions mainly due to the simple handling of these complexes and the cheap phosphine ligand.[11] Besides, some heterogeneous systems require the addition of phosphine ligands such as $PPh_3$ to reach reasonable catalytic activity.[12] Therefore, the heterogenization of triphenylphosphine-palladium complexes was extensively investigated. However, the benefits related to the separation of the catalyst and its reuse are reduced by the moderate activity of such systems, since a pronounced part of the active sites is not easily available for the reactants.[13] Thus there is still a demand to develop new protocols for ecologically benign C–C couplings which should fulfill the following requirements: a low amount of catalyst, high activity and selectivity, and an efficent recycling and reuse of the catalyst with consistent yields over a large number of experiments.

Nanoparticles that can be magnetized in the presence of an external magnet had first been explored for biological and medicinal applications.[14] Recently they also emerged as efficient catalyst supports for C–C bond-forming reactions,[15] hydrogenation,[16] hydroformylation,[17] oxidation[18] and organocatalytic[19] reactions. Due to the small particle size they possess high specific surface areas without porosity. This makes the catalytically active sites on the surface well accessible for the reactants. Since there is almost no limitation by diffusion, catalytic nanoparticles can be considered as quasi-homogeneous systems. Moreover, magnetic nanoparticles can simply be removed from the reaction mixture by application of a magnetic field (magnetic filtration).

In continuing our efforts to develop greener synthetic pathways for organic transformations,[20] we here report the synthesis of a novel, highly active, magnetically recoverable palladium-phosphine catalyst for the Suzuki–Miyaura cross-coupling. Its activity and stability were evaluated by comparison with similar active sites grafted on a conventional silica gel and a mesoporous MCM-41 support. Compared to palladium grafted on magnetic nanoparticles by simple ligands like amines or thiols,[6,8] the heterogenity is guarenteed in our system (Scheme 1). At the outset of this study no example of a magnetic nanoparticle-supported palladium-phosphine complex was reported despite the inherent high activity of such complexes in various coupling reactions.



**Scheme 1.** Synthesis of the palladium(II)-triphenylphosphine complex **3** functionalized with two trimethoxysilyl side chains.

## Results and Discussion

For this purpose, we synthesized magnetic nanoparticles (**MNP**) of approximately 10 nm in diameter by a co-precipitation method. The particles were subsequently coated with a dense silica layer, using tetraethoxysilane (TEOS) as the silica source and aqueous $NH_3$ as the hydrolyzing agent. The silica layered system **SMP** then offers the binding sites (Si–OH units) for the heterogenization of the molecular catalysts. The silylated derivative **2** of triphenylphosphine was achieved as reported by the solvent-free, NaOMe-catalyzed thermal aminolysis of 4-diphenylphosphinylbenzenecarboxylic acid methyl ester (**1**) with 3-trimethoxysilylpropylamine. The formation of the palladium(II)-phosphine complex (**3**) was realized by simply dissolving **2** in $CH_2Cl_2$ and treating it with half an equivalent of di(benzonitrile)dichloropalladium(II) (Scheme 1).[20a]

In the starting material **3** applied in the grafting process, two phosphine ligands are coordinated to one palladium centre. The catalytically active system **Pd@SMP** is then accessible by reacting **SMP** with **3** in toluene at 90 °C.

High-resolution transmission electron microscopy (HR-TEM) images of the **MNPs** depict relatively uniform $\gamma$-$Fe_2O_3$ particles with an average size of ~10 nm. TEM images of the silica-coated **SMP** show the typical core-shell structure with a uniform silica coating and a mean thickness of approximately 50 nm (see Supporting Information). The dense silica shell prevents leaching of iron from the core during the catalytic reactions and also assists in a stable anchoring of the silylated palladium complexes (Figure 1). FE-SEM images showed the spherical morphology of **Pd@SMP** with slight aggregation and spongy surfaces confirming the successful coating of **MNP** by a dense silica layer (Figure 1). Energy dispersive X-ray (EDX) analysis carried out with **SMP** showed the presence of silica and iron, while after the grafting reaction the presence of palladium was noted on **Pd@SMP**, confirming the successful anchoring of the palladium-phosphine complexes on the magnetic nanoparticles. Besides, elemental mapping analysis proves that the palladium species are uniformly dispersed over the magnetic silica nanocomposites (see Supporting Information).

XRD measurements of **MNP** exhibit diffraction peaks corresponding to the typical spinel maghemite structure while the silica-layered systems **SMP** and **Pd@SMP** showed an additional broad band ($2\theta = 20$–$30$) for the amorphous silica (Figure 2). The average crystallite size of the $\gamma$-$Fe_2O_3$ particles was calculated to be ~9.3 nm by Scherrer's equation for the (311) reflection, which is in well accordance with the HR-TEM results. No peaks characteristic for palladium nanoparticles were observed which proves the excel-

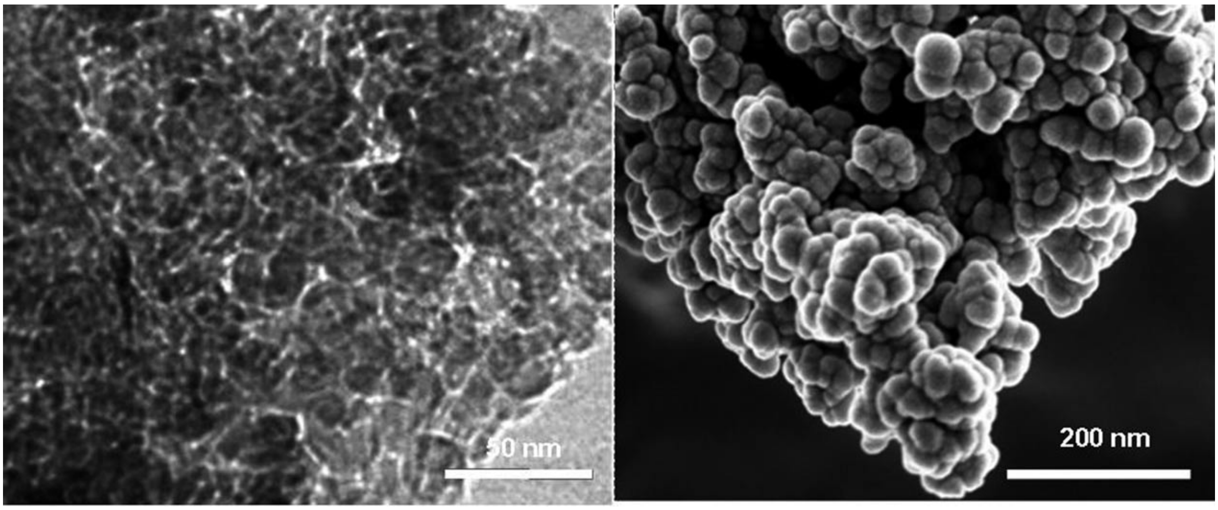


**Figure 1.** HR-TEM and FE-SEM images of **Pd@SMP**.

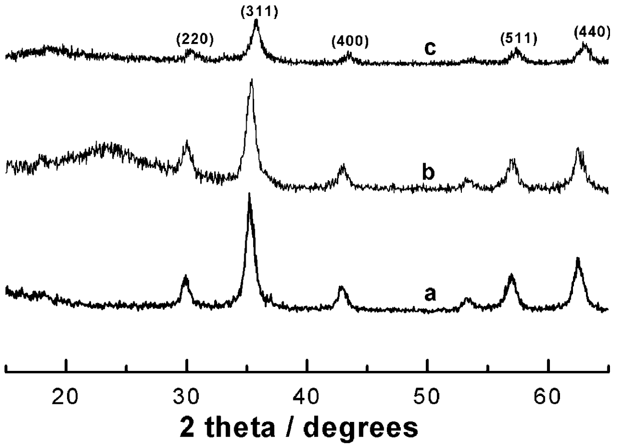


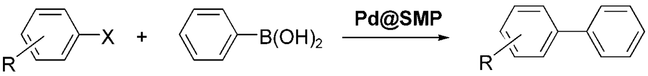
**Figure 2.** XRD patterns of (a) **MNP**, (b) **SMP** and (c) **Pd@SMP**.

lent dispersion of the palladium sites on the magnetic silica nanocomposites. The field-dependent magnetization curve at 300 K of the magnetic nanoparticles investigated by SQUID magnetometry, shows no hysteresis revealing that the materials exhibit superparamagnetic behaviour at room temperature with a saturation magnetization (*Ms*) of 50 emu g$^{-1}$ and 18 emu g$^{-1}$ for **MNP** and **SMP**, respectively, whereas Mössbauer spectroscopy identifies the superparamagnetic particles as $\gamma$-$Fe_2O_3$ since there is no evidence for spectral components representing Fe(II) ions.[20d]

The presence of magnetic iron oxide inside **Pd@SMP** prevents the analysis of organic functional groups by solid state NMR spectroscopy. Therefore, these hybrid materials were further analyzed by IR spectroscopy and elemental analysis. The IR spectrum of **MNP** shows the Fe–O stretching absorption at 576 cm$^{-1}$. After coating with silica a new sharp band appears for the Si–O vibration at 1080 cm$^{-1}$. In the IR spectrum of **Pd@SMP** absorptions at 3300 (N–H), 2930 cm$^{-1}$ ($CH_2$), 1640 cm$^{-1}$ (C=O) and a weak amide band at 1540 cm$^{-1}$ were observed indicating the presence of silylated palladium-phosphine groups (see Supporting Information).[21] By determination of the nitrogen content (C,H,N elemental analysis), a palladium-phosphine complex loading of approximately 0.20 mmol g$^{-1}$ was calculated for **Pd@SMP**. To confirm alternatively the structural integrity after the grafting processes, compound **3** was grafted on a silica gel support and the stability of this system was analyzed by solid state $^{31}$P MAS NMR spectroscopy (see Supporting Information). The results confirm the retention and stability of the palladium-phosphine precusor (**3**): the phosphorus resonance of **3** (24.6 ppm) is only slightly shifted in comparison to 23.6 ppm for the silica gel-supported palladium-phosphine complex **Pd@SG**.

The magnetically separable nanocomposite **Pd@SMP** was then used as catalyst for the Suzuki–Miyaura cross-coupling of phenyl halides and phenylboronic acid (Scheme 2).

Initial experiments with bromobenzene and phenylboronic acid were performed to optimize the reaction conditions (base, solvent, reaction temperature). As shown in Table 1 and Table 2, $Cs_2CO_3$ gave better conversions than other bases like $K_2CO_3$, $Na_2CO_3$, KF or $CH_3COONa$ and dioxane and DMF are the first choice among a series of other solvents. The solvent



**Scheme 2.** Suzuki–Miyaura cross coupling of aryl halides and phenylboronic acid in presence of **Pd@SMP**.

**Table 1.** Suzuki–Miyaura coupling of phenyl bromide and phenylboronic acid using different bases.[a]

| Base | $Cs_2CO_3$ | $K_2CO_3$ | KF | $Na_2CO_3$ | $CH_3COONa$ |
|---|---|---|---|---|---|
| Yield [%][b] | >99 | 71 | 62 | 47 | 42 |

[a] *Reaction conditions:* PhBr (1 mmol), $PhB(OH)_2$ (1.5 mmol), base (1.2 mmol), catalyst (1 mol%), dioxane (5 mL), 80 °C, 15 h.

[b] Determined by GC-MS using *n*-decane as the internal standard.

**Table 2.** Suzuki–Miyaura coupling of phenyl bromide and phenylboronic acid using different solvents.[a]

| Solvent | dioxane | DMF | DMA | EtOH | THF |
|---|---|---|---|---|---|
| Yield [%] | >99 | 95 | 91 | 63 | 34 |

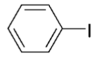
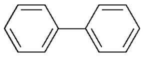
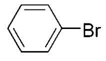
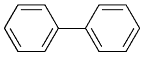
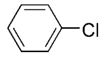
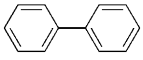
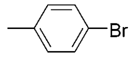
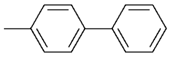
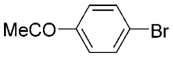
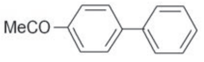
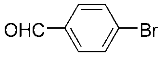
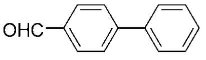
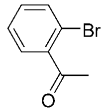
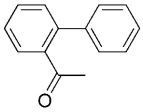
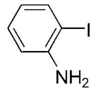
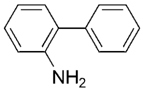
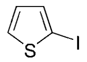
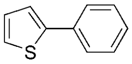
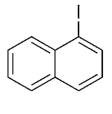
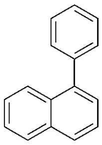
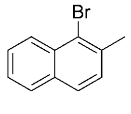
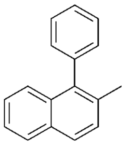
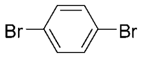
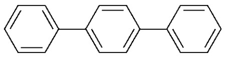
[a] *Reaction conditions:* PhBr (1 mmol), $PhB(OH)_2$ (1.5 mmol), $Cs_2CO_3$ (1.2 mmol), catalyst (1 mol%), solvent (5 mL), 80 °C, 15 h.

effect is probably determined by the solubility of the base. Reducing the amount of catalyst 0.5 mol% still gives a good yield of coupled products (see Supporting Information). Since biphenyl might result from a cross-coupling or homo-coupling reaction, we used 4-bromoacetophenone to prove the chemoselectivity of the catalyst. The formation of the homo-coupled product was not significant under the given reaction conditions (<5%).

Further optimization studies revealed that the catalysts were inactive at room temperature, while heating the mixture to 80–100 °C gave high conversions. Increasing the reaction temperature to >120 °C decreases the activity of the catalysts (<50% of conversion after 15 h) probably due to decomposition of the palladium-phosphine sites.

With the optimized reaction conditions ($Cs_2CO_3$, dioxane, 80 °C, 15 h) we examined the scope of the palladium-catalyzed Suzuki–Miyaura coupling on a series of different substrates (Table 3). Control experiments carried out in the absence of **Pd@SMP** confirmed the crucial role of palladium (0% of conversion after 24 h). The coupling of phenyl iodide and phenyl bromide with phenylboronic acid afforded the formation of biphenyl in >99% yield. Notably, the less reactive and less expensive phenyl chloride also showed moderate reactivity in the presence of **Pd@SMP**. Various 4-substituted aryl bromides as well as heteroaromatic substrates like iodothiophene also led to high yields of coupled products. The reaction rate is clearly influenced by the impact of other substitutents at Ar–X: electron-withdrawing groups enhance, while electron-donating groups decrease the rate (e.g., Table 3, entry 4 *vs.* entry 5). Attempts to couple 2-substituted Ar–X derivatives gave the desired products in only low yields probably due to the steric hindrance (entries 7 and 8). Only 1-bromo-2-methylnaphthalene could be converted with high activity. The Br–Ar–Br substrate 1,4-dibromobenzene gave 73% of conversion with selectivities of 41% and 59% for 4-bromobiphenyl and terphenyl.

**Table 3.** Substrate scope of the Suzuki–Miyaura coupling with phenylboronic acid.[a]

| Entry | Substrate | Product | Yield [%] |
|---|---|---|---|
| 1 |  |  | >99 (96) |
| 2 |  |  | >99 (95) |
| 3 |  |  | 34 |
| 4 |  |  | 73 |
| 5 |  |  | 90 (83) |
| 6 |  |  | 93 |
| 7 |  |  | 35 |
| 8 |  |  | 24 |
| 9 |  |  | 93 |
| 10 |  |  | 89 (80) |
| 11 |  |  | 75 |
| 12[b] |  |  | 73 |

[a] *Reaction conditions:* substrate (1 mmol), $PhB(OH)_2$ (1.5 mmol), $Cs_2CO_3$ (1.2 mmol), Pd (1 mol%), solvent (5 mL), 80 °C, 15 h; values in parenthesis shows the isolated yield.

[b] Selectivity: 41% for binary and 59% for ternary product.

For the practical application of a heterogeneous catalyst system its stability and reusability are important factors. The literature demonstrates that many immobilized catalysts behave homogeneously in their reactions (leaching of the active site), which is particularly true for palladium-based systems.[22] To ensure that the high activity of **Pd@SMP** arises from the palladium sites on the surface and not from the leached palladium species, the heterogenity of **Pd@SMP** was first tested by hot filtration. For this, the coupling reaction of phenyl bromide and phenylboronic acid was carried out until a conversion of 30%. Then the catalyst was separated magnetically from the solution at the reaction temperature and half of the hot solution was transferred to another batch reactor set under identical reaction conditions. The portion containing the suspended catalyst proceeded to 99% of conversion where as the catalyst-free portion reacted only to an additional 10% after 15 h. This shows that the leaching of palladium from the magnetic silica nanocomposite is not a serious concern. However, as shown in Table 4, the reactivity of **Pd@SMP** slightly reduces after the first run and then stays constant. We assign this to a slight leaching process parallel to the formation of palladium nanoparticles, which carry on the reactivity from the second run (Figure 3).

For investigations on the recyclability of the catalyst, it was recovered by magnetic separation, washed three times with an ethanol/$CH_2Cl_2$ mixture, dried in air and reused for the next reaction. More than 98% of the catalyst could simply be recovered by fixing a magnet near to the reaction vessel (Figure 4). This method avoids the inherent problems of filtration such as loss of catalytically active particles and oxidation of sensitive metal complexes. **Pd@SMP** could be reused seven times by simple magnetic separation almost without any deterioration in catalytic activity (Table 4). In our opinion, the high catalytic activity and stability of the palladium catalyst relates to the efficient site isolation, to the optimal dispersion of the active sites on the particle surface and to the relatively strong interaction between the phosphine ligands and the palladium centre supported on the magnetic silica nanoparticles. Due to the preformation of the palladium(II)-phosphine complex all phosphines are grafted on the surface in a ideal position for complexing the palladium centre. In combination with the surface they can be considered as a chelating ligand system.

**Table 4.** Reusability test for **Pd@SMP** in the Suzuki–Miyaura coupling of phenyl bromide and phenylboronic acid.[a]

| Recycle | I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|---|
| Yield [%] | >99 | 94 | 94 | 94 | 93 | 93 | 92 |

[a] *Reaction conditions:* PhBr (1 mmol), $PhB(OH)_2$ (1.5 mmol), $Cs_2CO_3$ (1.2 mmol), Pd (1 mol%), solvent (5 mL), 80 °C, 15 h.

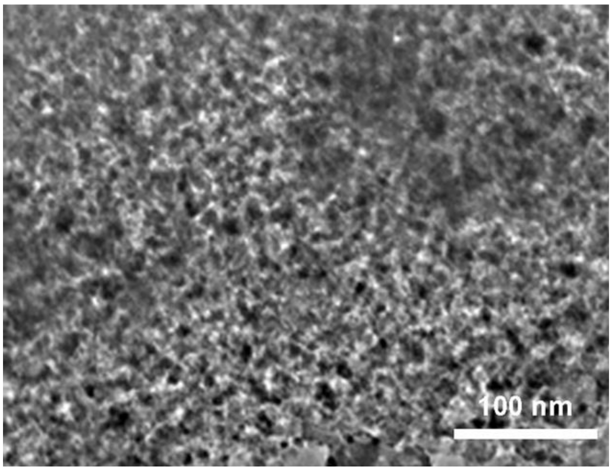


**Figure 3.** TEM image of heterogenized palladium nanoparticles after a third recycling.

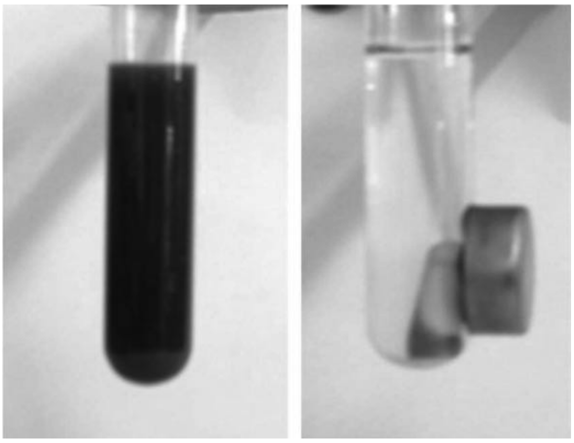


**Figure 4.** Magnetofiltration of finely dispersed superparamagnetic **Pd@SMP** nanoparticles (*left*: before application of the magnet; *right*: 2 min later).

In a previous study we noted that a catalyst system wherein the palladium(II)-phosphine complex **3** is simply grafted on a commercially available silica turns gradually darker during its consecutive reuse.[20a] This effect arises from the presence of metallic palladium nanoparticles and is well documented in the literature for various palladium-ligated catalysts.[23] However, the presence of the phosphines in ideal positions on the silica surface assists in the stabilization of the nanoparticles and hence they do not diffuse into the reaction mixture (Figure 3). To confirm this, we had anayzed the used **Pd@SG** catalyst by means of $^{31}$P MAS NMR spectroscopy. The $^{31}$P MAS NMR spectrum (see Supporting Information) shows sharp signals at 33.5 ppm and 3.9 ppm with a weak shoulder at −3.1 ppm. These results prove that the phosphine ligands gets partially oxidized to phosphine oxide (peak at 33.5 ppm) whereas the peak at 3.9 ppm is assigned to triphenylphosphine ligands coordinated to the palladium(0) nanoparticles and the weak shoulder at −3.1 ppm arises for palladium-free phosphine ligands. However, the triphenylphosphine ligand as well as phosphine oxide developed during the reaction are able to assist in the stabilization of palladium nanoparticles which, in turn, explains the good reusability of this catalyst system.

Furthermore, it has been reported that metal nanoparticles aggregate into large clusters in the absence of stabilizing agents, resulting in a decrease of their specific surface area, which is equivalent to a loss of active sites and thus one main reason for catalyst deactivation. The consistent catalytic performance of **Pd@SMP** again proves the stabilization of the palladium nanoparticles and explains the excellent reusability of this catalyst system. The amount of palladium and ligand on the reused catalyst is identical to that of the fresh catalyst. AAS analysis only showed $<0.5\%$ of leached palladium in the reaction filtrate and elemental analysis data confirmed the retention of the phosphine/phosphine oxide ligands on the surface after catalyst recycling. On the other hand, a direct grafting of palladium species on the magnetic silica nanoparticles by application of $PdCl_2(PhCN)_2$ leads to severe leaching of active sites during the recycling (a 50% conversion in first run changed to zero activity for the second run) which additionally confirms the stabilizing role of the phosphine ligands.

To compare the activity and stability of **Pd@SMP**, the palladium(II)-phosphine precursor (**3**) was heterogenized on two further supports: a commercially available silica gel (**Pd@SG**) and a mesoporous MCM-41 sample (**Pd@MCM-41**). It could be shown that activity and stability of the three catalysts follows the order **Pd@SMP** > **Pd@MCM-41** > **Pd@SG** (Table 5). Obviously the high catalytic activity of **Pd@SMP** arises from its unique quasi-homogeneous nature due to its nanoscale particle size and the location of the active sites on the surface of a dense and almost non-porous silica shell, which prevents limitating effects of diffusion. Alternatively, we tried to compare the results obtained from a magnetic nanoparticle-supported NHC-Pd(II) complex with our **Pd@SMP** catalyst under similar experimental conditions.[15a] The **Pd@SMP** shows an only slightly reduced performance compared to heterogenized NHC-Pd(II) catalyst (see Supporting Information).

**Table 5.** Suzuki–Miyaura coupling of phenyl bromide and phenylboronic acid using different supports.[a]

| Entry | Sample | Yield [%] | |
|---|---|---|---|
| | | 1st run | 4th run |
| 1 | **Pd@SMP** | >99 | 94 |
| 2 | **Pd@MCM-41** | 88 | 78 |
| 3 | **Pd@SG**[b] | 85 | 73 |

[a] *Reaction conditions:* PhBr (1 mmol), $PhB(OH)_2$ (1.5 mmol), $Cs_2CO_3$ (1.2 mmol), Pd (1 mol%), solvent (5 mL), 80 °C, 15 h.

[b] From ref.[20a]

## Conclusions

To summarize, it could be shown that **Pd@SMP** obtained by grafting of the palladium(II)-phosphine complex **3** on magnetic silica nanoparticles is an efficient and simply recoverable catalyst for the Suzuki–Miyaura cross-coupling reaction. The synthesis of the nanocomposite is straightforward and there is no degradation of activity during multiple reuse. We anticipate that this synthesis strategy can now be extended for the heterogenization of other homogenous ligands/catalysts, which we are presently investigating.

## Experimental Section

### Synthesis of the Magnetic Nanoparticles (MNP)

Ferrous chloride (0.25 g) and ferric chloride (0.5 g) were added under stirring to 20 mL of a nitrogen purged 2-propanol solution resulting in a yellowish orange reaction mixture. After 15 min of stirring, the temperature of the solution was raised to 80 °C and 10 mL of aqueous $NH_3$ were slowly added. The colour of the solution turned to dark brown and the stirring was continued for another 2 h. The magnetic nanoparticles formed were protected by the addition of 10 mM of oleic acid in 30 mL methanol, removed from the solution by magnetic separation, washed with methanol and then redispersed in ethanol.

### Synthesis of the Silica-Coated Magnetic Nanoparticles (SMP)

2 g of a suspension of **MNP** in ethanol were diluted with 4 mL of deionized water and 20 mL of 2-propanol and the mixture was sonicated for approximately 5 min. To this well dispersed MNP solution, 1 mL of $NH_4OH$ followed by 1 g of tetraethoxysilane was slowly added and stirred for further 4 h at room temperature. The material was then separated by centrifugation and redispersed in deionized water.

### 4-Diphenylphosphinylbenzenecarboxylic Acid 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 under vacuum and the residue was dissolved in $CH_2Cl_2$. After removing the solvent, 1.67 g of **2** were obtained as a yellow oily residue. The spectroscopic data were in accordance with the published data.[20a]

### Dichloridobis{(4-diphenylphosphinylbenzene-carboxylic Acid 4-[*N*-(3-Trimethoxysilypropyl)amide]}palladium(II) (3)

178 mg (0.46 mmol) of di(benzonitrile)dichloropalladium(II) dissolved in 30 mL of dry $CH_2Cl_2$ were 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 and

the filtrate was evaporated to dryness under reduced pressure. The residue was washed with ether to obtain a pale yellow solid. The spectroscopic data were in accordance with the published data.[20a]

### Synthesis of Pd@SMP, Pd@MCM-41 and Pd@SG

0.15 g of **3** dissolved in 5 mL of dry $CH_2Cl_2$ were added to a suspension of 0.3 g of **SMP** in 30 mL of dry toluene. The mixture was then stirred at 90 °C under an atmosphere of nitrogen for 12 h. The solid material obtained was magnetically separated, washed repeatedly with toluene and $CH_2Cl_2$ to remove any unanchored species and then dried under vacuum.

A similar procedure was adopted for the grafting of **3** on MCM-41 and silica gel giving 0.22 $mmol\,g^{-1}$ and 0.20 $mmol\,g^{-1}$ loading of the palladium(II)-phosphine complex, respectively. The catalyst loadings were determined by elemental analysis.

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