



# The first synthesis of stable palladium(II) PCP-type catalysts supported on silica—application to the Heck reaction

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## Abstract

An efficient method for the formation of a silica-immobilized tridentate diphosphinoaryl ligand (PCP-type) palladium(II) complex (**11**) is described and successfully used as a catalyst for the Heck reaction. Commercially available 5-amino-isophthalic acid dimethyl ester was converted to *N*-acetyl-3,5-bis(chloromethyl)aniline (**4**) in three steps, by reduction, acetylation, and chlorination (Scheme 1). Arbuzov reaction of **4** led to the diphosphine oxide (**5**). Deprotection and functional group manipulations allowed the transformation of **5** into *N*-[3,5-bis-(diphenyl-phosphino)ylmethyl]-phenyl-succinamic acid (**7**). Subsequent reduction of **7** with  $\text{HSiCl}_3$  afforded the diphosphine (**8**) attached to silica by transforming compound **8** to *N*-{3,5-bis[(diphenyl-phosphanyl)methyl]-phenyl}-succinamic acid 2,5-dioxo-pyrrolidin-1-yl ester (**9**). Palladium(II) trifluoroacetate was used to form the PCP-type palladium(II) complex. This complex shows high catalytic activity in the Heck reaction for aryl iodides, and it is also active with aryl bromides. The catalyst is thermally stable and it is also stable towards oxygen and moisture. In addition, it can be recycled by simple filtration in air and reused with moderate loss of activity. © 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** PCP-type Pd(II) catalysts; Heck reaction; Silica-immobilized catalysts

## 1. Introduction

Homogeneous catalysis is widely used in organic chemistry as the pre-catalysts are usually commercially available and well defined [1,2], and some catalysts exhibit high selectivity and activity [3–5], although product separation and especially catalyst recovery can be difficult. On the other hand, heterogeneous catalysts can be easily separated and recycled [6], thus making some processes more economical, and environmentally friendly. Immobilization of the homogeneous catalyst by means of a heterogeneous

support can, in principle, retain the properties observed for the homogeneous system and allow simple separation from the reaction mixture.

The Heck reaction is an important method for C–C bond formation [7,8]. However, this reaction usually requires quite high catalyst loading (up to 10 mol% of Pd). Recently, supported catalysts, including dendrimers, have displayed to be very useful in organic synthesis [9,10]. It was also shown that palladium complexed dendrimers immobilized on silica are good catalysts for the Heck reaction [11]. It has also been reported that palladium complexes with pincer ligands are excellent catalysts for the Heck reaction [5,12–14]. Compound **1** (Fig. 1), prepared by direct cyclometallation, has been shown to be a highly active catalyst for the Heck reaction. It is also thermally stable

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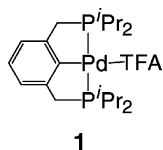


Fig. 1. Complex 1.

up to 180 °C and not sensitive to oxygen and moisture [5]. Furthermore, it was reported that when the alkyl substituents on phosphorus were substituted for the weakly electron-withdrawing phenyl groups, direct cyclometallation could proceed at room temperature [15].

In this paper, we report the successful immobilization of a PCP-type palladium(II) complex onto silica under mild conditions; an approach that combines the advantages of heterogeneous and homogeneous catalysts. This complex is a good catalyst for the Heck reaction and can easily be recycled. It is also thermally stable up to 170 °C and quite air stable.

## 2. Experimental

### 2.1. General

All manipulations of air-sensitive materials were carried out using standard Schlenk techniques. Solvents were appropriately dried and distilled before use. All other reagents and *N*-methyl-pyrrolidinone (NMP) were obtained from commercial sources and were used without further purification. 3,5-bis(Hydroxymethyl)aniline (**2**) [16], *N*-acetyl-3,5-bis(hydroxymethyl)aniline (**3**) [17], and *N*-acetyl-3,5-bis(chloromethyl)aniline (**4**) [17] were prepared by literature procedures.

Solution NMR spectra were recorded at 20.5 °C, unless otherwise indicated, on a Varian Gemini-200 (<sup>1</sup>H at 199.97 MHz and <sup>13</sup>C{<sup>1</sup>H} at 50.28 MHz) or a Bruker 300 NMR spectrometer (<sup>1</sup>H at 300.13 MHz, <sup>13</sup>C{<sup>1</sup>H} at 75.48 MHz and <sup>31</sup>P{<sup>1</sup>H} at 121.49 MHz). The <sup>13</sup>C and <sup>31</sup>P CP/MAS (cross-polarization/magic angle spinning) NMR spectra, frequency 50.32 and 81.00 MHz, respectively, were recorded on a Bruker ASX-200 spectrometer. Solid samples were prepared by transfer of the relevant material to a 5 mm o.d. pyrex NMR tube and connected to a high vacuum

stopcock in an M. Braun GmbH glovebox. The sample was then removed from the drybox, placed under high vacuum and, without breaking vacuum, sealed off at 30 mm lengths. The tubes were then placed in zirconia rotors that were used in the Bruker ASX-200 instrument.

### 2.2. Procedure

#### 2.2.1. Synthesis of *N*-[3,5-bis-(diphenyl-phosphino)ethyl]-phenyl]-acetamide (**5**)

A modified literature procedure was used [18] In a two-necked 100-ml round bottom flask, a stirred suspension of Ph<sub>2</sub>POEt (7.4 g, 32 mmol) and compound **4** (1.8 g, 8.0 mmol) in toluene (90 ml) was refluxed for 20 h. The reaction mixture was cooled to room temperature and the white precipitated solid was filtered, washed with benzene, and dried in vacuo to afford compound **5** as a white solid, which was sufficiently pure for further synthesis. Yield: 4.4 g (90%). <sup>1</sup>H NMR (300.13 MHz, CD<sub>3</sub>OD) δ (ppm) 7.78–7.48 (m, 20H, ArH), 7.21 (s, 2H, ArH), 6.73 (s, 1H, ArH), 3.71 (d, *J* = 14 Hz, 4H, PhCH<sub>2</sub>), 2.02 (s, 3H, CH<sub>3</sub>C=O); <sup>13</sup>C{<sup>1</sup>H} (75.48 MHz, CD<sub>3</sub>OD) δ (ppm) 170.3 (C=O), 138.9, 132.4, 132.1, 132.0, 131.2, 131.1, 131.0, 129.0, 128.9, 128.8, 128.1, 120.5, (ArC), 37.1, 36.3, (PhCH<sub>2</sub>), 22.7 (CH<sub>3</sub>C=O); <sup>31</sup>P NMR (121 MHz, CD<sub>3</sub>OD) δ (ppm) 34.7; EI MS for C<sub>34</sub>H<sub>31</sub>NO<sub>3</sub>P<sub>2</sub> 563 (M<sup>+</sup>).

#### 2.2.2. Synthesis of 3,5-bis-(diphenyl-phosphino)ethyl]-phenylamine (**6**)

A modified literature procedure was used [17]. To a solution of **5** (4.2 g, 7.5 mmol) in 95% EtOH (100 ml) was added NaOH (1.5 g, 37.5 mmol). The mixture was refluxed for 48 h and the solution was cooled with an ice bath, neutralized with concentrated HCl, and the majority of the solvent was removed under reduced pressure. The remaining residue was filtered, washed with water, and dissolved in methanol. The solvent was removed under reduced pressure affording the compound **6** as a yellow solid, which was sufficiently pure for further synthesis. Yield: 3.1 g (80%). <sup>1</sup>H NMR (300.13 MHz, CD<sub>3</sub>OD) δ (ppm) 7.74–7.47 (m, 20H, ArH), 6.44 (s, 2H, ArH), 6.37 (s, 1H, ArH), 3.63 (d, *J* = 14 Hz, 4H, PhCH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} (50 MHz, CD<sub>3</sub>OD) δ (ppm) 137.3, 133.6, 133.5,

132.6, 132.5, 132.3, 131.2, 131.1, 131.0, 130.9, 129.1, 128.9, 120.6 (ArC), 36.8, 35.9, (PhCH<sub>2</sub>); <sup>31</sup>P NMR (121 MHz, CD<sub>3</sub>OD) δ (ppm) 34.4; Electrospray MS for C<sub>32</sub>H<sub>29</sub>NO<sub>2</sub>P<sub>2</sub> 522 (M + H<sup>+</sup>).

### 2.2.3. Synthesis of *N*-[3,5-bis-(diphenyl-phosphinoylmethyl)-phenyl]-succinamic acid (**7**)

A modified literature procedure was used [17]. To a suspension of **6** (3.1 g, 6.0 mmol) and triethylamine (3.0 g, 30.0 mmol) in THF (150 ml) was added succinic anhydride (0.7 g, 7.0 mmol). The mixture was refluxed for 48 h, cooled, and the solvent was removed under reduced pressure. The residue was dissolved in ethanol (120 ml) followed by addition of NaOH (8 M, 12 ml). The solvent was removed under reduced pressure, yielding an off-white solid material. This solid was washed with diethyl ether and then added to a 6N HCl aqueous solution (30 ml). The residue was filtered, washed with water, and then dissolved in methanol. The solvent was removed under reduced pressure, affording **7** as an off-white solid, which was sufficiently pure for subsequent reaction. Yield: 3.0 g (80%). <sup>1</sup>H NMR (300.13 MHz, CD<sub>3</sub>OD) δ (ppm) 7.74–7.48 (m, 20H, ArH), 7.20 (s, 2H, ArH), 6.72 (s, 1H, ArH), 3.71 (d, *J* = 13 Hz, 4H, PhCH<sub>2</sub>), 3.46 (m, 1H, NH), 2.65–2.50 (m, 4H, CH<sub>2</sub>C=O); <sup>13</sup>C{<sup>1</sup>H} (50 MHz, CD<sub>3</sub>OD) δ (ppm) 176.3, 172.5 (C=O), 140.0, 133.7, 133.4, 133.1, 132.9, 132.3, 132.1, 131.7, 130.0, 129.8, 128.9, 121.4 (ArC), 38.4, 37.1, (PhCH<sub>2</sub>), 32.3, 30.1 (CH<sub>2</sub>C=O); <sup>31</sup>P NMR (121 MHz, CD<sub>3</sub>OD) δ (ppm) 34.7; Electrospray MS for C<sub>36</sub>H<sub>33</sub>NO<sub>5</sub>P<sub>2</sub> 621 (M<sup>+</sup>).

### 2.2.4. Synthesis of *N*-{3,5-bis-[(diphenyl-phosphanyl)-methyl]-phenyl}-succinamic acid (**8**)

A modified literature procedure was used [18]. In a three-necked 500-ml round bottom flask, a suspension of **7** (1.6 g, 2.6 mmol) in 1,2-dichlorobenzene (90 ml) was refluxed at 180 °C until the solution became homogeneous. The reaction solution was then cooled to 140 °C and HSiCl<sub>3</sub> (5 ml, 49 mmol) was added dropwise. The reaction mixture was then stirred at 140 °C for 2 h. This solution was cooled to 0 °C, and an aqueous NaOH (4 M, 98 ml) was slowly added under vigorous stirring. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried (MgSO<sub>4</sub>), and then concentrated

in vacuo to ca. 2 ml. Hexane was slowly added to precipitate an off-white solid, which was filtered and washed with hexane several times. Yield: 1.1 g (72%). <sup>1</sup>H NMR (300.13 MHz, CD<sub>3</sub>OD) δ (ppm) 7.46–7.15 (m, 20H, ArH), 6.79 (s, 1H, ArH), 6.74 (s, 2H, ArH), 3.29 (s, 4H, PhCH<sub>2</sub>), 2.79 (s, 4H, CH<sub>2</sub>C=O); <sup>13</sup>C{<sup>1</sup>H} (75.48 MHz, CDCl<sub>3</sub>) δ (ppm) 175.0 (C=O), 139.0, 138.9, 138.8, 133.5, 133.2, 128.8, 128.7, 128.4, 128.1, 125.2 (ArC), 36.3, 36.1, (PhCH<sub>2</sub>), 28.1 (CH<sub>2</sub>C=O); <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ (ppm) –9.0; Electrospray MS for C<sub>36</sub>H<sub>33</sub>NO<sub>3</sub>P<sub>2</sub> 590 (M + H<sup>+</sup>).

### 2.2.5. Synthesis of compound **10**

A solution of **8** (1.0 g, 1.7 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.21 g, 1.7 mmol) in dichloromethane (20 ml) was added with 1,3-dicyclohexylcarbodiimide (DCC) (0.35 g, 1.7 mmol) in dichloromethane (1 ml) and *N*-hydroxysuccinimide (0.2 g, 1.7 mmol) at 0 °C. The mixture was stirred at room temperature for 18 h. The white solid was filtered and the solvent was removed under reduced pressure, affording compound **9** as a yellow solid. DMAP (0.21 g, 1.7 mmol) in dichloromethane (50 ml) and aminopropyl silica (0.5 g, 0.45 mmol) were added, the reaction was stirred at room temperature for 1 day and then heated at 45 °C for 4 days. The suspension was filtered, washed with dichloromethane several times, and dried in vacuo to afford **10** as a pale yellow solid. Yield: 0.6 g (78%). <sup>31</sup>P CP/MAS NMR δ (ppm) –10.5 (br s) and 31.1 (phosphine oxide); <sup>13</sup>C CP/MAS NMR δ (ppm) 172.1, 157.8, 140.7, 110.1, 41.5, 23.6, 10.7.

### 2.2.6. Synthesis of complex **11**

A suspension of compound **10** (0.6 g, 0.35 mmol), and Pd(TFA)<sub>2</sub> (0.06 g, 0.17 mmol) in THF (50 ml) was stirred at room temperature for 3 days. The suspension was filtered and washed with THF several times, dried in vacuo to afford complex **11** as a dark yellow solid. Yield: 0.6 g (94%). <sup>31</sup>P CP/MAS NMR δ (ppm) 37.9 (br s) and 28.7 (phosphine oxide); <sup>13</sup>C CP/MAS NMR 173.4, 156.9, 141.9, 130.3, 108.7, 50.6, 41.9, 33.5, 26.0, 11.2; ICP analysis mass% Pd 1.67.

## 2.3. General procedure for the Heck reactions

A solution of bromoarene (2 mmol) or iodoarene (12 mmol), olefin (2.4 mmol for bromoarene or

14.4 mmol for iodoarene), sodium carbonate (5 mmol for bromoarene or 30 mmol for iodoarene), and catalyst **11** (100 mg, 0.8 mol% for bromoarene or 25 mg, 0.03 mol% for iodoarene) in 10 ml of NMP for bromoarene, or 50 ml of NMP for iodoarene, was heated at 140 °C for 24 h (bromoarene) or 6 h (iodoarene) under nitrogen. After the reaction, the mixture was allowed to cool, and filtered to separate the catalyst from the liquid phase. The catalyst was washed several times with water and diethyl ether. The aqueous phase was extracted with diethyl ether several times and the combined organic phase was washed with saturated NaCl aqueous solution and water, and then dried (MgSO<sub>4</sub>). The catalyst was dried under reduced pressure before being recycled.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of a silica-bound PCP-type palladium(II) complex and catalytic properties of the immobilized palladium(II) complex

Complex **13** [15] was synthesized from 1,3-bis-diphenylphosphanylmethylbenzene and palladium(II) trifluoroacetate (Pd(TFA)<sub>2</sub>) at room temperature (Eq. (1)). Crystals suitable for X-ray analysis were obtained for **13** (Fig. 2).

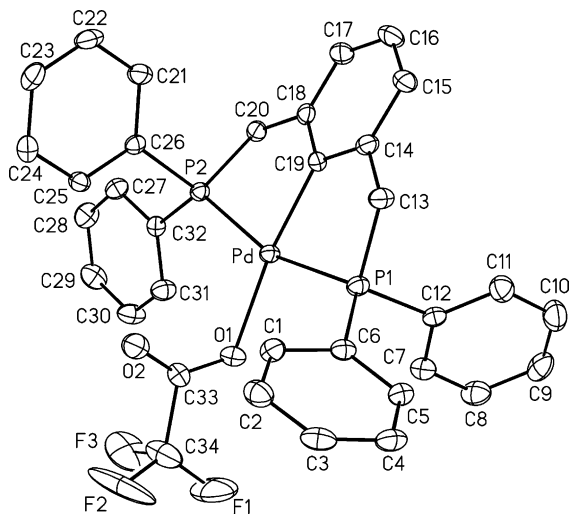


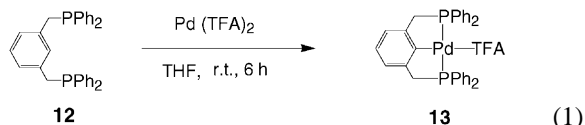
Fig. 2. ORTEP diagram of complex **13** (hydrogen atoms omitted for clarity).

Table 1  
Heck reaction of iodobenzene and butyl acrylate catalyzed by **1** or **13**<sup>a</sup>

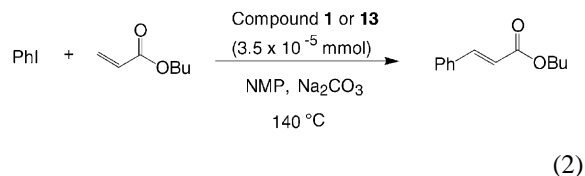
Complex	Time (h)	Yield (%) <sup>b</sup>	TON (mol product/mol Pd)	TOF (mol product/mol Pd/h)
<b>1</b>	88	88	108000	1227
<b>13</b>	70	>99	138000	1983

<sup>a</sup> Reactions were conducted using 5 mmol iodobenzene in NMP.

<sup>b</sup> Determined by GC.



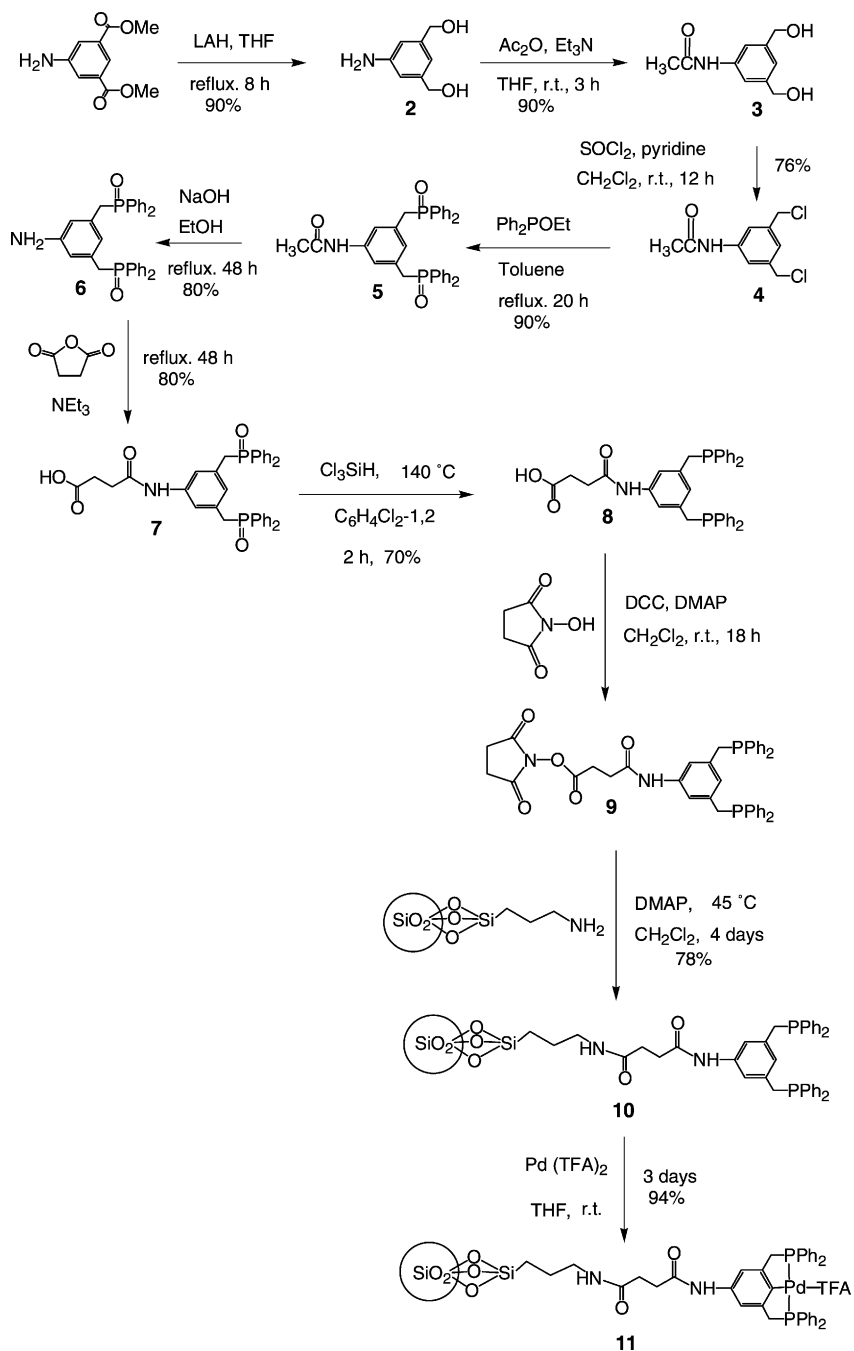
The catalytic activity of **13** was tested and compared with complex **1** (Eq. (2) and Table 1). It was found that the reactivity of **13** is better than **1**. This could be due to the electron-withdrawing effect of the phenyl groups.



The diphosphine PCP-type ligand anchored to silica was then prepared as shown in Scheme 1.

As mentioned previously, *N*-acetyl-3,5-bis(chloromethyl)aniline (**4**) was prepared in three steps (reduction, acetylation, and chlorination) according to the literature, starting from commercially available 5-amino-isophthalic acid dimethyl ester [16,17]. The diphosphine oxide compound (**5**) was synthesized by Arbuzov-type reaction of **4** instead of the analogue diphosphine because it is sufficiently stable for the subsequent deprotection, and reaction with succinic anhydride provided the *N*-[3,5-bis-(diphenylphosphinoylmethyl)-phenyl]-succinamic acid (**7**). Compound **7** was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>31</sup>P{H} NMR, and X-ray crystallography (Fig. 3).

Reduction of **7** with HSiCl<sub>3</sub> afforded the diphosphine compound (**8**), which is transformed into *N*-hydroxysuccinimide ester (**9**). Reaction with commercial aminopropyl silica gel gave the supported ligands. CP/MAS <sup>31</sup>P NMR was used as a tool for the determination of the successful binding to the silica,



Scheme 1.

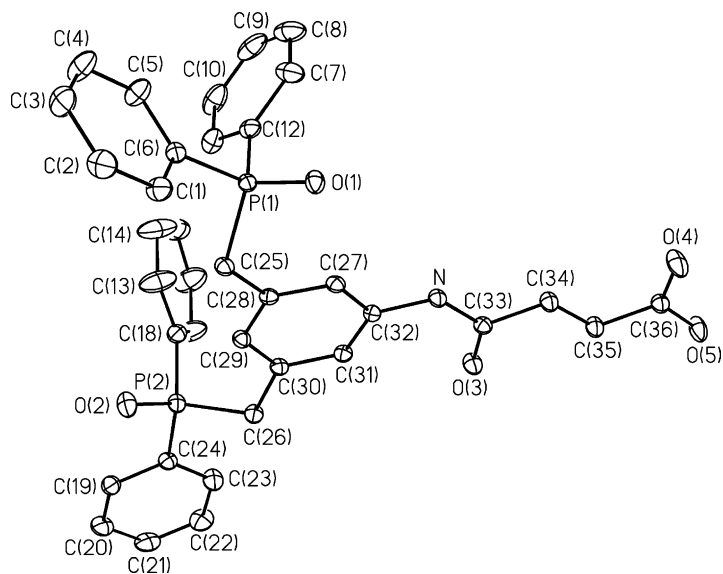


Fig. 3. ORTEP diagram of compound **4** (hydrogen atoms omitted for clarity).

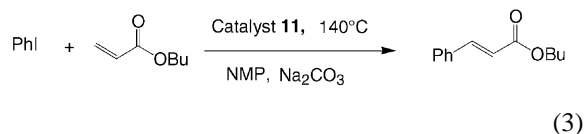
as the chemical shift values are very sensitive to small changes in the microenvironment. The CP/MAS  $^{31}\text{P}$  NMR spectrum of compound **10** showed a broad signal at  $-10.5$  ppm and a small broad signal (phosphine oxide) at  $31.1$  ppm, whereas the  $^{31}\text{P}$  NMR solution spectrum of compound **8** gave a signal at  $-9.0$  ppm (phosphine oxide at  $34.7$  ppm). Also the CP/MAS  $^{13}\text{C}$  NMR spectrum of compound **10** shows aromatic peaks.  $\text{Pd}(\text{TFA})_2$  was then reacted with **10** to form the PCP-type palladium(II) complex **11**. A phosphine/palladium ratio of 4:1 was used to avoid the formation of other complexes along with the PCP-type palladium(II) complex, such as palladium bound to the amino groups of the aminopropyl silica gel. While complexation of  $\text{Pd}(\text{TFA})_2$  with **12** was completed in 6 h (rt) to form complex **13**, 3 days were necessary for the immobilized system. The  $^{31}\text{P}$  NMR spectra of **11** and **13** show peak at  $37.9$  and at  $37.2$  ppm, respectively (there is also a low intensity signal in the NMR of **11**, at  $28.7$  ppm due to phosphine oxide impurity). It has been reported that the chemical shifts of the silica-bound late transition metal species which bond with phosphine ligands are similar to those of their molecular precursors [19]. The percentage of palladium in **11** was determined from ICP.

The preparation of complex **11** was also attempted by effecting cyclometallation of the phosphine ligands

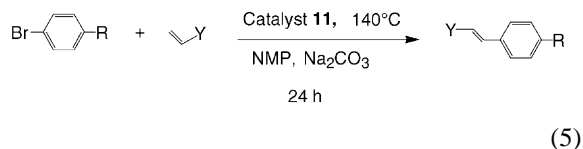
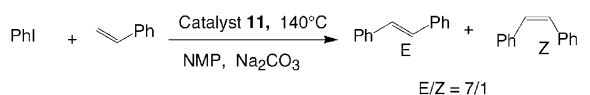
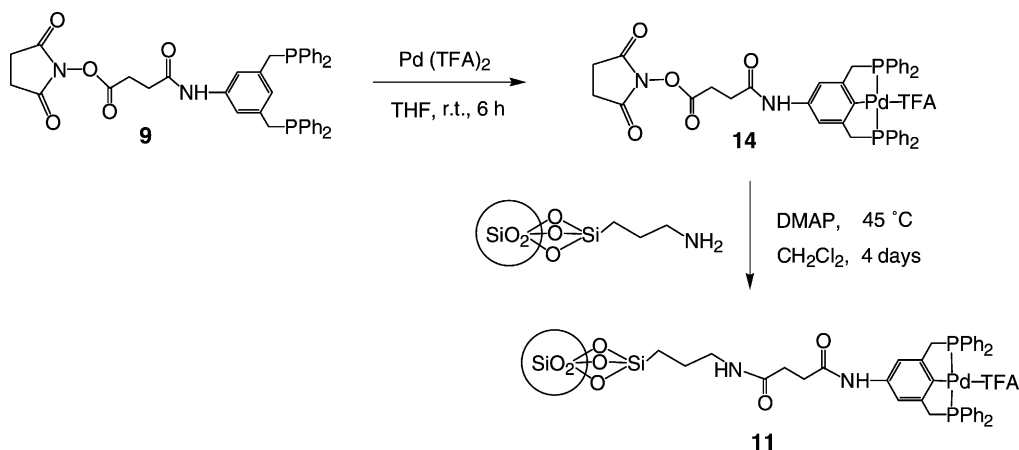
with the Pd complex prior to binding with silica (Scheme 2).

Nevertheless, due to the reactivity of the *N*-hydroxy-succinimide ester, problems were encountered in the purification of the Pd complex (**14**) obtained by this route. In the previous method, the purification of the silica-bound ligand is more facile.

The silica-PCP-type palladium(II) complex **11** was used as a catalyst for the Heck reaction. The coupling reaction of iodobenzene and butyl acrylate was optimized by varying the temperature, base, and solvent. The best conditions were similar to those reported for compound **1** [5]. The reaction was carried out at  $140^\circ\text{C}$ , using sodium carbonate as base in NMP (Eq. (3) and Table 2).



High turnover numbers (TON) were obtained (3030 mol product/mol Pd), and the catalyst was recycled three times with high activity. Lower reactivity was observed when changing the substrate from butyl acrylate to styrene (TON = 1320 mol product/mol Pd) (Eq. (4) and Table 3). Both *E/Z* stilbenes were formed in a ratio of 7:1.



Bromobenzene and several *para*-substituted bromobenzenes were also used as substrates with methyl or butyl acrylate. High activities and good recycling properties were observed here (Eq. (5) and Tables 4 and 5). A *para*-substituent on the benzene ring has no significant effect on the reaction. Chlorobenzene was found to react poorly with the acrylate (TON = 16 mol product/mol Pd). The rate-determining step of the reaction may involve oxidative addition.

Table 2  
Heck reaction of iodobenzene and butyl acrylate catalyzed by **11**<sup>a</sup>

Run number	Time (h)	Yield (%) <sup>b</sup>	TON (mol product/mol Pd)	TOF (mol product/mol Pd/h)
1	3	88	2611	897
1	6	>99 (90) <sup>c</sup>	3030	505
2	6	84 (75) <sup>c</sup>	2958	493
3	6	70	– <sup>d</sup>	– <sup>d</sup>

<sup>a</sup> Reactions were conducted using 25 mg ( $3.9 \times 10^{-3}$  mmol) of catalyst, and 12 mmol iodobenzene in NMP.

<sup>b</sup> Determined by GC.

<sup>c</sup> Isolated yield.

<sup>d</sup> Palladium loading was not measured.

Table 3  
Heck reaction of iodobenzene and styrene catalyzed by **11**<sup>a</sup>

Run number	Time (h)	Yield (%) <sup>b</sup>	TON (mol product/mol Pd)	TOF (mol product/mol Pd/h)
1	6	44	1344	224
1	15	72	1335	89
1	30	85	1320	44
2	30	80	– <sup>c</sup>	– <sup>c</sup>

<sup>a</sup> Reactions were conducted using 25 mg ( $3.9 \times 10^{-3}$  mmol) of catalyst, and 12 mmol iodobenzene in NMP.

<sup>b</sup> Determined by GC.

<sup>c</sup> Palladium loading was not measured.

ICP analysis showed that the total palladium content was 1.45 mass% Pd after the catalyst was used three times (entry 10, Table 5). However, a higher loading of catalyst ( $1.6 \times 10^{-2}$  mmol Pd, 100 mg of catalyst) was necessary and in the case of 4-bromotoluene, a lower yield was found after the reaction was run three times (entry 12, Table 5) (58% yield). ICP analysis showed that there was only 0.7 mass% Pd. A control experiment was carried out using a palladium–silica system catalyst obtained by stirring Pd(TFA)<sub>2</sub> and silica (10% by weight of palladium to silica) in THF solution. This system displayed poor stability as it decomposed to

Table 4

Heck reaction of bromobenzene and *para*-substituted bromobenzenes, and butyl or methyl acrylate catalyzed by **11**<sup>a</sup>

Entry	R group	Y group	Run number	Yield (%) <sup>b</sup>	TON (mol product/mol Pd)	TOF (mol product/mol Pd/h)
1	H	C(O)O <sup>n</sup> Bu	1	86	109	4.6
2	OMe	C(O)OMe	1	95	120	5.0
3	OMe	C(O)O <sup>n</sup> Bu	1	90	115	4.8
4	C(O)OMe	C(O)O <sup>n</sup> Bu	1	>99	127	5.3
5	Me	C(O)O <sup>n</sup> Bu	1	>99	127	>5.3

<sup>a</sup> Reactions were conducted using 100 mg ( $1.6 \times 10^{-2}$  mmol) of catalyst, and 2 mmol of *para*-substituted bromobenzenes for 24 h in NMP.<sup>b</sup> Determined by GC or NMR.

Table 5

Heck reaction of bromobenzene and *para*-substituted bromobenzenes, and butyl or methyl acrylate catalyzed by **11**,<sup>a</sup> a recycling study

Entry	R group	Y group	Run number	Yield (%) <sup>b</sup>
1	H	C(O)O <sup>n</sup> Bu	2	86
2			3	79
3			4	70
4			5	79
5	OMe	C(O)OMe	2	92
6			3	94
7	OMe	C(O)O <sup>n</sup> Bu	2	81
8			3	83
9	C(O)OMe	C(O)O <sup>n</sup> Bu	2	98
10			3	94
11	Me	C(O)O <sup>n</sup> Bu	2	85
12			3	58

<sup>a</sup> Reactions were conducted using 100 mg ( $1.6 \times 10^{-2}$  mmol) of catalyst, and 2 mmol *para*-substituted bromobenzenes for 24 h in NMP.<sup>b</sup> Determined by GC or NMR.

black Pd particles during a 20-h reaction and could not be recycled without loss of activity (99% yield for the first, 68% yield for the second, and 29% yield for the third runs). These results clearly confirm that stable PCP-type Pd catalysts were formed for **11** and **13** (no visible decomposition of **11** after 3 days in solution). Another control experiment was also carried out under the same conditions, but using compound **13** plus silica (2% by weight of palladium to silica) as a catalyst. We found only 38% yield in the third run (>99% yield for the first and 75% yield for the second runs).

#### 4. Conclusions

We have shown that the species obtained by immobilization of a PCP-type palladium(II) complex onto

silica is an active catalyst for the Heck reaction. In addition, the system displays good stability and can be recycled effectively.

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