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Oxime Carbapalladacycle Covalently Anchored to High Surface Area Inorganic Supports or Polymers as Heterogeneous Green Catalysts for the Suzuki Reaction in Water

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An oxime carbapalladacycle known as an extremely active homogeneous catalyst for the Suzuki coupling in water has been conveniently modified and anchored on high surface area SiO_2, MCM-41, and polystyrene-divinylbenzene and ethylenglycol dimethylacrylate polymers. The resulting solids were characterized by analytical and spectroscopic (UV−vis and IR) techniques and tested as catalysts for the reaction of 4-chloroacetophenone with phenylboronic acid in water, dioxane, and a mixture of both. Differences in activity depending on the support were remarkable, the palladium complex being more active for the reactions in water when supported on SiO_2 or MCM-41. The catalysts were truly heterogeneous (no leached palladium) and when anchored on SiO_2 were reused seven times without loosing activity. Palladium complex anchored in SiO_2 was also tested as Suzuki catalyst for a wide range of bromo-, chloro-, and even fluoroaromatics.

Introduction

In a series of papers Nájera and co-workers have reported a highly active water-soluble Pd-oxime carbapalladacycle catalyst that is able to effect the Suzuki reaction of arylboronic acids and aryl chlorides in water.[1,2] The problem with homogeneous catalysis is the difficulty to separate the catalyst from the reaction mixture and the impossibility to reuse it in consecutive reactions. In contrast, solid catalysts can be easily separated from the reaction mixture by simple filtration and reused in successive reactions provided that the active sites have not become deactivated. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes.[3,4]

One general methodology to transform a successful homogeneous transition metal complex catalyst into a heterogeneous catalyst consists of the anchoring the conveniently modified complex onto an insoluble support. Two types of insoluble solids are among the most useful supports to anchor complex catalysts, inorganic oxides[5−7] and polymers.[8,9] Inorganic oxides have the advantage that they can be prepared with larger surface areas, have periodic structured porosity, and can resist thermal regeneration. In contrast, polymers present a high hydrophobicity that makes them more suitable for reactions in organic solvents.

In a preliminary communication we reported the anchoring of a 10-undecenyl derivative of carbapalladacycle complex **5** on silica and found that the resulting Pd on silica is an active catalyst for the reaction of boronic acid for 4-bromo- or 4-chloroacetophenone.[10] Herein we have expanded the initial results to the preparation of a related catalyst using MCM-41 as support and another series in which PdL has been anchored to a polymeric backbone. The results obtained confirm the high activity of the supported carbapalladacycle on inorganic oxides that can be used for a wide range of substrates, reaching high conversion and selectivity.

Results and Discussion

The route followed to prepare the solid catalysts is depicted in Schemes 1 and 2. The preparation is based on the synthesis of an oxime carbapalladacycle having a terminal C═C double bond group in a long alkyl chain that will enable the anchoring of the complex. This undecenyl derivative of the Pd complex was prepared from the corresponding oxime starting from 4-hydroxyacetophenone (Scheme 1). Other alternatives in which Pd complexation was not accomplished in the last step

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(1) Botella, L.; Najera, C. *J. Organomet. Chem.* **2002**, *663*, 46−57.

(2) Botella, L.; Najera, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 179−181.

(3) Poliakoff, M.; Fitzpatrick, J. M.; Farren, T. R.; Anastas, P. T. *Science* **2002**, *297*, 807−810.

(4) Anastas, P. T.; Kirchhoff, M. M. *Acc. Chem. Res.* **2002**, *35*, 686−694.

(5) Corma, A. *Chem. Rev.* **1995**, *95*, 559−614.

(6) Van Rhinj, W. M.; De-Vos, D.; Jacobs, P. A. *Fine Chemicals through Heterogeneous Catalysis*; Wiley-VCH: Weinheim, 2001; Vol. 106.

(7) Corma, A.; Garcia, H. *Chem. Rev.* **2002**, *102*, 3837−3892.

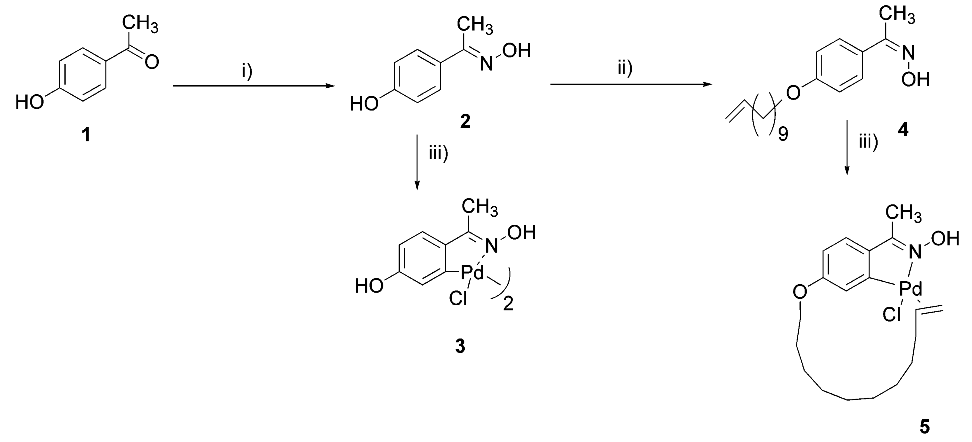
(8) Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217−3274.

(9) McNamara, C. A.; Dixon, M. J.; Bradley, M. *Chem. Rev.* **2002**, *102*, 3275−3300.

(10) Baleizao, C.; Corma, A.; Garcia, H.; Leyva, A. *Chem. Commun.* **2003**, 606−607.

10.1021/jo030302u CCC: $27.50

SCHEME 1[a]



[a] (i) NH_2OH, NaOAc, H_2O, reflux, 1 h; (ii) $CH_2{=}CH(CH_2)_9Br$, K_2CO_3; (iii) Li_2PdCl_4, NaOAc, MeOH, rt, 72 h.

SCHEME 2. Anchoring Procedure of Oxime Carbapalladacycle 5 onto Mercaptopropyl-Modified High Surface Silica Supports

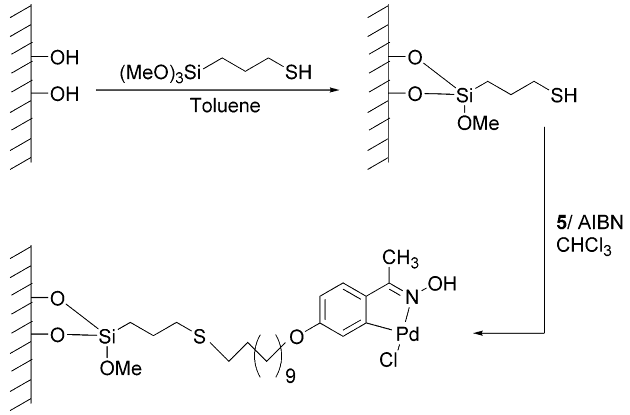


TABLE 1. Analytical and Spectroscopic Data of Solid Catalysts Used

catalyst	BET surface (m^2 g^{-1})	combustion analysis (mmol g^{-1})	Pd content (mmol g^{-1})
PdL@SiO_2	380	C 5.97; N 0.29; S 0.8	0.27
PdL@MCM-41	720	C 8.14; N 0.41; S 0.77	0.41
PdL@PS		C 74 H 81 N 0.16	0.15
PdL@PEA		C 48 H 70 N 0.37	0.35

but in an earlier stage of the synthesis led to poor complex yields. The reaction intermediates and the final oxime carbapalladacycle **5** were fully characterized by analytical and spectroscopic means. Particularly informative were the data corresponding to the Pd complex. The FAB-MS spectrum exhibits the characteristic molecular cluster[11] due to the different palladium isotopes from 404 to 410 amu corresponding to the mass of the monomeric carbapalladacycle after losing a Cl^- anion. This indicates that, in our case, the complex **5** is in a monomeric form rather than a dimer as previously reported for the 4-hydroxy derivative of complex **3**.[10] The monomeric nature of complex **5** suggests that the terminal C═C double bond is somehow interacting with the Pd, disfavoring the dimer formation, but a definitive confirmatory structure determination based on a single-crystal XRD has not yet being possible. Also important is the information obtained by ^1H and ^{13}C NMR. In ^1H NMR the characteristic pattern for the aromatic protons was observed for the ligand, and they shift toward lower δ values, indicating that the Pd is bonded to the aryl ring. Also in support of the C═C double bond interaction with the Pd some variations in the chemical shift of these hydrogens were observed. The ^{13}C NMR was also in good agreement with the data previously reported for the 4-hydroxy derivative **3**,[1] but some additional studies are still necessary to address the bonding of Pd with the terminal C═C double bond. Complex **5** having the terminal C═C double bond can be easily anchored through a radical chain mechanism onto 3-mercaptopropyl-modified silicas, which are easily obtained by reacting 3-mercaptopropyl trimethoxysilane with silicas silanol groups (Scheme 2). Both reactions, mercaptopropyl silylation and radical-chain anchoring of mercapto groups on terminal C═C double bonds, have been widely used in precedents in which organic molecules and complexes have been successfully bound to inorganic surfaces.[12] This procedure was applied to amorphous silica (PdL@SiO_2) and to an MCM-41 silicate having a large surface (720 m^2) and a pore diameter of 38 Å (PdL@MCM-41). The two solids were characterized by chemical analysis (Pd, C, N, S) and optical and IR spectroscopy.

The most relevant analytical data of the solid catalysts are summarized in Table 1. Comparison of the palladium and nitrogen content of the solids gives a similar ratio as in the precursor **5**, suggesting that the Pd complex has survived the anchoring procedure. The complex loading of the silica samples is around 0.3 mmol g^{-1}. On the other hand, comparison of the sulfur to nitrogen atomic ratio establishes that less than 50% of the mercaptopropyl groups of the modified silica or MCM-41 have reacted and must contain the Pd oxime complex. About 50% of unreacted mercaptopropyl groups remain free. Oversilylation with mercaptopropylsilyl groups serves to mask free silanol groups that could introduce some weak Brönsted acidity in the solids. A test reaction using the mercaptopropyl-modified silica lacking an-

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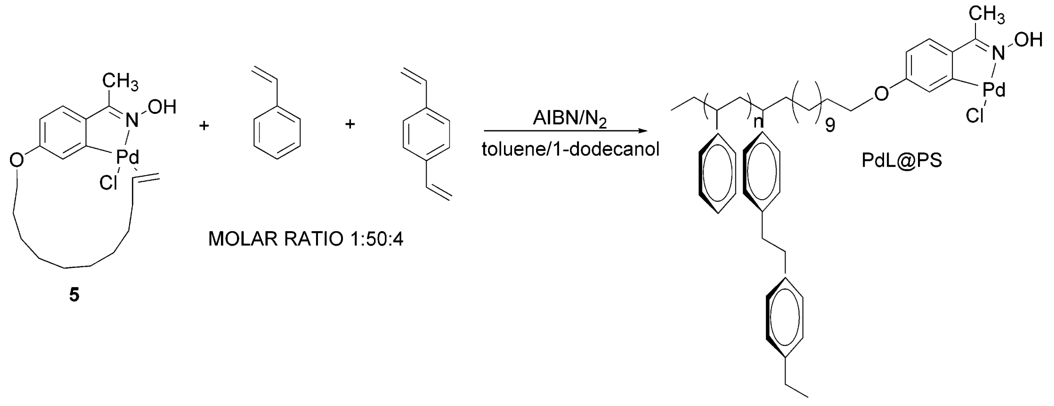
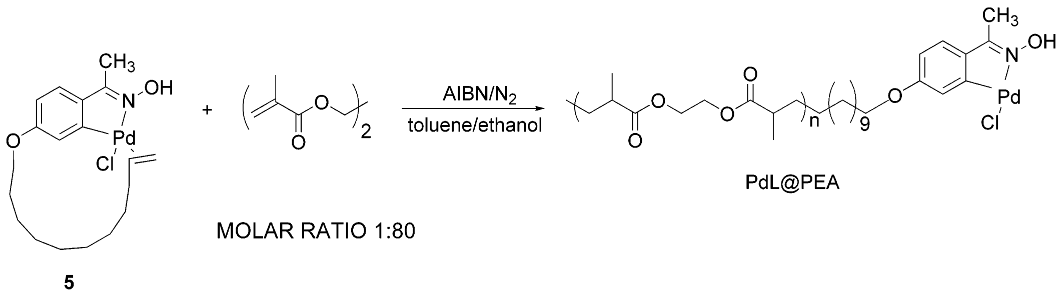
[11] McLafferty, F. W. *Interpretation of Mass Spectra*, 3rd ed.; University Science Books: Mill Valley, 1980.

[12] Baleizao, C.; Gigante, B.; Garcia, H.; Corma, A. *J. Catal.* **2003**, *215*, 199–207.

SCHEME 3. Formation of PdL@PS by in Situ Radical Copolymerization



SCHEME 4. Formation of PdL@PEA by in Situ Radical Copolymerization



chored PdL as catalyst was performed without reactant conversion. Diffuse reflectance UV−vis spectra of PdL@SiO$_2$ and PdL@MCM-41 exhibit a peak at λ_{max} 380 nm characteristic of the carbapalladacycle complex in solution. This absorption band is absent in the mercaptopropyl modified solids. The IR spectra of the PdL@MCM-41 coincides with that previously reported by us[10] for PdL@SiO$_2$ where, in addition to strong vibration bands at 2950 and 2900 cm^{-1} corresponding to the CH$_2$ groups of the spacer connecting the complex to the silica walls, other absorption bands in the aromatic region compatible with the structure of the carbapallacycle complex are also recorded.

A different type of solid catalyst where the oxime carbapalladacycle complex is anchored on two different polymeric backbones was also prepared. One of these polymeric catalysts termed as PdL@PS was obtained starting from complex **5** having the terminal C═C double bond upon copolymerization with styrene and *p*-divinylbenzene (Scheme 3). The latter monomer acts as cross-linker of the polymeric backbone and increases the insolubility of the polymer, allowing easier recovery of the heterogeneous catalyst. Polymerization of the C═C double bond was carried out through a radical chain mechanism using azobisisobutyronitrile (AIBN) as radical initiator in the absence of oxygen, and a mixture of toluene and 1-dodecanol as solvent. The presence of 1-dodecanol in the medium increases the porosity and the surface area of the polystyrene.[13]

The second polymer (PdL@PEA) was obtained starting from ethylene glycol bis(methacrylate) (EA) as monomer through copolymerization with lesser amounts of ω-terminal C═C double bond complex **5**. Radical polymerization was also effected using AIBN as initiator and toluene/ethanol as solvent (Scheme 4). The palladium loading of the two polymeric solid catalysts based on the ligand content is also contained in Table 1. Noteworthy from these data is that the Pd loading is in the same range for the four samples, thus allowing a straightforward comparison between the catalytic activity of the PdL supported on silicates or polymers.

The two solid catalysts in which PdL was anchored on the polymeric scaffold were also characterized by diffuse reflectance UV−vis spectroscopy. The PdL@PS and PdL@PEA samples exhibit the metal to ligand charge-transfer band at about 350 nm (Figure 1), which is somewhat shifted with respect to the λ_{max} recorded for the same complex supported on silicates (380 nm). This variation in λ_{max} may reflect differences in the polarity/hydrophobicity of the polymers compared to that of silicates. The IR spectra of the solid catalysts PdL@PS and PdL@PEA contain some bands characteristic of complex **5** embedded within much more intense vibrations corresponding to the polymeric backbone (Figure 2).

To determine the catalytic activity of the samples the Suzuki reaction of phenylboronic acid with 4-chloroacetophenone was carried out in water as well as dioxane or a 3:2 water/dioxane mixture. Figures 3 and 4 show the time conversion plot for the formation of 4-phenylacetophenone in water and dioxane, respectively. Table 2 summarizes the results obtained for each solid catalyst. As expected in view of the reported influence of the solvent polarity on the activity of oxime carbapalladacycle complex, the reaction in water was much faster and led to higher conversions than in dioxane.[14] An intermediate situation is observed for mixtures of water/dioxane. Since

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[13] Bevington, J. C. *J. Polym. Mater.* **1993**, *10*, 195−202.

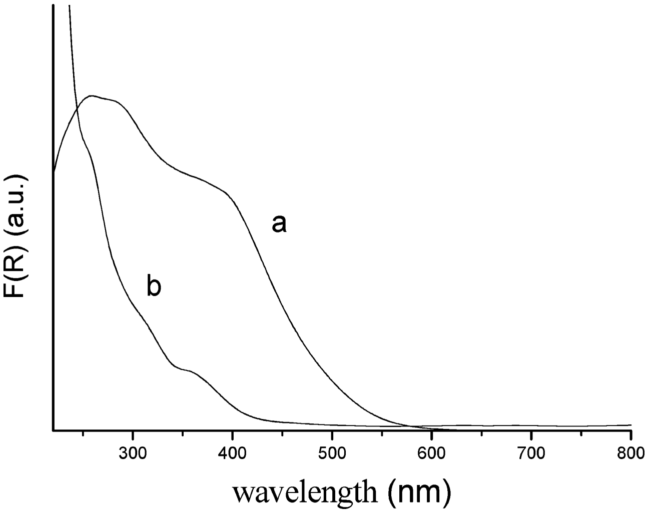

FIGURE 1. Diffuse reflectance UV−vis spectra (plotted as the Kubelka−Munk function of the reflectance, *R*) of PdL@MCM-41 (a) and PdL@PEA (b).

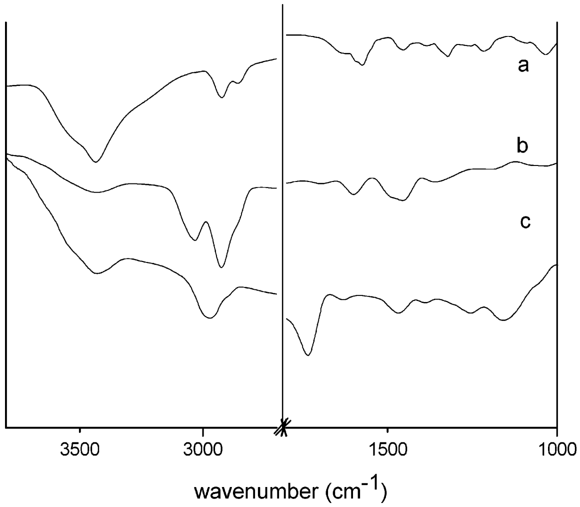

FIGURE 2. Infrared spectra of oxime carbapalladacycle **5** (a), PdL@PS (b), and PdL@PEA (c).

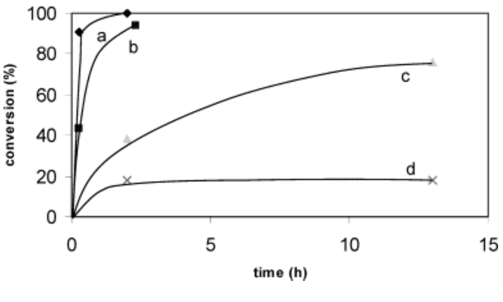

FIGURE 3. Time conversion plot for the Suzuki reaction of *p*-chloroacetophenone (31 mg, 0.2 mmol), phenylboronic acid (36 mg, 0.3 mmol), and K_2CO_3 (55 mg, 0.4 mmol) in neat water (5 mL) at 100 °C using PdL@SiO$_2$ (a), PdL@MCM-41 (b), PdL@PS (c), and PdL@PEA (d) as catalysts.

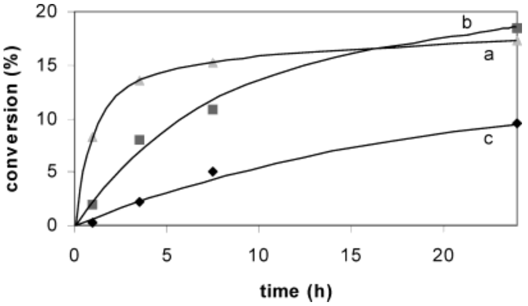

FIGURE 4. Time conversion plot for the Suzuki reaction of *p*-chloroacetophenone (31 mg, 0.2 mmol), phenylboronic acid (36 mg, 0.3 mmol) and K_2CO_3 (55 mg, 0.4 mmol) in dioxane (5 mL) at 100 °C using PdL@PEA (a), PdL@PS (b), and PdL@SiO$_2$ (c) as catalysts.

potassium carbonate is not fully soluble in dioxane, one obvious factor decreasing the reaction rate in this solvent as compared to that in water is the lower base concentration. However, this cannot be the only factor since the solvent polarity changes the relative activity of the catalysts, the influence being considerably higher for PdL anchored on silicates than anchored on polymers. In fact, PdL@PEA is the most active solid catalyst in dioxane and its activity is only 0.75 times lower in dioxane than in water. In contrast, the activities for PdL@SiO$_2$ and PdL@MCM-41 are reduced at least 0.002 times going from water to dioxane. Although the influence of solvent polarity on the activity of the oxime carbapalladacycle in solution has been previously reported,[14] we believe that solvent polarity only does not explain the dramatic effect observed in the activity when PdL is anchored on silicates compared to that on polymers. Leaching of palladium species for PdL anchored on silicates was considered and disregarded (vide infra). In other words, the support plays a critical role on the activity of the complex depending on the solvent. PdL anchored on polymers is relatively insensitive to the polarity of the medium since the minor decrease can be explained just by considering the lower carbonate solubility.

In view of the above results, we propose that the carbapalladacycle complex in the polymeric scaffold is entangled and embedded within the hydrophobic polymer chains, being protected from water. This would explain the low activity of PdL in water when anchored on polymer. On the other hand, the much higher hydrophilicity of silica and MCM-41 permits free access of this solvent to all of the pores, effectively surrounding the PdL complex. In other words, PdL will interact more freely with water when anchored on silicates than in polymers. The above findings constitute a remarkable example of the influence of the nature of the support in heterogeneous catalysis, this effect arising from the intrinsic dramatic change of the PdL activity as a function of the solvent.

We have expanded the study to other substrates using water as solvent and PdL@SiO$_2$ and PdL@MCM-41 as catalysts. To cover a wide range of substrates, brominated, chlorinated, and fluorinated aromatic compounds were tested. The results are summarized in Table 3. In some cases, particularly with low reactive chloro derivatives and at long reaction times, significant amounts of biphenyl arising from the homocoupling of phenylboronic acid[15] were observed accompanying the corresponding

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[14] Alonso, D. A.; Najera, C.; Pacheco, M. C. *J. Org. Chem.* **2002**, *67*, 5588−5594.

[15] Kochi, J. K. *J. Organomet. Chem.* **2002**, *653*, 11−19.

TABLE 2. Results for Suzuki Reaction of *p*-Chloroacetophenone (31 mg, 0.2 mmol), Phenylboronic Acid (36.6 mg, 0.3 mmol), and K_2CO_3 (55.3 mg, 0.4 mmol) in Neat Water (5 mL) at 100 °C in the Presence of Solid Catalyst (30 mg)[a]

catalyst	time (h)	conversion (%)
PdL@SiO_2	0.25	91
	2	>99
PdL@MCM-41	0.25	43
	2	94
PdL@PS	2	38
	13	76
PdL@PEA	2	18
	13	18

[a] The only product observed was the corresponding 4-phenylacetophenone. Selectivity >95%.

cross-coupling product. As expected,[16,17] the bromo derivatives react much faster to give high yields of the Suzuki product in short reaction times. However, it is worth remarking that moderate to high yields are also obtained with chloro compounds, particularly those having electron-withdrawing groups. The activity of the PdL anchored on silicates is so high that even conveniently substituted fluoroaromatics can undergo coupling with phenylboronic (see Table 3, last entry).

Leaching and Reuse Tests

With a heterogeneous catalyst, two issues need to be addressed. The first is to demonstrate the heterogeneity of the process and the absence of catalytically active species in solution leached from the solid. This crucial point was addressed in three different ways. In one of the approaches the Suzuki coupling of phenylboronic acid and 4-bromoacetophenone in water was performed in the presence of the most active PdL@SiO_2, and the solid was filtered at 22% conversion while hot, observing that the reaction completely stops when the resulting clear solution was heated for 24 h. In the second approach, chemical analysis of a PdL@SiO_2 catalyst reused in eight consecutive runs (see below for reusability) showed within the experimental error the same palladium content as the fresh catalyst.

In the third more elaborated strategy, the "boomerang" leaching mechanism, proposed by Lipshutz as operating on related catalysts of Pd metal supported on carbon, was scrutinized and disregarded.[18,19] According to the Lipshutz's proposal, catalytically significant amounts of supported Pd metal can be dissolved during the reaction and would redeposit quickly on the solid during the filtration as a result of unavoidable minor temperature decreases during the filtration workup. To determine the occurrence of the homogeneous catalysis, Lipshutz proposed the so-called "three-phase test" consisting of anchoring one of the reagents onto a solid in addition to using the solid catalyst. In this way, if the process is completely heterogeneous, no transformation should be observed for the anchored reagent, whereas if during the course of the reaction some active palladium species is present in the solution, the anchored reagent will be converted in some degree. To completely rule out the occurrence of the leaching, we prepared a modified silica functionalized with *p*-chlorobenzamide as well as *p*-iodobenzamide (Scheme 5). Control reactions in homogeneous phase using *p*-iodo-*N*-butylbenzamide as model compound established that the Suzuki reaction of this substrate with phenylboronic acid is readily catalyzed by the oxime carbapalladacycle and that the hydrolysis of 4-phenyl-*N*-butylbenzamide can be performed in basic media (Scheme 6).

As a matter of fact, when the Suzuki reaction of phenylboronic acid and 4-chloroacetophenone using PdL@SiO_2 as catalyst was performed in the presence of silica-bound ClPhCONH, after workup the Suzuki product was not detected. 4-Chlorobenzoic acid was the only compound observed besides the 4-phenylacetophenone. However, in the case of IPhCONH@SiO_2, together with 4-iodobenzoic and 4-hydroxybenzoic acid, the predominant product observed in the basic hydrolysis of the solids was the corresponding Suzuki coupling product 4-phenylbenzoic acid.

The above results using the three-phase methodology clearly indicates that although some palladium species sufficiently active to promote the coupling with iodoaromatics has to be present in the solution, the Suzuki product from 4-chloroacetophenone is a completely heterogeneous process. In other words, the leached species is not sufficiently active to catalyze the Suzuki coupling of chloroaromatics. It is well-documented[20−22] that reaction of chloroaromatics requires more active palladium catalysts than those required for iodocompounds. The above explanation is also compatible with the "conventional" leaching experiment consisting of filtration of the catalyst while hot and also with the lack of detectable palladium depletion on the solid and with the reusability of the catalyst (see below).

Reusability of the PdL@SiO_2 catalyst was demonstrated by performing a series of reactions using 4-chloroacetophenone and phenylboronic acid as substrates in which the catalyst PdL@SiO_2 was filtered at the end of the reaction; washed consecutively with aliquots of distilled water, ethanol, and ethyl ether; dried over reduced pressure, and reused for a new batch. Up to eight consecutive reactions were carried out with the same catalyst at the same substrate-to-catalyst ratio without observing any decrease in the final conversion or selectivity of the process.

Conclusions

Covalent attachment of the oxime carbapalladacycle catalyst to silicates renders solid catalysts that are extremely active for the Suzuki cross-coupling and can be reused for a series of consecutive runs without

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(16) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(17) Fu, G. C.; Littke, A. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176−4211.

(18) Davies, I. W.; Matty, L.; Hughes, D. L.; Reider, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 10139−10140.

(19) Lipshutz, B. H.; Tasler, S.; Chrisman, W.; Spliethoff, B.; Tesche, B. *J. Org. Chem.* **2003**, *68*, 1177−1189.

(20) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

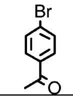
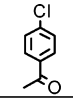
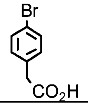
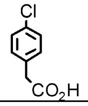
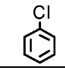
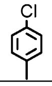
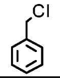
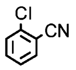
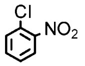
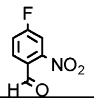
(21) Tsuji, J. Wiley: New York, 1995.

(22) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359−1469.

(23) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; et al. *J. Am. Chem. Soc.* **1992**, *114*, 10834−10843.

(24) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710−712.

TABLE 3. Results for Suzuki Reaction of Aryl Halides (0.2 mmol), Phenylboronic Acid (0.3 mmol), and K_2CO_3 (0.4 mmol) in Neat Water (5 mL) in the Presence of PdL@SiO_2 (30 mg) or PdL@MCM-41 (24.4 mg) as Catalysts

Substrate	Time (h)	Product yield(%)		Biphenyl yield(%)[a]	
		PdL@SiO_2	PdL@MCM-41	PdL@SiO_2	PdL@MCM-41
	<0.1	>99		-	
	0.25	91	43	-	-
	2	>99	94		
	0.25	>99		-	
	6	77		36	
	6	>99	>99	-	18
	6	73		38	
	5	>99	63	25	34
	4	63	46	-	18[b]
	48	>99	93	25[b]	55[b]
	0.25	26	10	-	-
	2	89	40	-	11
	4	34		3	
	24	30[c]			

[a] Biphenyl comes from homocoupling reaction of phenylboronic excess, and the % value is referred to the initial amount. [b] 4-Methylphenylboronic acid was used as reagent instead of phenylboronic acid and 4,4′-dimethylbiphenyl was resulting as by-product. [c] Products coming from SN_{Ar} are also found. Carboxylic acids and diols together with aldehydes are present as final reaction products.

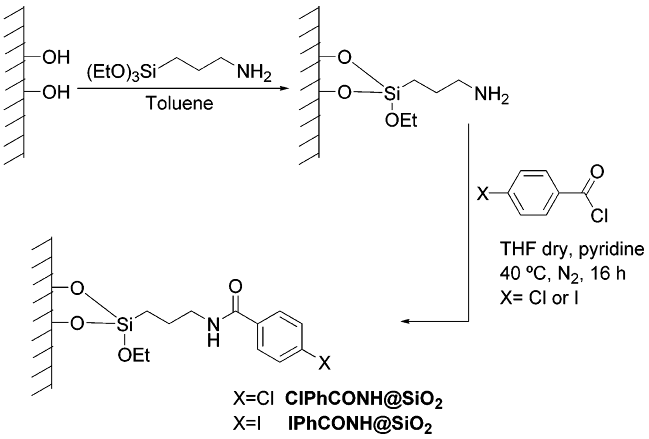
deactivation or leaching. Silica is a particular suitable support that can effect the Suzuki reaction with chlorinated substrates. No advantages of using mesoporous MCM-41 as support were apparent. In contrast to this, anchoring of the palladium complex on polymeric backbones derived from styrene or methyl acrylate gives much less active solid catalysts. The present results show the importance of the support, solvent, and reaction conditions on the catalytic activity. Based on PdL@SiO_2, "green" Suzuki reaction using water as solvent and a reusable catalyst can be developed.

Experimental Section

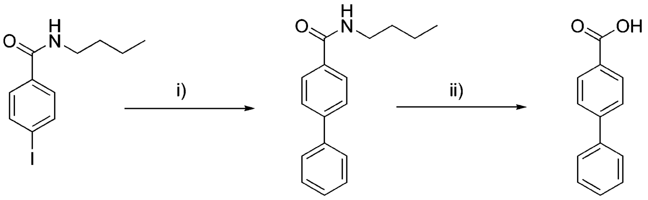
For reagents, general instrumentation, characterization, recovery, and reuses of the catalysts and leaching tests see Supporting Information.

Synthesis of 2. To a solution of hydroxylamine hydrochloride (5.13 g, 0.074 mol) and sodium acetate (10.26 g, 0.125 mol)

SCHEME 5. Anchoring Procedure of *p*-Chloro- or *p*-Iodo-*N*-butyl Benzamide onto the Aminopropyl-Modified High Surface Silica



SCHEME 6[a]



[a] (i) $PhB(OH)_2$, **3**, K_2CO_3, water, 100 °C; (ii) KOH, ethanol/water (2:1), 90 °C

in water (26 mL) was added 4-hydroxy-acetophenone (3 g, 0.022 mol). The solution was stirred at reflux temperature for 1 h. After this time, the aqueous solution was extracted exhaustively with diethyl ether. The organic phase was dried, and the solvent was evaporated under vacuum. To the resulting crude was added hexane, and 1-(4-hydroxyphenyl)-ethanone oxime (**2**) started to precipitate as a white solid (3.25 g, 0.0215 mol, 98%). Mp: 146−147 °C. IR (KBr, cm^{-1}): 3324, 1642, 1603, 1514, 1444, 1316, 1240, 1176, 940, 825, 589. ^1H NMR (ppm, 300 MHz, CD_3OD): δ 7.49 (2H, d, J = 5 Hz), 6.77 (2H, d, J = 5 Hz), 2.18 (3H, s). ^{13}C NMR (ppm, 300 MHz, CD_3OD): δ 159.9, 156.7, 130.2, 128.9, 116.5, 12.55. MS (FAB): m/z 151. Anal. Calcd for $C_8H_9NO_2$ (151.15): C, 63.5; H, 5.95; N, 9.26. Found: C, 63.19; H, 6.22; N, 9.35.

Synthesis of 3. To a solution of Li_2PdCl_4 (524.1 mg, 2 mmol) in methanol (4 mL) was added a methanolic solution (2 mL) of **2** (302 mg, 2 mmol) and sodium acetate (0.164 g, 2 mmol). The mixture was stirred at room temperature for 72 h. The mixture was filtered, and after water (5 mL) was added, the cyclopalladated complex (**3**) started to precipitate as a yellow solid (75%). IR (KBr, cm^{-1}): 3429, 1627, 1584, 1472, 1430, 1375, 1326, 1260, 1211, 1037, 873, 799, 608. ^1H NMR (ppm, 300 MHz, DMSO-d^6): δ 10.38(1H, s), 9.88(1H, s), 9.77(1H, s) 9.63(1H, s), 7.3 (2H, s), 7.15 (2H, d, J = 8 Hz), 6.5 (2H, d, J = 8 Hz), 2.23 (6H, s). ^{13}C NMR (ppm, 300 MHz, DMSO-d^6): δ 167.5, 157.3, 154.7, 133.1, 128.3, 122.1, 111.8, 11.6. MS (FAB): m/z 584. Anal. Calcd for $C_{16}H_{16}N_2O_4Pd_2Cl_2$ (584.04): C, 32.87; H, 2.74; N, 4.79. Found: C, 32.12; H, 2.87; N, 4.59.

Synthesis of 4. A mixture of **2** (2.5 g, 16.55 mmol), 11-bromoundecene (3.695 g, 16.55 mmol), and K_2CO_3 (11.27 g, 82.78 mmol) in acetone (30 mL) was heated to reflux for 24 h. The suspension was filtered, and the solvent was evaporated under vacuum. The crude was dissolved in AcOEt and extracted with water and brine. The organic phase was dried, and the solvent evaporated under vacuum. To the resulting crude was added hexane was added, and the mixture was heated under reflux for 30 min. The solution was filtered, and 1-[4-(undec-10-enyloxy)-phenyl]-ethanone oxime (**4**) started to precipitate as a white solid (3.97 g, 13 mmol, 80%). Mp: 67−69 °C. IR (KBr, cm^{-1}): 3449, 2929, 2841, 1640, 1606, 1505, 1471, 1316, 1248, 1174, 1012, 938, 904, 830, 635. ^1H NMR (ppm, 300 MHz, $CDCl_3$): δ 8.8 (1H, brs), 7.56 (2H, d, J = 7 Hz), 6.89 (2H, d, J = 7 Hz) 5.82 (1H, m), 4.95 (2H, m) 3.97 (2H, t, J = 6.5 Hz), 2.27 (3H, s), 2.05 (2H, m), 1.78 (2H, m), 1.43 (14H, m). ^{13}C NMR (ppm, 300 MHz, $CDCl_3$): δ 160.1, 155.6, 139.2, 128.8, 127.6, 127.3 (2C), 115.4, 114.4 (2C), 114.1, 68.1, 33.8, 29.5, 28.9, 26.0, 12.1. MS (FAB): m/z 304 (peaks at 286 and 151). Anal. Calcd for $C_{19}H_{29}NO_2$ (305.15): C, 74.72; H, 9.50; N, 4.59. Found: C, 74.53; H, 9.78; N, 4.62.

Synthesis of 5. To a solution of Li_2PdCl_4 (1.048 g, 4 mmol) in methanol (8 mL) was added a methanolic solution (4 mL) of **4** (1.212 g, 4 mmol) and sodium acetate (0.328 g, 4 mmol). The mixture was stirred at room temperature for 72 h. The mixture was filtered, and after water (10 mL) was added, the cyclopalladated complex (**5**) precipitated as a yellow solid. Mp: 135−137 °C. IR (KBr, cm^{-1}): 3435, 2922, 2848, 1633, 1584, 1560, 1458, 1340, 1263, 1211, 1033, 960, 800, 636. ^1H NMR (ppm, 300 MHz, $CDCl_3$): δ 8.4 (1H, s), 7.1 (1H, s), 6.85 (1H, d, J = 8 Hz), 6.35 (1H, d, J = 8 Hz), 5.35 (2H, s), 3.9 (2H, t), 2.2 (2H,d), 1.9 (3H, s), 1.7 (2H, brs), 1.6 (2H, brs), 1.4 (10H, m), 0.9 (2H, m). ^{13}C NMR (300 MHz, $CDCl_3$) δ_C (ppm): δ 165.0, 157.2, 154.1, 134.2, 131.6, 125.0, 117.4, 114.4, 111.1, 67.9, 34.7, 32.5, 29.6, 29.4, 29.3, 29.1, 26.0, 17.9, 14.0. MS (FAB) m/z (M − Cl); typical isotopic distribution for Pd: 406(17%), 407(22%), 408(27%), 410 (24%), 412(6%). Anal. Calcd for $C_{19}H_{28}NO_2PdCl$ (445.02): C, 51.12; H, 6.28; N, 3.14. Found: C, 52.10; H, 6.53; N, 3.18.

General Procedure for Anchoring the Cyclopalladated Complex on the Surface of the Modified Solids. To a solution of **5** (178 mg) in degassed chloroform were added the modified solid (1 g, see Supporting Information) and AIBN (6.5 mg, 10%) in a nitrogen atmosphere. The suspension was stirred magnetically at 80 °C under nitrogen for 20 h. The solid was filtered and Soxhlet extracted with dichloromethane for 24 h. After drying of the solids (at 45 °C under 10^{-1} Torr for 2 h), the quantity of palladium was determined by quantitative atomic absorption spectroscopy.

Procedure for Synthesis of the PdL@PS Polymer. A mixture of styrene (0.545 g, 5.23 mmol), Pd complex **5** (50 mg), divinylbenzene (50 mg, 0.38 mmol), toluene (0.3 mL), and 1-dodecanol (1.5 mL) was placed in a vessel and purged with nitrogen for 15 min. After that time, 2,2′-azobisisobutyronitrile (75 mg) was added, and the vessel was closed and heated at 80 °C for 24 h. The polymer was removed by filtration and Soxhlet extracted with dichloromethane for 24 h. The content of complex was determined by chemical analysis.

Procedure for Synthesis of the PdL@PEA polymer. Pd complex **5** (50 mg) and ethylene glycol dimethacrylate (EGDMA) (1.5 mL) were dissolved in toluene (2.1 mL) and ethanol (0.9 mL). The polymerization mixture was bubbled with nitrogen for 30 min. 2,2′-Azobisisobutyronitrile (25 mg) was added, and the mixture was heated at 80 °C for 24 h. The polymer was removed by filtration and Soxhlet extracted with dichloromethane for 24 h. The content of complex was determined by elemental analysis.

Typical Procedure for Suzuki Coupling of Aryl Bromides, Chlorides, and Fluorides. Suzuki reactions in water were carried out by stirring magnetically the corresponding aryl halide (0.2 mmol), boronic acid (0.3 mmol, 1.5 equiv), and K_2CO_3 (0.4 mmol, 2 equiv) in water, water/dioxane, or dioxane (5 mL) in the presence of the solid catalyst (5 mol % Pd) at reflux temperature. In neat water and water/dioxane the course of the reaction was followed periodically by extracting aliquots (0.5 mL) of the aqueous phase with ethyl acetate and analyzing the extract with GC using nitrobenzene as external standard. When pure dioxane was the test reaction solvent, the aliquots (0.1 mL) were analyzed as taken using nitrobenzene as external standard.

Procedure for Synthesis of $ClPhCONH@SiO_2$ and $IPhCONH@SiO_2$. To anchor the *p*-chloro- or *p*-iodobenzamide, a solution of the corresponding acyl chloride (*p*-chloro, 0. 919 g, 5.25 mmol; *p*-iodo, 1.4 g, 5.25 mmol) in dry THF (10 mL) was placed in a round-bottomed flask in the presence of aminopropyl-modified solid (1 g, see Supporting Information) and pyridine (404 μL, 5 mmol) under nitrogen atmosphere. The suspension was stirred magnetically at 40 °C under nitrogen atmosphere for 12 h. The solid was separated by centrifugation and washed with 20 mL of HCl/H_2O (5% v/v, 3 times), 20 mL of K_2CO_3/H_2O (0.02 M, 2 times), neat water (2 times), and ethanol (2 times). Then the solid was Soxhlet extracted with CH_2Cl_2 for 24 h. After drying the solids (at 45 °C under 10^{-1} Torr for 2 h), the anchored amount was determined by combustion chemical analysis and confirmed by thermogravimetric analysis. $ClPhCONH@SiO_2$: 0.40 mmol/g; $IPhCONH@SiO_2$: 0.88 mmol/g.

Three-Phase Tests. A solution of 4-chloroacetophenone (0.2 mmol), phenylboronic acid (0.3 mmol, 1.5 equiv), and K_2CO_3 (0.4 mmol, 2 equiv) in water (5 mL) ewas magnetically stirred in the presence of $PdL@SiO_2$ (30 mg) and $ClPhCONH@SiO_2$ or $IPhCONH@SiO_2$ (200 mg) at 100 °C for 2 h. At this time, the supernatant was analyzed by GC (conversion >99%), and the solid was separated by filtration under vacuum while hot, washed with ethanol, and Soxhlet extracted with ethanol for 24 h. After that, the solid was hydrolyzed in a 2 M solution of KOH (1.68 g) in ethanol/water (10:5 mL) at 90 °C for 3 days. The solution was neutralized with HCl 10% v/v (9.1 mL), extracted with CH_2Cl_2, concentrated and, analyzed by GC−MS.

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Supporting Information Available: General procedure for the preparation of mercaptopropyl- and aminopropyl-functionalized solid supports as well as catalyst characterization and reuse and leaching test data. This material is available free of charge via the Internet at http://pubs.acs.org.

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