

Hybrid Organic-Inorganic Materials from Di-(2-pyridyl)methylamine-Palladium Dichloride Complex as Recoverable Catalysts for Suzuki, Heck and Sonogashira Reactions

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Abstract: Hybrid silica materials containing the di-(2-pyridyl)methylamine-palladium dichloride complex, prepared by sol-gel cogelification, are efficient recyclable catalysts for Suzuki (aryl bromides and chlorides), Heck (aryl bromides) and Sonogashira reactions (aryl iodides and bromides). Formation of palladium(0) nanoparticles is observed in the Suzuki

and Heck reactions but not in the Sonogashira coupling.

Keywords: catalyst immobilization; C–C coupling; organic-inorganic hybrid materials; palladium; sol-gel process

Introduction

Palladium-catalyzed carbon-carbon bond forming processes such as the Suzuki–Miyaura^[1] cross-coupling, Heck^[2] and Sonogashira^[3] reactions are key steps in the synthesis of natural products and a great variety of complex organic molecules used in many fields, such as drugs, agrochemicals or in materials science. On the other hand, the heterogenization of homogeneous catalysts by their immobilization on polymeric organic^[4] or inorganic^[5] supports offers the advantages of easy product separation and catalyst recycling. Phosphanes are common ligands used in palladium-catalyzed processes, but they are readily oxidized to their corresponding phosphane oxides, which can prevent the easy recovery and reuse of the catalytic systems. Thus, phosphane-free palladium catalysts have superior stability.

Some of us discovered^[6] air- and moisture-stable phosphane-free macrocyclic triolefinic palladium(0) complexes. We have described their immobilization onto cross-linked polystyrene,^[7] and onto a silica matrix,^[8] and the activity of these supported versions as recyclable catalysts in Suzuki cross-couplings and telomerization reactions. However, the drawback of

our heterogenized macrocyclic palladium(0) complexes was that they were efficient in Suzuki couplings with activated and deactivated aryl iodides but not for the more challenging aryl bromides and chlorides, the ideal substrates for coupling reactions being the more eco-friendly aryl chlorides.^[9]

Several phosphane-free palladium systems have been reported as robust and efficient catalysts or precatalysts (high TON and TOF)^[10] for the coupling reactions with aryl chlorides (palladacycles, N-heterocyclic carbenes and bipyridine-based systems). We focused our attention on bipyridin-2-ylmethane-type ligands to prepare immobilized palladium catalysts onto a silica matrix. Such inorganic supports constitute an interesting alternative for the preparation of heterogeneous catalysts because of their mechanical and thermal stability and chemical inertia.^[11] The formation of organic-inorganic hybrids by sol-gel chemistry^[12] is a convenient route to solid materials with catalytic properties.^[5,13]

Palladium(II) complexes of di-2-pyridylamine-derived ligands **1** (Figure 1) have been developed by Buchmeiser^[14] as catalysts for C–C and C–N bond formation and they have been covalently grafted to a matrix resulting from a ROMP polymerization.

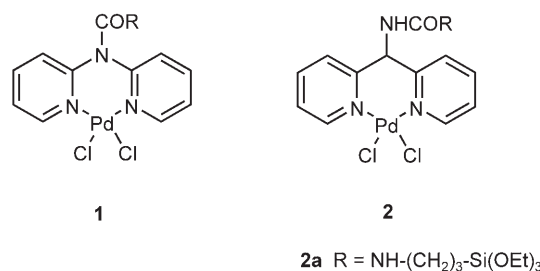


Figure 1. Palladium dichloride complexes of di-2-pyridylamine and di-(2-pyridyl)methylamine ligands.

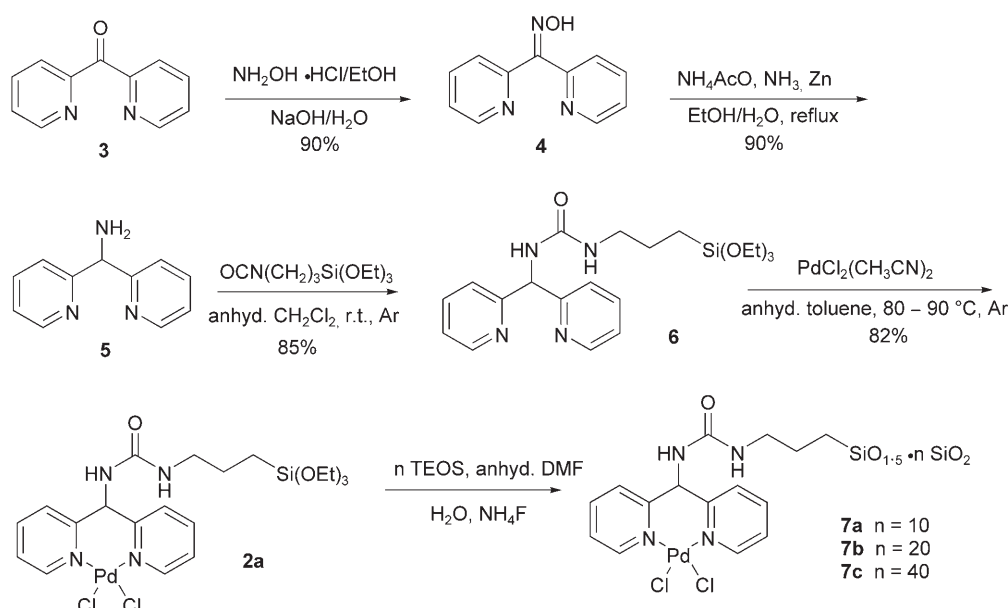
Nájera^[15] has described related palladium(II) complexes **2** (Figure 1) as efficient catalysts for Heck, Suzuki and Sonogashira reactions in organic and aqueous solvents under homogeneous conditions. The same group has covalently anchored this type of complexes **2** to a styrene-maleic anhydride copolymer providing a recyclable catalyst for those reactions.^[16] Prompted by the publication of this report we have presented our preliminary results on the preparation of hybrid silica materials from the silylated monomer **2a** (Figure 1) and their activity and recyclability in Suzuki cross-couplings.^[17] We describe here the full details of our work and its extension to Heck and Sonogashira reactions.

Results and Discussion

Monomer Synthesis and Catalysts Preparation

The monosilylated palladium(II) complex **2a** and the hybrid silica catalytic materials derived thereof were

prepared as summarized in Scheme 1. Zinc reduction^[18] of the oxime **4** derived from commercial di-(2-pyridyl)methanone (**3**) gave di-(2-pyridyl)methylamine (**5**) which was immediately reacted overnight under stirring with freshly distilled 3-(triethoxysilyl)propyl isocyanate in anhydrous dichloromethane at room temperature. The resulting silylated urea **6** was treated overnight with PdCl₂(CH₃CN)₂ in anhydrous toluene at 80–90 °C to furnish complex **2a**. Palladium-containing hybrid silica materials **7a–c** were obtained by standard co-gelification of monomer **2a** with different amounts of tetraethyl orthosilicate (TEOS) (1:10, 1:20, 1:40) in dimethylformamide, using the stoichiometric amount of water and ammonium fluoride as catalyst. A standard nucleophilic fluoride catalysis was considered appropriate for the sol-gel co-gelification of TEOS with the complex **2a**, it has been widely used by many authors and avoids the acidic or basic medium involved in alternative acid or basic catalysis. The materials were characterized by solid-state ²⁹Si NMR and ¹³C NMR, surface area BET measurements, IR and elemental analysis, the amount of palladium being determined by inductively coupled plasma (ICP) (Table 1). From analytical data we obtained a molar ratio Pd/N of about 1/4 for complex **2a** as expected. As for the materials **7a–c** the experimental molar ratios Pd/N were found to be about 1/7, partial decomplexation has occurred in the formation of materials by the sol-gel process. Large amounts of TEOS were used (10, 20 and 40 molar equivalents with respect to **2a**) in order to favour solid formation with high BET surface areas, because heterogeneous catalysts with higher specific surface areas are usually more efficient. Similar surface areas ranging from 165 to 176 m² g⁻¹ were obtained for all three materials ac-



Scheme 1. Preparation of hybrid silica materials **7a–c**.

Table 1. Some analytical and textural data of hybrid materials **7a–c**.

7	²⁹ Si CP MAS NMR T ³ Q ³ Q ⁴	S _{BET} [m ² g ^{−1}]	Pore Diameter ^[a] [Å]	Pore Volume ^[b] [cm ³ g ^{−1}]	% Pd	mmol Pd/g
7a	−65.4 −101.9 −109.4	165	61	0.274	6.05	0.569
7b	−65.7 −102.2 −110.6	171	99	0.454	3.88	0.365
7c	−64.6 −100.8 −109.4	176	97	0.464	2.63	0.247

^[a] Adsorption average pore diameter.

^[b] Adsorption cumulative volume of pores.

cordingly to the BET adsorption-desorption measurements. The presence of the organic ligand in the hybrid materials was ensured by the solid-state NMR spectra (²⁹Si and ¹³C). The ²⁹Si spectra of **7a–c** show two groups of chemical shifts: T units at around −55 to −75 ppm, resulting from the hydrolysis-condensation of **2a**, and Q units ranging from −100 to −120 ppm, formed from TEOS as exemplified by the ²⁹Si solid-state NMR of **7a** (Figure 2, a). The T:Q intensities diminish from **7a** to **7c** with decreasing amount of **2a** to TEOS (not shown). Only the solid-state ¹³C NMR of **7a** was performed, the organics in **7b** and **7c** being of too little intensity in the corresponding hybrids to be measured in a reasonable time. The spectrum of **7a** exhibits an absorption at 8.7 ppm (CH₂–Si) which confirms the covalently bonded ligand to silica. Other signals attributable to the chemical shifts of the organic part of **7** appear at 16.6 (CH₃ from residual ethoxy groups), 23.0 (CH₂–CH₂–Si), 42.6 (CH₂–N), 58.1 (CH₂ from residual ethoxy groups), 74.3 (CH–N), 126.8, 141.7, 154.5 (3 C from pyridine rings) and 158 (C=O) ppm (Figure 2, b).

Assay of Supported Catalysts **7a–c** in Suzuki, Heck and Sonogashira Reactions

The activity and recyclability of catalysts **7a–c** was assayed in the Suzuki cross-coupling of phenylboronic acid (**8**) with *p*-bromoacetophenone (**9a**), and with the aryl chlorides *m*-chlorobenzonitrile (**11a**) and chlorobenzene (**11b**) (Scheme 2, Table 2 and Table 3). Three different sets of conditions were tested for aryl bromide **9a** with material **7b** (Table 2): A) KOH, MeOH/H₂O (3:1), 60 °C; B) K₂CO₃, toluene, 110 °C; C) K₂CO₃, DMF/H₂O (95:5), 110 °C. The faster reaction (0.75 h for full conversion) and the best recycling in up to five consecutive runs was achieved with conditions C (96% isolated yield in the fifth run). Thus, they were also adopted for the other two catalytic materials **7a** and **7c**. Ten consecutive cycles with the same batch of catalyst were performed for every catalyst, maintaining the same reaction time in every run. The isolated yields of 4-phenylacetophenone (**10**) for every catalytic material are summarized in Table 2.

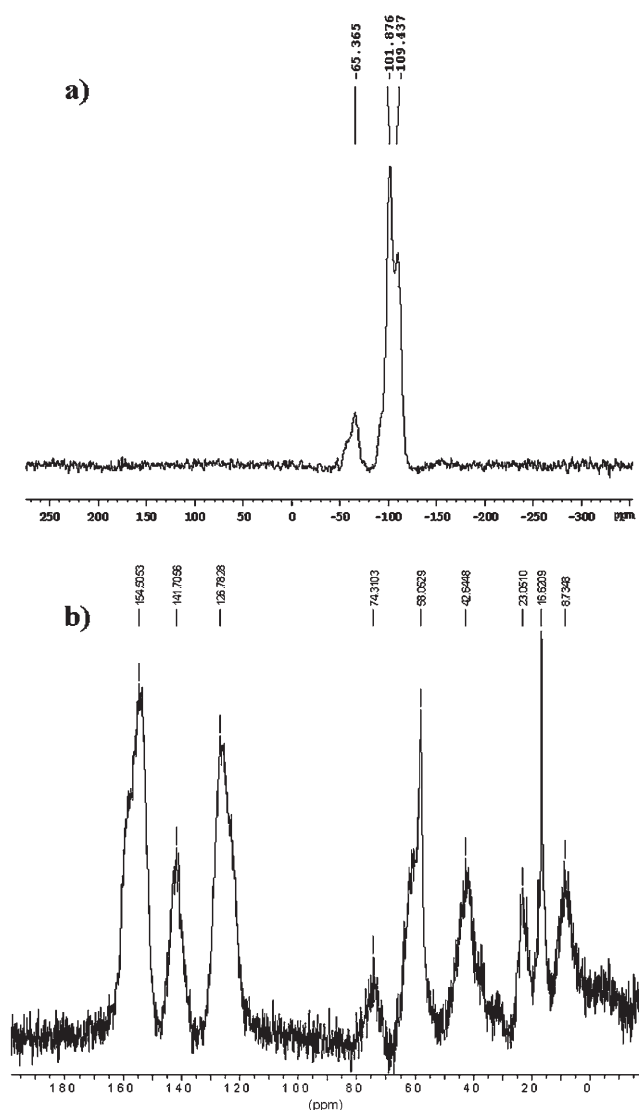
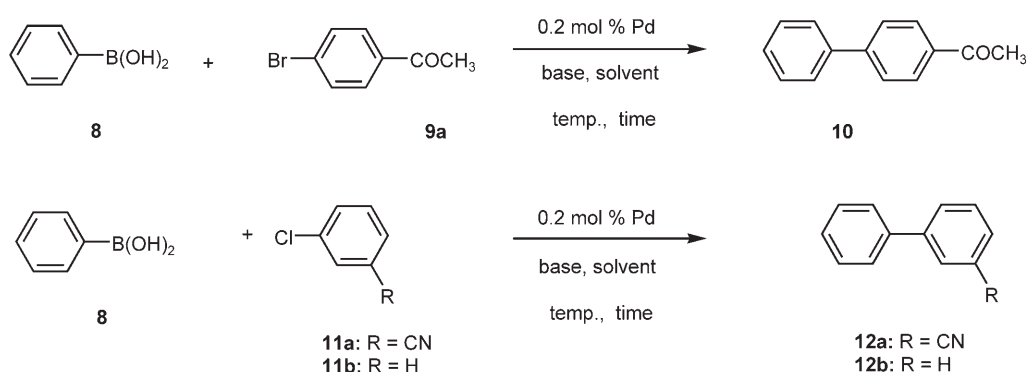


Figure 2. Solid state CP-MAS ²⁹Si (a) and ¹³C NMR (b) spectra for **7a**.

No significant differences were found within the materials with respect to their recyclability, which was excellent in all cases, but the reaction time required to achieve complete conversion of the aryl bromide was longer with **7c** containing a lower percentage of palladium. This Suzuki cross-coupling was also as-



Scheme 2. Suzuki cross-couplings tested with catalysts **7a–c**.

Table 2. Suzuki couplings between **8** and **9a** with catalysts **7a–c** giving rise to **10** (Scheme 2).

Run	Conditions A ^[a] 7b		Conditions B ^[b] 7b		Conditions C ^[c] 7a		Conditions C ^[c] 7b		Conditions C ^[c] 7c	
	<i>t</i> [h]	Conversion [%] ^[d]	<i>t</i> [h]	Conversion [%] ^[d]	<i>t</i> [h]	Yield [%] ^[e]	<i>t</i> [h]	Yield [%] ^[e]	<i>t</i> [h]	Yield [%] ^[e]
1	0.75	100	3	98	0.75	100	0.75	100	1	100
2	0.75	78	3	94	0.75	100	0.75	100	1	99
3	0.75	74	3	89	0.75	96	0.75	99	1	98
4	0.75	73	3	91	0.75	97	0.75	96	1	98
5					0.75	96	0.75	96	1	97
6					0.75	95	0.75	94	1	98
7					0.75	97	0.75	96	1	96
8					0.75	98	0.75	96	1	97
9					0.75	97	0.75	97	1	95
10					0.75	94	0.75	96	1	95

^[a] 0.2% molar of Pd, [ArX]=0.5 M, PhB(OH)₂ (1.5 equiv.), KOH (2 equiv.), MeOH/H₂O (3:1), 60 °C.

^[b] 0.2% molar of Pd, [ArX]=0.5 M, PhB(OH)₂ (1.5 equiv.), K₂CO₃ (2 equiv.), toluene, 110 °C.

^[c] 0.2% molar of Pd, [ArX]=0.5 M, PhB(OH)₂ (1.5 equiv.), K₂CO₃ (2 equiv.), DMF/H₂O (95:5), 110 °C.

^[d] GLC conversions (undecane as internal standard).

^[e] Isolated yield.

Table 3. Suzuki couplings between **8** and **11a** with catalyst **7b** giving rise to **12a** (Scheme 2).

Run	Conditions C ^[a] 7b			
	<i>t</i> [h]	Conversion [%] ^[b]	<i>t</i> [h]	Conversion [%] ^[b]
1	7	61	24	82
2	7	44	24	59
3	7	34	24	38
4	7	31	24	34
5	7	25	24	26

^[a] 0.2% molar of Pd, [ArX]=0.5 M, PhB(OH)₂ (1.5 equiv.), K₂CO₃ (2 equiv.), DMF/H₂O (95:5), 110 °C.

^[b] GLC conversions (undecane as internal standard).

sayed under the same conditions C with the material **7bSi**, obtained by refluxing **7b** with excess of bis(trimethylsilyl)amine for capping surface silanol groups, but the reaction was slower, four hours being required to afford a 97% isolated yield of **10**. Nájera^[16] has used water or methanol-water as solvent systems in their recycling experiments with the di-(2-pyridyl)me-

thylamine complex anchored to organic polymer, increasing reaction times being described for successive cycles. In our case, the use of a lower amount of water, dimethylformamide instead of methanol and potassium carbonate as base instead of KOH improved the recyclability (conditions C are better than conditions A).

It must be mentioned that the initial pale yellow solids **7a–c** turned grey after the first run and darkened progressively to black after several runs which is possibly due to the formation of metallic particles. In order to confirm this we studied the recycled materials through electron microscopic techniques. Indeed high-resolution transmission electron microscopy (HR-TEM) showed the formation of metal nanoparticles in the materials (diameter around 5 nm). Electron diffraction (ED) of the sample exhibited the characteristic pattern of face-centered cube (fcc) palladium(0). Both the inorganic matrix and the organic ligand of the hybrids can have a contribution to the nanoparticle stabilization.^[19] To ensure that the nano-

particles were inside the silica material and not only adsorbed on the external surface, a sample for TEM measurement was also prepared by using ultramicrotomy techniques instead of only depositing a drop of a suspension of the solid onto the copper grid. In Figure 3 we show an example of HR-TEM micrographs of one of the samples (material **7c** after the fourth cycle, conditions C of Table 2), a TEM observation using ultramicrotomy techniques and the size distribution of the particles. The nanoparticles were not observed by TEM in the materials before the catalysis, but darkening of the recovered catalytic materials in successive runs took place under any conditions used for the Suzuki couplings. Palladium nanoparticles observed by TEM in supported bipyridyl complexes have also been described by Nájera.^[16]

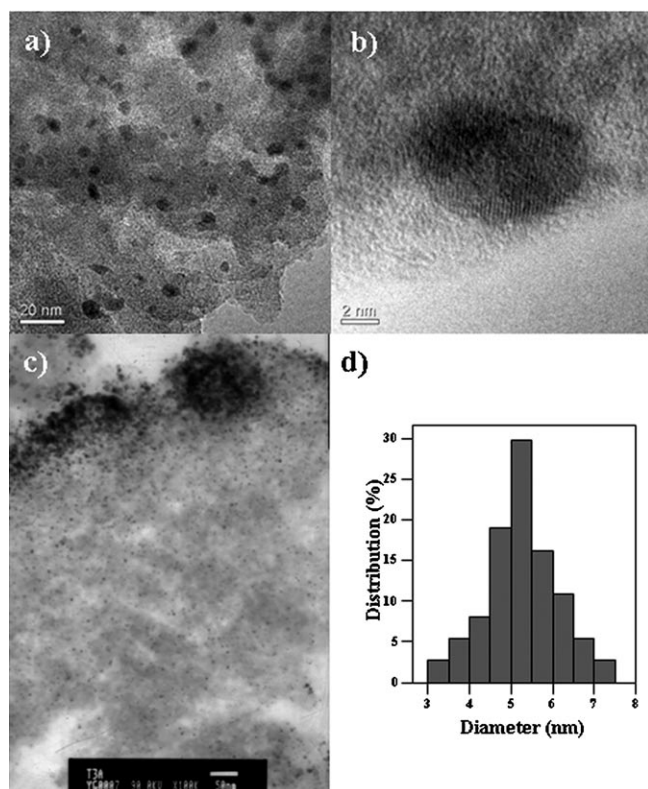
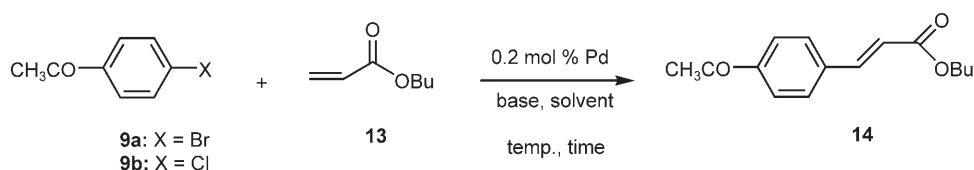


Figure 3. a) and b) HR-TEM micrographs of Pd nanoparticles formed in the Suzuki reaction; c) TEM observation by using ultramicrotomy techniques; d) particle size distribution (104 particles; mean particle size: 5.1 ± 0.9 nm).

The amounts of Pd determined by ICP-MS in the product **10** isolated from the first cycle performed with catalyst **7a** under conditions C and in the solid mixture obtained in this cycle by evaporation of the filtrate were found to be 12 and 80 ppm, respectively. Some authors have pointed out^[20] that released Pd under reaction conditions acts as the true catalyst in immobilized palladium systems and redeposition of the metal after completion of the reaction is claimed. When the catalyst **7b** was filtered off from the hot reaction mixture under conditions C after 15 min (47% GLC conversion of **9a**) and the remaining filtrate was made to react at the same temperature, the conversion raised to 80% (GLC) after 6 h. Thus, a homogeneous pathway due to metal release in the reaction conditions is, in part, responsible for the catalysis, but as the reaction is much slower, the heterogeneous pathway plays a significant role.

Material **7b** was also tested in the more challenging Suzuki coupling with aryl chlorides (Scheme 2). Treatment of phenylboronic acid (**8**) with *m*-chlorobenzonitrile (**11a**) under conditions C (Table 3) afforded 3-cyanobiphenyl (**12a**)^[21] but a complete conversion could not be achieved after one day. Conversions of **11a** were determined by GLC at two reaction times (7 and 24 h) for each of the five consecutive runs. In this case, a significant decrease of conversion upon recycling was observed, prolonged reaction times being not useful. When conditions C were adopted with catalyst **7a** for the reaction of phenylboronic acid (**8**) with chlorobenzene (**11b**) to yield **12b**, a modest conversion of 36% (GLC) was obtained after 6 h. Heating at higher temperature (150 °C) with the same base and solvent system did not improve very much the result (42% conversion after 6 h). However, our results are even better than those previously reported,^[16] where the recycling was performed with an activated aryl chloride, *p*-chloroacetophenone, at higher temperature (130 °C) and higher amount of Pd (4.4%) in H₂O and K₂CO₃ as base, with decreasing activities of the recovered catalyst, as only modest yields were obtained from the second run even on increasing the reaction times from 3 to 14 h.

Next we performed the Heck reaction between *p*-bromoacetophenone (**9a**) and *n*-butyl acrylate (**13**) to give 4-acetyl-*trans*-cinnamic acid butyl ester (**14**) (Scheme 3). Three different bases (tributylamine, sodium acetate and potassium carbonate) were tested



Scheme 3. Heck reactions tested with catalysts **7a–c**.

Table 4. Heck reactions between **9a** and **13** with catalysts **7a–c** giving rise to **14** (Scheme 3).

Run	Conditions A ^[a] 7b		Conditions B ^[b] 7b		Conditions C ^[c] 7a	
	<i>t</i> [h]	Conversion [%] ^[d]	<i>t</i> [h]	Conversion [%] ^[e]	<i>t</i> [h]	Conversion [%] ^[e]
1	1	100	1	100	1	100
2	1	49	1	16	1	16
3	1	48	1	12	1	10
4	1	47	1	8	1	5
5	1 (7)	50 (95)	1	0	1	0

[a] 0.2% molar of Pd, [ArX]=0.5 M, *n*-butyl acrylate (1.5 equiv.), NBU₃ (1.5 equiv.), DMF, 150 °C.

[b] 0.2% molar of Pd, [ArX]=0.5 M, *n*-butyl acrylate (1.5 equiv.), NaOAc (1.5 equiv.), DMF, 150 °C.

[c] 0.2% molar of Pd, [ArX]=0.5 M, *n*-butyl acrylate (1.5 equiv.), K₂CO₃ (1.5 equiv.), DMF, 150 °C.

[d] GLC conversions (undecane as internal standard).

[e] ¹H NMR conversions.

in dimethylformamide at 150 °C (conditions A, B and C in Table 4). In all cases a fast reaction took place on the first cycle (complete conversion of **9a** after one hour), but very significant differences were observed on subsequent runs with the same batch of material. When the organic base tributylamine was used, the conversion is maintained around 50% in cycles 2 to 5 for the same reaction time (1 h). Thus, it seems that another catalytic species is formed after the first cycle, which would react slower while maintaining the recyclability properties. Upon prolonged reactions times (7 h), an almost complete conversion is achieved on the fifth cycle (95%). On the contrary, the recovered material after the first cycle under conditions B and C exhibits a poor recyclability, a fast decrease in conversion being obtained from runs 2 to 5. We made another important observation that can explain these differences on the catalyst behaviour. The solid recovered under conditions A was grey-black and contained palladium nanoparticles (15.1 ± 2.6 nm), whereas the material recovered under conditions B and C maintained the pale yellow initial colour and nanoparticles were not observed. In Figure 4 we show an example of HR-TEM micrographs of one of the samples (material **7b** after the first cycle, conditions A of Table 4), the ED image (*d*-spacings=0.226, 0.197, 0.139, 0.119 nm) and the size distribution of the particles. From the HR-TEM micrographs we could clearly see that the nanoparticles were not well spread inside the silica matrix but agglomerated on the external surface of the material. The stabilizer must be in this case the tributylammonium bromide formed in the Heck reaction. Indeed, the stabilization of palladium nanoparticles by ammonium salts is well documented in the literature.^[22] As this salt is not formed when sodium acetate and potassium carbonate are used as bases, this can explain the unsuccessful recycling found for conditions B and C. Probably most of the palladium is not retained onto the silica material after the first cycle. A test for Pd leaching was also performed under conditions A.

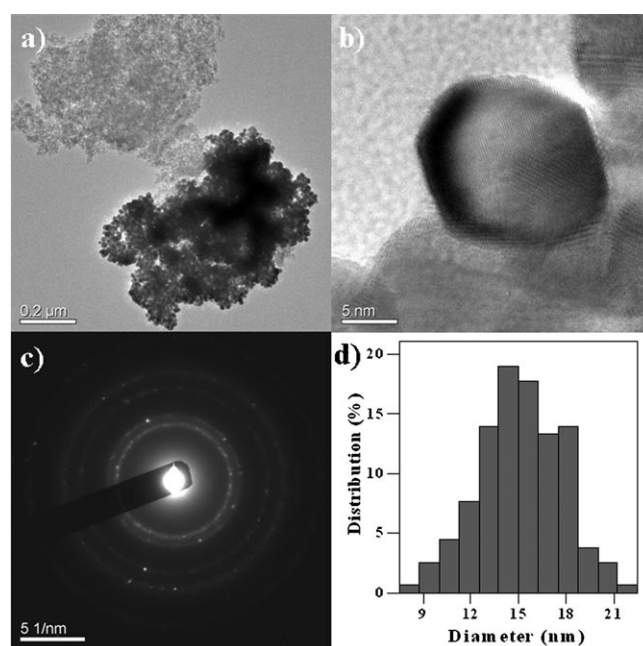


Figure 4. a) and b) HR-TEM micrographs of Pd nanoparticles formed in the Heck reaction (conditions A of Table 4); c) ED image; d) particle size distribution (158 particles; mean particle size: 15.1 ± 2.6 nm).

By filtration of the hot mixture after 20 min of reaction (26% GLC conversion) and heating again the filtrate at 150 °C for 15 h a 100% conversion of **9a** was achieved, showing that an homogeneous pathway is, in part, responsible of the reaction. The corresponding aryl chloride **9b** failed to react with **13** under conditions A.

Nájera^[16] used water as solvent at 100 °C in the presence of diisopropylamine as base and added TBAB for Heck recycling with the organic polymeric version of the palladium catalyst and increasing reaction times were required in successive cycles for full conversion (6 h in first cycle, 22 h from the second cycle). With our silica-anchored palladium complex

the use of organic solvent at higher temperature instead of water was advantageous, but in our hands, an organic base was also the best choice for good recyclability and the activity of the catalyst decreased also from the first to the second cycle and it was maintained in successive runs.

The hybrid material **7b** was assayed as catalyst in the Sonogashira reaction between phenylacetylene (**15**) and aryl halides **9a**, **b** and **17** to afford disubstituted acetylenes **16** and **18** (Scheme 4). After a screening of some bases and solvents (pyrrolidine, NMP, 110 °C, 4 h, 50% conversion; Bu₄NOAc, NMP, 110 °C, 1 h, 93% conversion on the first run and 86% on the second run; K₂CO₃, DMF/H₂O 95:5, 110 °C, 5 h, 74%; Bu₄NOAc, EtOH, 100 °C, 6 h, 25%; K₂CO₃, Bu₄NBr, DMF, 110 °C, 5 h, 77%; Bu₄NOAc, CH₃CN, 100 °C, 1.5 h, 89%; NaOAc, DMF, 110 °C, 1 h, 70%; KF, DMF, 110 °C, 3 h, 70%) on the reaction with the bromide **9a**, the conditions A of Table 5 were adopted (tetrabutylammonium acetate as base, dimethylformamide, 110 °C). Under these conditions *p*-bromoacetophenone (**9a**) and *p*-iodoanisole (**17**) underwent a fast reaction to give full conversion to 1-(4-acetylphenyl)-2-phenylacetylene (**16**) and 1-(4-methoxyphenyl)-2-phenylacetylene (**18**) in 1.5 and 0.5 h, respectively. However, the recycling was best accomplished with the bromide **9a** as shown in Table 5. The iodide **17** seemed to have some deleterious effect on the activity of the recovered catalyst and a significant decrease of conversion was observed in successive runs. Nonetheless, the *p*-chloroacetophenone (**9b**) did not react with **15** in an appreciable extent under prolonged heating in analogous conditions. The Nájera group's^[16] choice for the Sonogashira coupling with the supported catalyst was again refluxing water, with an organic base such as pyrrolidine and the addition of TBAB. In our hands, an organic solvent such as DMF was superior for the silica anchored complex and our results are comparable with theirs, if we take into account that they described increasing reaction times in successive cycles to maintain the conversion.

It is worthwhile to notice that the recovered catalytic material **7b** of the Sonogashira reactions did not

Table 5. Sonogashira reactions between **15** and the aryl halides **9a** and **17** with catalyst **7b** giving rise to **16** and **18** (Scheme 4).

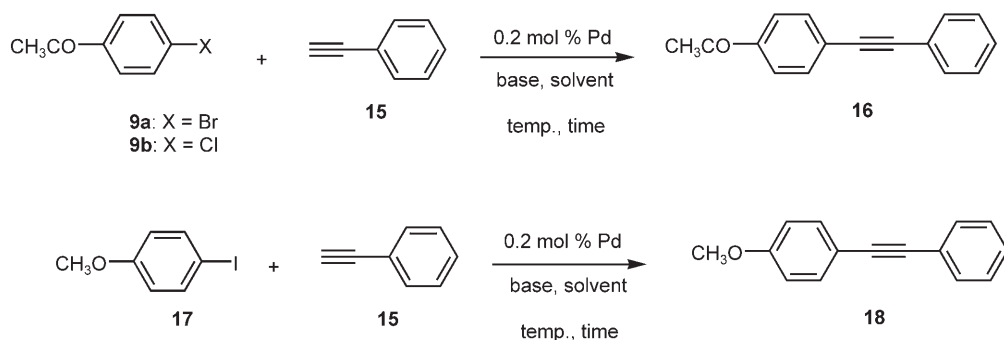
Run	Conditions A ^[a] 17 to 18		Conditions A ^[a] 9a to 16	
	<i>t</i> [h]	Conversion [%] ^[b]	<i>t</i> [h]	Conversion [%] ^[b]
1	0.5	100	1.5	100
2	0.5	68	1.5	96
3	0.5	50	1.5	92
4	0.5	48	1.5	92
5	0.5	43	1.5	85

^[a] 0.2% molar of Pd, [ArX]=0.5 M, **15** (1.5 equiv.), Bu₄NOAc (1.5 equiv.), DMF, 110 °C.

^[b] GLC conversions (undecane as internal standard).

contain nanoparticles and it did not darken on successive cycles. In this case, contrary to what we have previously observed in Suzuki and Heck reactions, the formation of nanoparticles is not required for good recycling. As a consequence, the real catalytic species formed from the bipyridyl-type palladium complex and which are responsible for the catalysis should be different in every reaction studied. The infrared spectra on the region of 30–700 cm⁻¹ of the silylated monomer **2a**, the material **7a** before the catalysis and the same material after Sonogashira and Suzuki reactions are summarized in Figure 5. The infrared vibrations for the Pd–Cl bond appear^[23] in the range 350–330 cm⁻¹ and the less intense vibrations for the Pd–N bond are in the range 530–430 cm⁻¹. The absorptions at *ca.* 336 cm⁻¹ of complex **2a** and at *ca.* 338 cm⁻¹ of material **7a** should be attributed to vibrations of Pd–Cl bond (Figure 5, a). The IR spectrum of recovered material **7a** after Sonogashira reaction is more similar to that of the original **7a** before catalysis (Figure 5, b) than to the IR spectrum of recovered **7a** after Suzuki reaction (Figure 5, c), in accordance with the fact that palladium(0) nanoparticles are formed in the Suzuki process but not in the Sonogashira reaction.

A test for Pd leaching was also performed for the Sonogashira reaction between **9a** and **15** (conditions A of Table 5). By filtration of the hot mixture after



Scheme 4. Sonogashira reactions tested with catalysts **7a–c**.

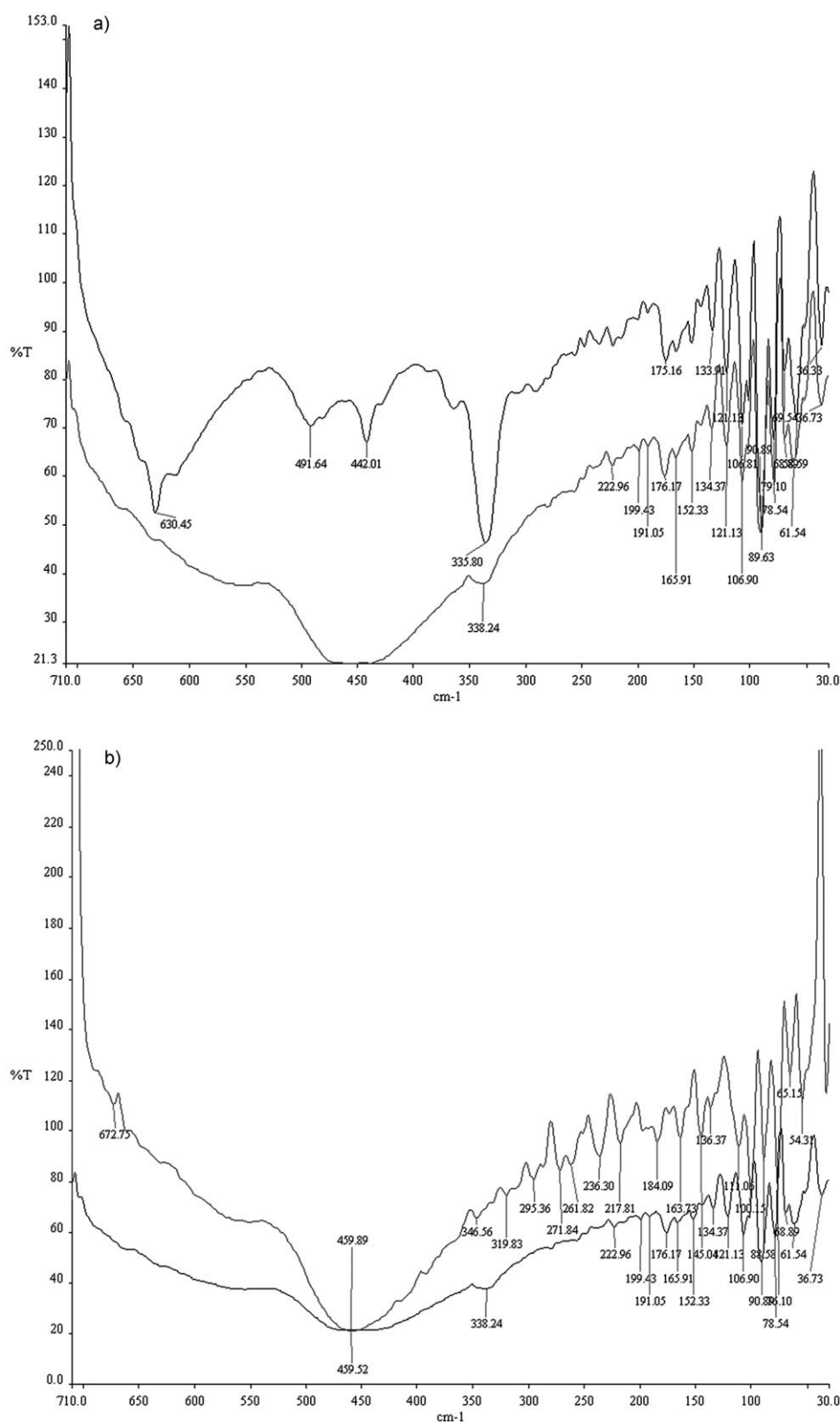
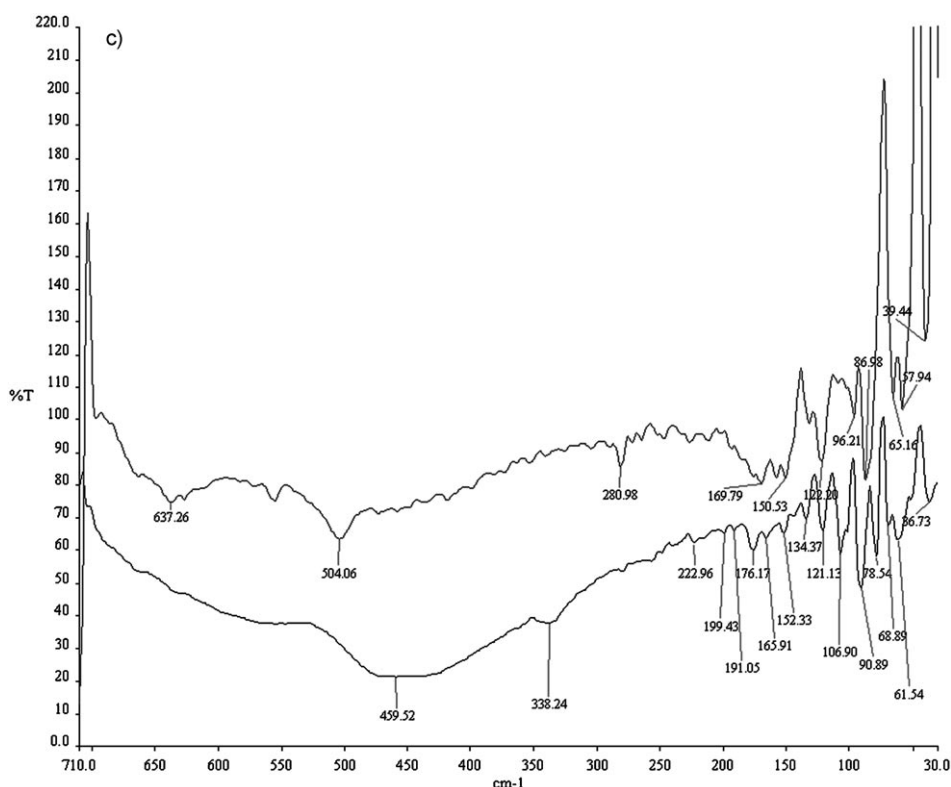


Figure 5. a) IR spectra (30–700 cm⁻¹) of monomeric complex **2a** (upper trace) and polymeric complex **7a** (lower trace). b) IR spectra (30–700 cm⁻¹) of recovered material **7a** after Sonogashira reaction (upper trace) and **7a** before catalysis (lower trace). c) IR spectra (30–700 cm⁻¹) of recovered material **7a** after Suzuki reaction (upper trace) and **7a** before catalysis (lower trace).



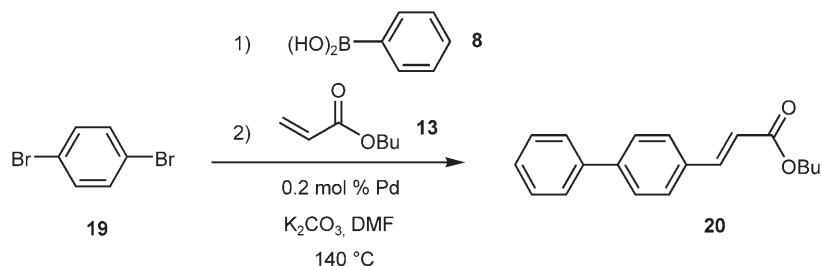
20 min of reaction (49% GLC conversion) and heating again the filtrate at 110°C a 95% GC conversion of **9a** was obtained after 6 h, showing that a homogeneous pathway is, in part, responsible of the reaction. Some soluble catalytic palladium species should have been formed, but as the reaction was slower, a heterogeneous pathway should also participate in the catalytic process.

Finally, a two-step tandem Suzuki–Heck process was also undertaken with catalyst **7b** on *p*-dibromobenzene (**19**) by sequential treatment with phenylboronic acid (**8**) and *n*-butyl acrylate (**13**) in dimethylformamide at 140°C in the presence of potassium carbonate as base (Scheme 5). The 4-phenyl-*trans*-cinnamic acid *n*-butyl ester (**20**) was obtained in a clean and efficient one-pot process in 97% isolated yield.

The products resulting from the catalytic processes were checked by GC and characterized by NMR (pu-

urities by GC: 100% for compound **10**, 97% for compound **14**, 97% for compound **16**, 96% for compound **18** and 94% for compound **20**). The analytical or spectroscopic data were coincident with that reported in the literature (see supporting information for NMR spectra of **10**, **14**, **16**, **18** and **20**).

Some reports are available in the recent literature about the use of silica anchored palladium(II) or Pd(0) complexes in Suzuki,^[8,17,24] Heck^[24b,f,k,i,o,r,s,25] and Sonogashira^[25w,26] coupling reactions. Many of these works deal with the use of aryl iodides as substrates and do not report the recycling in Sonogashira reactions with aryl bromides. Wang^[26c] had described the Sonogashira coupling of terminal alkynes with aryl iodides and bromides in the presence of a recoverable 3-(2-aminoethylamino)propyl-functionalized silica-gel immobilized palladium(II) catalyst. They claim a very efficient recycling of the silica-supported palladium,



Scheme 5. Tandem Suzuki–Heck coupling process with catalyst **7b**.

but the text is general and ambiguous and it is not clear if it refers to aryl iodides or also to aryl bromides. Efficient recovery and reuse with aryl chlorides in Suzuki coupling has only been achieved in few cases^[24d,e,l] for oxime palladacycles and N-heterocyclic carbenes anchored to the silica matrix. In the case of Heck reactions, although some examples involving aryl iodides and bromides have been found, only few of them report the recycling with the more challenging aryl bromides.^[24f,s,25e,j,m,r,t] Even if phosphane ligands are more prone to oxidation, there are some examples of heterogeneous phosphane-containing catalysts. Thus, silica sol-gel entrapped dichlorobis(tri-phenylphosphane)palladium worked out^[27] as an efficient recyclable catalyst in Heck reactions^[27a] and Suzuki cross-couplings^[27b]. However, this system failed with aryl chlorides in the Suzuki coupling and low conversions were attained with aryl bromides in the Heck reaction. Our heterogeneous catalysts **7a–c** are competitive compared with the other silica-anchored systems in terms of performance and reusability, giving faster reactions, and only oxime palladacycles^[24d,e] and N-heterocyclic carbenes^[24l] remain superior.

Conclusions

In summary, we have described the synthesis of hybrid silica materials with covalently attached di-(2-pyridyl)methylamine-palladium dichloride complex by sol-gel methodology and their use as efficient and recoverable catalysts for carbon-carbon bond formation reactions. They were very active in the Suzuki cross-coupling of phenylboronic acid with *p*-bromoacetophenone, being efficiently reused for up to ten cycles with no decrease of activity. The reaction has also been performed with *m*-chlorobenzonitrile, although the activity and recyclability were lower, five consecutive runs with decreasing activities being achieved. The Heck reaction between *p*-bromoacetophenone and *n*-butyl acrylate was very effective with these supported catalysts. The catalytic system was recyclable (five runs) when tributylamine was used as base. Suitable conditions were found for very fast copper- and phosphine-free Sonogashira couplings between phenylacetylene and aryl bromides and iodides. The recyclability of the catalyst (five runs) was much better for *p*-bromoacetophenone than for *p*-iodoanisole. A clean one-pot two-step Suzuki–Heck process between *p*-dibromobenzene, phenylboronic acid and *n*-butyl acrylate has been successfully carried out. Hot filtration tests performed with all these coupling reactions showed that both homogeneous and heterogeneous pathways participate in the catalysis. Nonetheless, our systems show excellent performance and good reusability, giving fast reactions with low amounts of

palladium. Formation of fcc Pd(0) nanoparticles during the Suzuki and Heck reactions has been shown by HR-TEM and ED. In the Sonogashira coupling the formation of nanoparticles was not observed.

Experimental Section

General Remarks

When required, experiments were carried out with standard high vacuum and Schlenk techniques. Solvents were dried and distilled just before use. Ammonium fluoride was purchased from Aldrich, 3-(triethoxysilyl)propyl isocyanate was purchased from Lancaster, tetraethyl orthosilicate, was purchased from Acros. IR data were obtained in the following spectrophotometers: Bruker Tensor 27 with ATR Golden Gate and Perkin–Elmer (System 2000 FT-IR). The CP-MAS ²⁹Si solid state NMR spectra were recorded on a Bruker FT-AM 400. The repetition time was 5 seconds with contact times of 5 milliseconds. Surface areas were determined by the Brunauer–Emmett–Teller (BET) method on a Micromeritics Tristar 3000 analyzer, and the average pore diameter was calculated by the BJH method. Elemental analysis have been performed at the Serveis Científic-Tècnics of the Universitat de Barcelona. The content of palladium was determined at the Serveis Científic-Tècnics of the Universitat de Barcelona by inductively coupled plasma (ICP). Transmission electron microscopy (TEM) observations by using ultramicrotomy techniques were carried out in Montpellier with a JEOL 1200 EXII (100 kV). High resolution transmission electron microscopy (HR-TEM) observations were carried out at “Servei de Microscòpia de la UAB” with a JEOL JEM 2010 (200 kV).

Oxime **4**^[18,28] and amine **5**^[18] were prepared as previously described.^[18]

Synthesis of *N*-(Di-2-pyridylmethyl)-*N'*-(3-(triethoxysilyl)propyl)urea (**6**)

Freshly distilled (3-triethoxysilyl)propyl isocyanate (565 μ L, 0.559 g, 2.26 mmol) was added at room temperature under an argon atmosphere to a stirred solution of freshly prepared amine **5** (0.419 g, 2.26 mmol) in anhydrous dichloromethane (2 mL). The reaction mixture was stirred at room temperature overnight, the solvent was evaporated and the white solid residue was thoroughly washed with anhydrous pentane and dried under vacuum to afford pure **6**^[17] yield: 0.829 g (85%); mp 113–114 °C; ¹H NMR (CDCl₃, 250 MHz): δ = 0.52–0.59 (m, 2H), 1.18 (t, *J* = 7.0 Hz, 9H), 1.54 (m, 2H), 3.14 (m, 2H), 3.76 (q, *J* = 7.0 Hz, 6H), 5.11 (br t, *J* = 5.6 Hz, 1H), 6.07 (d, *J* = 6.6 Hz, 1H), 6.91 (d, *J* = 6.6 Hz, 1H), 7.10 (ddd, *J* = 7.5, 4.9 and 1.1 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.58 (td, *J* = 7.7 and 1.8 Hz, 2H), 8.46 (d, *J* = 4.9 Hz, 2H); ¹³C NMR (CDCl₃), 62.5 MHz): δ = 7.9, 18.6, 23.8, 43.3, 58.6, 60.4, 122.5, 122.6, 137.1, 149.2, 157.9, 160.2; IR (ATR): ν = 3353, 3281, 2973, 2875, 1626, 1561, 1076, 950, 758 cm^{−1}; anal. calcd. (%) for C₂₁H₃₂N₄SiO₄: C 58.31, H 7.46, N 12.95, Si 6.49; found: C 57.43, H 8.52, N 12.93, Si 6.43.

Synthesis of the Palladium(II) Complex 2a

A stirred mixture of **6** (0.199 g, 0.46 mmol), PdCl₂(CH₃CN)₂ (0.119 g, 0.46 mmol) and anhydrous toluene (5 mL) was heated at 80–90 °C under argon overnight. The solvent was evaporated affording **2a**^[17] as a pale yellow solid; yield: 0.230 g (82%); ¹H NMR (CD₃SOCD₃, 250 MHz, 329 K): δ = 0.52–0.70 (m, 2H), 1.17 (t, *J* = 7.0 Hz, 9H), 1.43–1.67 (m, 2H), 3.12–3.24 (m, 2H), 3.77 (q, *J* = 7.0 Hz, 6H), 6.30–6.52 (m, 1H), 7.09–7.28 (m, 1H), 7.55 (t, *J* = 6.5 Hz, 2H), 7.66–7.96 (m, 3H), 8.03–8.24 (m, 2H), 8.83–9.00 (m, 2H); IR (ATR): ν = 3331, 3109, 2973, 2882, 1630, 1563, 1471, 1070, 953, 764 cm⁻¹; anal. calcd. (%) for C₂₁H₃₂N₄SiCl₂O₄Pd: C 41.35, H 5.29, N 9.19, Si 4.60, Pd 17.45; found: C 41.25, H 5.43, N 9.10, Si 4.46, Pd (ICP) 16.52.

Synthesis of Materials 7a, 7b and 7c; Typical Procedure

A solution of ammonium fluoride (168 mL of a 1 M solution, 0.168 mmol of fluoride, 9.33 mmol of water), anhydrous DMF (6.8 mL) and distilled and deionized water (1035 mL, 57.5 mmol) were added to a solution of **2a** (0.252 g, 0.413 mmol) and TEOS (3.489 g, 16.4 mmol) in anhydrous DMF (10 mL). The mixture was stirred manually for a minute to get an homogeneous solution and was left at room temperature without stirring. Gelation occurred after 2 h and the gel was allowed to age for 3 days, after which it was powdered and washed successively twice with water and 3 times with ethanol. The solid was dried under vacuum overnight (2 mm Hg, 60 °C), affording **7c** as a yellow powder; yield: 1.274 g; IR (KBr): ν = 3447, 1655, 1564, 1079, 959, 799, 459 cm⁻¹; anal. (%) found: C 8.38, H 1.24, N 1.86, Si 35.00, Pd (ICP) 2.63.

Materials **7a** and **b** were obtained in a similar manner except for the molar ratio **2a**:TEOS. Material **7a**: Anal. (%) found: C 11.77, H 1.90, N 4.43, Si 26.82, Pd (ICP) 6.05. Material **7b**: Anal. (%) found: C 10.32, H 1.24, N 2.66, Si 29.51, Pd (ICP) 3.88.

Synthesis of 10 by Suzuki Reaction between 8 and 9a with Catalyst 7b under Conditions C of Table 2; Typical Procedure

Potassium carbonate (1.935 g, 14 mmol) was added to a stirred mixture of **7b** (0.0384 g, 0.014 mmol of Pd), 4-bromoacetophenone **9a** (1.422 g, 7 mmol), and phenylboronic acid **8** (1.306 g, 10.5 mmol) in DMF/H₂O (95:5) (14 mL) and heated at 110 °C for 45 min (GLC monitoring). Product **10** precipitated by addition of water to the crude mixture. The filtered solid was washed with water and then it was taken in ethyl acetate. Insoluble **7b** was filtered. The filtrate was dried with anhydrous sodium sulphate and the solvent was evaporated to give pure **10** (100% by GC); yield: 1.374 g (100%); mp 120–121 °C (lit.^[29] mp 120.5 °C); ¹H NMR (CDCl₃, 250 MHz): δ = 2.65 (s, 3H), 7.40–7.51 (m, 3H), 7.63 (d, 2H, *J* = 6.7 Hz), 7.69 (d, 2H, *J* = 8.4 Hz), 8.04 (d, 2H, *J* = 8.4 Hz); IR (ATR): ν = 3067, 2994, 1674, 1594, 1357, 1257, 955, 835, 761 cm⁻¹. The catalyst **7b** was washed successively with water, ethanol and diethyl ether, it was dried under vacuum (2 mm Hg) and reused in the next run.

Synthesis of 14 by Heck Reaction between 9a and 13 with Catalyst 7b under Conditions A of Table 4; Typical Procedure

Tributylamine (1075 μL, 0.776 g mL⁻¹, 4.5 mmol) was added to a stirred mixture of **7b** (0.0164 g, 0.006 mmol Pd), 4-bromoacetophenone **9a** (0.6093 g, 3 mmol) and *n*-butyl acrylate **13** (655 μL, 0.890 g mL⁻¹, 4.5 mmol) in DMF (6 mL) and it was heated at 150 °C for 60 min (GLC monitoring). Insoluble **7b** was filtered, washed with water, ethanol and diethyl ether, it was dried under vacuum (2 mm Hg) and reused in the next run (0.0160 g of recovered catalyst). The product was extracted from the filtrate with ethyl acetate, and the organic phase was washed with water. The organic layer was dried with anhydrous Na₂SO₄ and the solvent was evaporated to give pure (97% by GC) 4-acetyl-*trans*-cinnamic acid *n*-butyl ester **14**^[30] as an oil; yield: 0.736 g (100%). ¹H NMR (CDCl₃, 250 MHz): δ = 0.96 (t, 3H, *J* = 7.3 Hz), 1.36–1.51 (m, 2H), 1.63–1.74 (m, 2H), 2.61 (s, 3H), 4.22 (t, 2H, *J* = 6.6 Hz), 6.52 (d, 1H, *J* = 16.0 Hz), 7.60 (d, 2H, *J* = 8.3 Hz), 7.68 (d, 1H, *J* = 16.0 Hz), 7.96 (d, 2H, *J* = 8.3 Hz); ¹³C NMR (CDCl₃, 62.5 MHz): δ = 13.9, 19.4, 26.8, 30.9, 64.8, 121.0, 128.3, 129.0, 138.2, 139.0, 143.1, 166.7, 197.4.

Synthesis of 16 by Sonogashira Reaction between 9a and 15 with Catalyst 7b under Conditions A of Table 5

Phenylacetylene **15** (505 μL, 0.930 g mL⁻¹, 4.5 mmol) was added to a stirred mixture of **7b** (0.0164 g, 0.006 mmol Pd), 4-bromoacetophenone **9a** (0.6093 g, 3 mmol) and Bu₄NOAc (1.398 g, 4.5 mmol) in DMF (6 mL) and heated at 110 °C for 90 min (GLC monitoring). Insoluble **7b** was filtered, washed with water, ethanol and diethyl ether, it was dried under vacuum (2 mm Hg) and reused in the next run (0.0156 g of recovered catalyst). The product was extracted from the filtrate with ethyl acetate, and the organic phase was washed with water. The organic layer was dried with anhydrous Na₂SO₄ and the solvent was evaporated to give pure (97% by GC) 1-(4-acetylphenyl)-2-phenylacetylene **16**^[31] yield: 0.6463 g (98%); mp 94–96 °C (lit.^[31b] mp 94–96 °C); ¹H NMR (CDCl₃, 250 MHz): δ = 2.61 (s, 3H), 7.34–7.38 (m, 3H), 7.53–7.56 (m, 2H), 7.60 (d, 2H, *J* = 8.6 Hz), 7.94 (d, 2H, *J* = 8.6 Hz); ¹³C NMR (CDCl₃, 62.5 MHz): δ = 26.9, 88.9, 93.0, 123.0, 128.5, 128.6, 128.7, 129.1, 131.99, 132.04, 136.5, 197.6.

Synthesis of 18 by Sonogashira Reaction between 17 and 15 with Catalyst 7b under Conditions A of Table 5

Phenylacetylene **15** (505 μL, 0.930 g mL⁻¹, 4.5 mmol) was added to a stirred mixture of **7b** (0.0164 g, 0.006 mmol Pd), 4-iodoanisole **17** (0.7092 g, 3 mmol) and Bu₄NOAc (1.398 g, 4.5 mmol) in DMF (6 mL) and it was heated at 110 °C for 30 min (GLC monitoring). Insoluble **7b** was filtered, washed with water, ethanol and diethyl ether, it was dried under vacuum (2 mm Hg) and reused in the next run (0.0149 g of recovered catalyst). The product was extracted from the filtrate with ethyl acetate, and the organic phase was washed with water. The organic layer was dried with anhydrous Na₂SO₄ and the solvent was evaporated to give pure (96% by GC) 1-(4-methoxyphenyl)-2-phenylacetylene **18**^[15a]

yield: 0.605 g (97%); mp 50–53 °C (lit.^[15a] mp 51–53 °C); ¹H NMR (CDCl₃, 250 MHz): δ = 3.82 (s, 3H), 6.87 (d, 2H, *J* = 9 Hz), 7.32–7.35 (m, 3H), 7.45–7.52 (m, 4H); ¹³C NMR (CDCl₃, 62.5 MHz): δ = 55.6, 88.4, 89.7, 114.3, 115.7, 123.9, 128.2, 128.6, 131.8, 133.4, 159.9.

Synthesis of 20 by a Tandem Suzuki–Heck Process from *p*-Dibromobenzene (19)

A stirred mixture of 1,4-dibromobenzene **19** (0.9629 g, 4 mmol), phenylboronic acid **8** (0.4977 g, 4 mmol), K₂CO₃ (1.658 g, 12 mmol) and **7b** (0.0141 g, 0.008 mmol Pd) in DMF (8 mL) was heated at 140 °C for one day (GLC monitoring). *n*-Butyl acrylate **13** (875 μL, 0.890 g mL⁻¹, 6 mmol) was added. After one more day of heating at the same temperature, **7b** was filtered off and washed with water, ethanol and chloroform. The product was extracted from the filtrate with ethyl acetate, and the organic phase was washed with water. The organic layer was dried with anhydrous Na₂SO₄ and the solvent was evaporated to give 4-phenyl-*trans*-cinnamic acid *n*-butyl ester **20**,^[30a] yield: 1.0845 g (97%) (94% by GC); ¹H NMR (CDCl₃, 250 MHz): δ = 0.98 (t, 3H, *J* = 7.3 Hz), 1.38–1.53 (m, 2H), 1.65–1.76 (m, 2H), 4.23 (t, 2H, *J* = 6.6 Hz), 6.48 (d, 1H, *J* = 16.0 Hz), 7.34–7.40 (m, 1H), 7.43–7.49 (m, 2H), 7.60–7.63 (m, 6H), 7.72 (d, 1H, *J* = 16.0 Hz); ¹³C NMR (CDCl₃, 62.5 MHz): δ = 14.1, 19.5, 31.1, 64.8, 118.5, 127.3, 127.8, 128.2, 128.9, 129.2, 133.8, 140.5, 143.3, 144.4, 167.5.

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