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Silica-supported 3-4,5-dihydroimidazol-1-yl-propyltriethoxysilanedichloropalladium(II) complex: Heck and Suzuki cross-coupling reactions

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A novel mesoporous silica-nanotube-supported 3-4,5-dihydroimidazol-1-yl-propyltriethoxysilanedichloropalladium(II) complex was prepared and characterized. 3-4,5-Dihydroimidazol-1-yl-propyltriethoxysilanedichloropalladium(II) and mesoporous silica-supported 3-4,5-dihydroimidazol-1-yl-propyltriethoxysilanedichloropalladium(II) were tested for catalytic activity for Heck coupling reactions between styrene and several aryl halides and Suzuki coupling reactions between phenylboronic acid and several aryl halides. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: Heck reaction; Suzuki reaction; silica support; palladium catalyst; imidazoline

INTRODUCTION

Silica-based composite materials consisting of two distinct phases with entirely different properties and functionalities have been used extensively as catalysts. The literature contains numerous reports of novel composite materials that exhibit superior performances in many applications. Among them, transition-metal complexes with ligands containing nitrogen-donor atoms for successfully promoting the catalytic transformation of organic compounds have been successfully utilized.[1–3]

Extensively used in heterogeneous catalysts, silica-anchored metal catalysts possess many advantages over homogeneous systems. The recovery of the catalyst and its re-use in order to decrease production costs make metal complexes supported on silica important from the industrial point of view. Of the various alternatives to designing processable palladium-based catalysts that can be used, the introduction of an inorganic support or of functional silica that is converted to matrix by gelation or by co-condensation with tetraethoxysilane on which nitrogen or phosphine groups with palladium complexes were anchored have been tested for Heck and Suzuki reactions. Factors leading to re-use, ease of catalyst recovery and the selectivity offer an interesting alternative to homogeneous catalysts for industrial applications.

These discoveries motivate the search for new metal complexes with *N*-coordinated ligands and the evaluation of their catalytic properties. Our contribution to this field started with the syntheses of 2-imidazoline and benzimidazole complexes of platinum(II), rhodium(I) and ruthenium(II) that are capable of catalyzing the cyclopropanation of styrene with ethyl diazoacetate and intramolecular cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran in good yields.[4–10]

Here, we wish to report the preparation of a morphologically different silica supports prepared by the controlled hydrolysis of tetraethoxysilane in the presence of various organic agents, and their use for grafting of a palladium(II) complex of 3-4,5-dihydroimidazol-1-yl-propyltriethoxysilane (IMEO). Sol–gel methodology was chosen because of its mild conditions and ease. For these reasons, we wished to investigate the catalytic properties of palladium complexes as catalysts in Suzuki and Heck reactions.

EXPERIMENTAL

All reactions were performed using Schlenk-type flasks under argon and standard high-vacuum-line techniques. Solvents were analytical grade and distilled under argon from sodium benzophenone (Et_2O, dioxane). All aryl halides

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and phenylboronic acid (Aldrich) were simply degassed prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H) or 75.47 MHz (^{13}C). TUBITAK Microlab performed elemental analyses.

The grafting efficiency of the IMEO–palladium complex onto the mesoporous silica nanotube (MSN) particles was calculated using thermal gravimetric analysis (TGA). The thermal behavior was determined using a Shimadzu System 50 differential thermal analyzes and thermogravimetric analyzes. FT-IR analyses were performed on a Mattson 1100 FT-IR spectrometer. Specific surface areas were measured using a static process by means of a Micromeritics ASAP 2010 instrument. The specific surface area was calculated by the BET method and the average pore size was calculated using the Barrett, Joyner and Helenda (BJH) method.

Synthesis of 3-4,5-dihydroimidazol-1-yl-propyltriethoxysilanedichloropalladium(II) complex (1)

A solution of IMEO (0.29 g, 1.07 mmol) in toluene (20 ml) and $PdCl_2$ $(CH_3CN)_2$ (0.13 g, 0.53 mmol) was heated for 2 h under reflux. Upon cooling to room temperature, orange crystals were filtered off, washed with hexane (2 × 15 ml) and dried under vacuum. The crude product was recrystallized from CH_2Cl_2–Et_2O at room temperature; m.p. 103–104 °C, 0.36 g, 94% yield.

^{1}H NMR (δ, $CDCl_3$): 8.76 (s, 1H, $\mathrm{N{=}C}H\mathrm{N}$); 0.47 (t, $J = 8.2$ Hz, 2H, $\mathrm{SiC}H_2\mathrm{CH_2CH_2N}$); 1.66 (t, $J = 7.0$ Hz, 9H, $\mathrm{SiOCH_2C}H_3$); 1.49–1.53 (m, 2H, $\mathrm{SiCH_2C}H_2\mathrm{CH_2N}$); 3.08 (t, $J =$ 7.2 Hz, 2H, $\mathrm{SiCH_2CH_2C}H_2\mathrm{N}$); 3.25 and 3.79 8 (t, $J = 10.6$ Hz, 2H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$) 3.74 (q, $J = 7.0$ Hz, 6H, $\mathrm{SiOC}H_2\mathrm{CH_3}$).

^{13}C NMR (δ, $CDCl_3$): 160.24 ($\mathrm{N{=}CHN}$); 7.63 ($\mathrm{SiCH_2CH_2CH_2N}$); 18.67 ($\mathrm{SiOCH_2CH_3}$); 22.01 ($\mathrm{SiCH_2CH_2CH_2N}$); 47.31 and 50.29 ($\mathrm{NCH_2CH_2N}$); 53.37 ($\mathrm{SiCH_2CH_2CH_2N}$); 58.85 ($\mathrm{SiOCH_2CH_3}$).

Anal. Found: C, 39.49; H, 7.26; N, 7.61. Calc. for $C_{24}H_{52}Cl_2N_4O_6PdSi_2$: C, 39.66; H, 7.16; N, 7.71%.

Preparation of silica-nanotubes (MSN)

The reaction was carried out as follows; 10 g DL-tartaric acid and 30 g of water were dissolved in 2 l absolute ethanol. To this solution, 365 g of TEOS was added and the mixture was stirred for 5 min with a magnetic stirrer. After that, the system was allowed to stand 30 min and 1 l of 25% NH_3 solution was added. An opalescent white gel formed after 1 h. The gel was recovered by filtration and washed with 500 ml of distilled water three times and dried at 110 °C in a vacuum oven. BET surface area: 29 ± 6 m^2 g^{-1}; pore diameter: 1678 ± 23 Å; pore volume: 0.28 ± 0 ml g^{-1}.

Preparation of 3-4,5-dihydroimidazol-1-yl-propyltriethoxysilanedichloropalladium(II) complex-modified silica

In order to enhance the number of silanol (SiOH) groups that can be used to attach IMEO–Pd to the surface, etching of the above particles (grain size of 2–20 μm) with CH_3SO_3H was performed as given in the literature.[11] Grafting was carried out under nitrogen atmosphere with different amounts of IMEO–Pd complex and the MSN particles. 1 g of IMEO-Pd complex in 3 : 10 methanol/water was added dropwise to 2 g of MSN in 100 ml toluene. In order to avoid gel formation of IMEO–Pd, the solutions were prepared just before the process. The pH was adjusted to 8.6. The modified particles were then poured off and extracted with methanol in a Soxhlet apparatus for 12 h. Finally, the extracted particles were dried under reduced pressure at 120 °C for 24 h. The grafting efficiency of IMEO–Pd on silica support optimized as a function of IMEO–Pd concentration was in the range of 0.45 to 0.89 mmol g^{-1}.

General procedure for the Heck-type coupling reactions

Under an atmosphere of argon, 1.5 mmol% catalyst (based on palladium), aryl halide (1.0 mmol), styrene (1.5 mol), Cs_2CO_3 (1.5 mmol) and dioxane (3 ml) were placed in a 50 ml Schlenk tube containing a small stirring bar. The Schlenk tube was placed in an 80 °C oil bath and stirred for 2–3 h. After the desired time, conversion was determined by ^{1}H NMR. The mixture was diluted with Et_2O and filtered over a pad of silica. After the evaporation of the solvents, the residue was purified by flash chromatography.

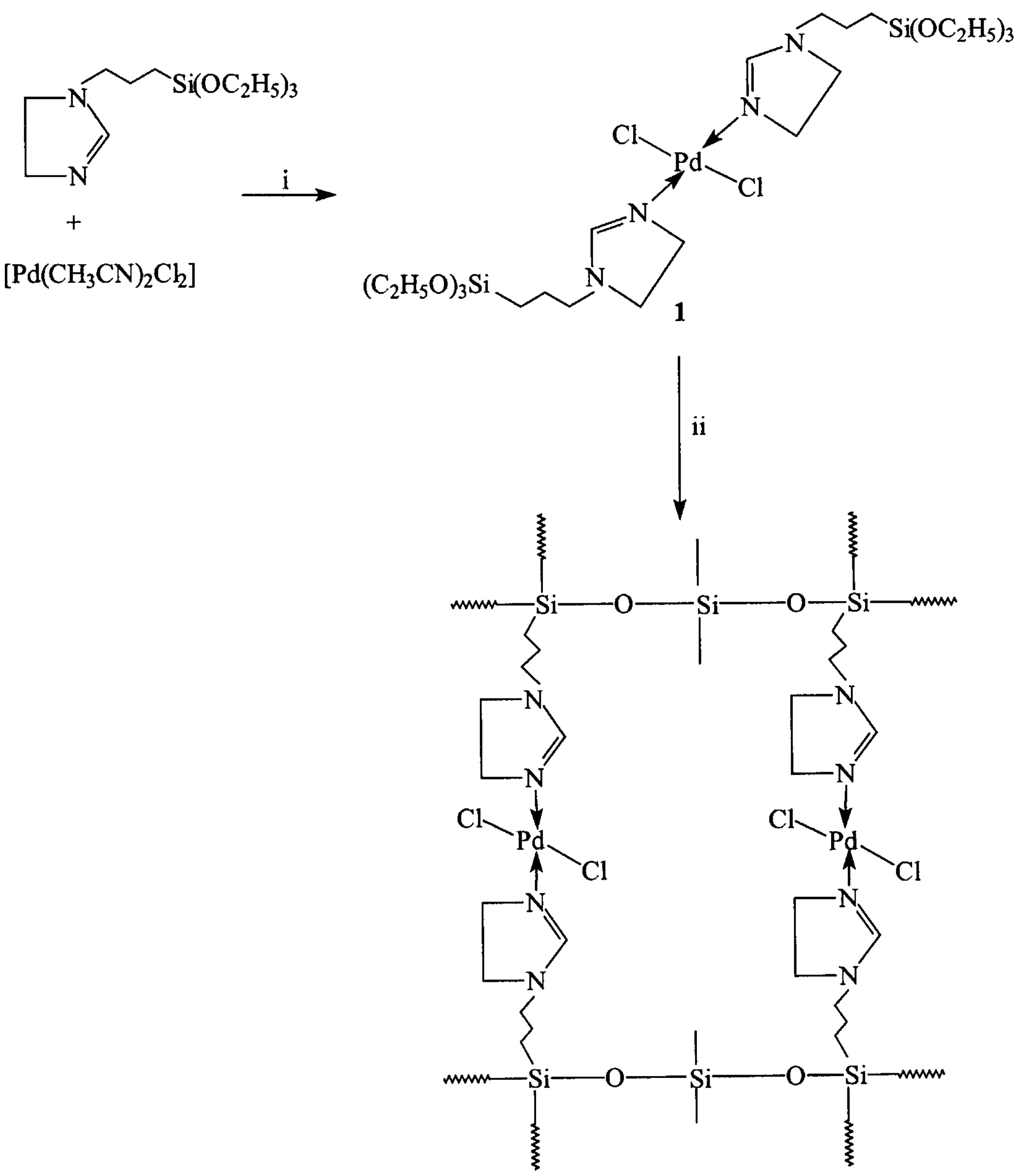
General procedure for the Suzuki-type coupling reactions

Catalyst (1.5 mmol%), aryl halide (1.0 mmol), phenylboronic acid (1.5 mol), Cs_2CO_3 (1.5 mmol) and dioxane (3 ml) were added in a 50 ml Schlenk tube under argon and the mixture was heated in an oil bath. The reaction mixture was cooled, diluted with Et_2O, filtered through a pad of silica gel with repeated washings, concentrated and purified by flash chromatography on silica gel.

RESULTS AND DISCUSSION

Dichloro-3-4,5-dihydroimidazol-1-yl-propyltriethoxysilane-palladium(II) catalyst was prepared from IMEO and $PdCl_2(CH_3CN)_2$ in toluene as shown in Scheme 1.

The results showed that three different morphological classes of silica xerogels were synthesized. Completely amorphous silicates were obtained in the presence of alcohols, whereas the material originating from DL-tartaric acid was silica nanotubes in a morphological state. Nonoporous silica spheres formation was noticed along with the nanotube formation. The characteristics of the products are given in the Experimental section. As expected, the silica nanotubes had the smallest BET area. The pore size distribution, calculated by the BJH method, indicates that nanotubes can be considered as essentially macroporous materials, whereas the majority of the pores in amorphous silica and silica foams fall into the mesoporous range.



Scheme 1. The synthetic route for the preparation of palladium–imidazoline complex and its immobilization: (i) PhMe, 110 °C; (ii) MSN and toluene.

The immobilization of dichloro-3-4,5-dihydroimidazol-1-yl-propyltriethoxysilanepalladium(II) by heating with MSN particles in a ratio of 0.60 mmol palladium per gram of silica for 12 h gave the modified silica product as shown in Scheme 1. Palladium analysis was performed on this sample and showed a palladium loading of 0.48 mmol μg^{-1}, indicating that 80% of the complex had been immobilized.

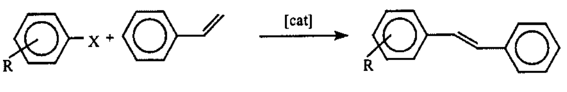
The silanol groups (SiOH) on the MSN surface that are the reactive sites for the silylation reaction play an important role in the surface modification process. Silica surfaces can be hydrophobic, as occurs when the surface chemical groups are mainly siloxane Si–O–Si groups, or hydrophilic, when the surfaces contain multiple silanol Si–OH groups. When silica is exposed to acid solution for an extended time, hydroxylation can be extensive. This produces polymeric chains of $Si(OH)_2$–O–$Si(OH)_2$–OH units, which can link in many different ways to form a three-dimensional network or silica gel. The chemistry and chemical reactions of silica surfaces in aqueous solutions are generally considered within the above framework. Therefore, mesoporous silica samples prepared in the presence of DL-tartaric acid result in completely amorphous silica xerogels. The gel consists of polymeric chains forming three-dimensional networks with hydroxyl groups present at the surface. The tentative assignments for the FT-IR spectra were as follows:

ν_{as}(Si–O–Si) 1174 cm^{-1}, ν(Si–OH) 1060 cm^{-1}, ν_s(Si–O–Si) 938, 785 cm^{-1}, ν_s(Si–O–Si) 620, 550 cm^{-1}. The TGA results revealed that the highest weight loss due to dehydroxylation was 0.95% for MSN.

The grafting efficiency of IMEO–Pd onto MSN has been studied. The amount of IMEO–Pd grafted onto the MSN was 0.5 wt% as determined by TGA.

The differential thermal analysis in air was performed on both MSN and IMEO–Pd-modified MSN. In the case of IMEO–Pd-modified MSN, exotherms were observed with maxima at around 250 and 440 °C. Moreover, a slight exotherm at 500 °C was observed due to decomposition of the adsorbed silane.

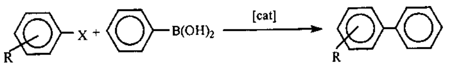
The olefination of aryl halides (Mizoroki–Heck, or simply the Heck reaction), one of the most important C–C coupling reactions in organic synthesis, is typically catalyzed by palladium complexes in homogeneous solution (Eqn (1)).[12–15] The use of monodentate phosphines in the palladium-catalyzed Heck reaction provides a most efficient catalytic system for the syntheses of substituted olefins. The reaction involving the less reactive aryl bromides and aryl chlorides requires electron-donating, bulky tertiary phosphines, such as $P(^tBu)_3$, as supporting ligand in order to assist in the initial oxidative-addition of C–X bonds.



(1)

However, under normal reaction conditions, phosphines and their palladium complexes are susceptible to decomposition. Hence, excess phosphine must be employed. This is undesirable for large-scale applications, since phoshines, especially electron-rich phosphines, are expensive. The use of excess ligand also reduces reaction rates; thus, in order to counterbalance this negative effect, a higher palladium loading is necessary to achieve acceptable catalytic activities.[16–20]

Coupling of aryl- and vinyl halides or triflates with aryl- or vinyl boron compounds, like boronic acids, boronic esters or boranes, is known as the Suzuki coupling reaction (Eqn (2)):



(2)

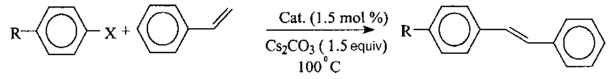
This reaction has proven extremely versatile for the preparation of unsymmetrical, bulky biaryls and has found extensive use in natural product synthesis. Although palladium complexes bearing tertiary phosphine ligands are commonly employed in Suzuki–Miyaura cross-coupling, these catalysts are often sensitive to air oxidation and therefore, require air-free handling to minimize ligand oxidation.[21,22]

Palladium complex **1** was found to be an active catalyst for the Heck reaction and proved to be thermally robust for high-temperature Heck olefination of aryl chlorides, bromides or iodides. Under our optimized reaction conditions (1.5% palladium–imidazoline complex, **1**, 1.5 equivalents of Cs_2CO_3, dioxane, 80 °C), excellent yields of coupled products could be obtained for a wide array of bromides or iodides with styrene (Table 1). For example, iodobenzene and *p*-iodoanisole, yields 94% and 93% respectively, could be reached in 0.5 h and 1 h respectively (Table 1). Electron-deficient 4-bromoacetophenone was converted completely to the coupled product in *ca* 1 h (Table 1, entry 2). It should be noted that in all cases only the trans products were selectively obtained, as confirmed by ^{1}NMR. The silica-supported IMEO–Pd matrix was found to be active in this reaction at 100 °C (Table 1, entries 5–10).

In a first test of the activity of complex **1** in the Suzuki-type coupling of para-substituted aryl halides with phenyl boronic acid, classical conditions for solvent and base were chosen (dioxane as solvent, Cs_2CO_3 as base, and reaction temperature of 80 °C).[23,24] The coupling of activated and deactivated aryl halides and phenylboronic acid proceeds in high yields and quite rapidly even with a low catalyst loading (Table 2). Under these conditions, 4-bromoacetophenone and *p*-chlorotoluene react very cleanly with phenylboronic acid in goods yields (Table 2, entries 2 and 5). Also, the palladium-anchored silica nanotubes were found to be an active catalyst under these reaction conditions (Table 2, entries 6–10).

In all cases where recycling of catalyst was attempted, small decreases in activity were observed from one run to the next. One plausible explanation for this was that the decomposition of the nanoparticles to the palladium metal was overcome. Therefore, the recovery of the catalyst was very high.

Table 1. Palladium-catalyzed Heck coupling reaction between styrene and several aryl halides



Entry	R	X	Time (h)	Yield[a] (%)
1	CH_3O	I	1.0	93
2	$COCH_3$	Br	1.0	91
3	CH_2Br	Br	1.0	85
4	H	I	0.5	94
5	CH_3O	I	4.0	89[b]
6	CH_3O	I	4.0	85[c]
7	CH_3O	I	4.0	79[d]
8	$COCH_3$	Br	4.0	87[b]
9	$COCH_3$	Br	4.0	85[c]
10	$COCH_3$	Br	4.0	81[d]

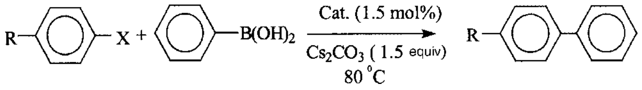
[a] Reaction conditions: 1.0 mmol of R-C_6H_4X-*p*, 1.5 mmol of styrene, 1.5 mmol Cs_2CO_3, 1.5 mmol% palladium catalyst, dioxane (3 ml). Isolated yields (purity of yield checked by NMR). All reactions were monitored by thin-layer chromatography (TLC).

[b] First use of MSN-supported catalysts.

[c] Second use of MSN-supported catalysts.

[d] Fifth use of the MSN-supported catalysts.

Table 2. Palladium-catalyzed Suzuki coupling reaction between phenylboronic acid and several aryl halides



Entry	R	X	Time (h)	Yield[a] (%)
1	CH_3O	I	1.0	95
2	$COCH_3$	Br	1.0	95
3	CH_2Br	Br	1.0	98
4	H	I	0.5	94
5	CH_3	Cl	2.0	82
6	$COCH_3$	Br	4.0	89[b]
7	$COCH_3$	Br	4.0	86[c]
8	$COCH_3$	Br	4.0	84[d]
9	$COCH_3$	I	4.0	91[b]
10	$COCH_3$	I	4.0	88[c]
11	$COCH_3$	I	4.0	86[d]

[a] Reaction conditions: 1.0 mmol of R-C_6H_4X-*p*, 1.5 mmol of phenylboronic acid, 1.5 mmol Cs_2CO_3, 1.5 mmol% palladium catalyst, dioxane (3 ml). Isolated yields (purity of yield checked by NMR). All reactions were monitored by TLC.

[b] First use of MSN-supported catalysts.

[c] Second use of MSN-supported catalysts.

[d] Fifth use of the MSN-supported catalysts.

CONCLUSION

In summary, we have found that the very easily synthesized, comparatively inexpensive complex **1** shows by far the highest activity yet reported in the Heck and Suzuki coupling of aryl halides, regardless of whether the substrates are electron rich or poor. Also, we have developed a convenient synthetic route to heterogenize catalytically active imidazoline complex by hydrolyzing and condensation of $-Si(OEt)_3$ group attached through $-(CH_2)_3-$ spacer to a nitrogen atom of the imidazoline via hydroxyl bonding on MSN particles showed catalytic activity for Heck and Suzuki coupling reactions. The heterogenized catalysts are easily separable from the reaction mixture by filtering and reusable many times without deactivating by leaching of palladium. Though the classical Pd/C catalyst deactivates after only three cycles, this novel catalyst has the same activity even after five cycles in the Heck or Suzuki reactions.

Therefore, the use of stable palladium complexes anchored on MSN particles may offer an interesting alternative to homogeneous catalysts for industrial applications.

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