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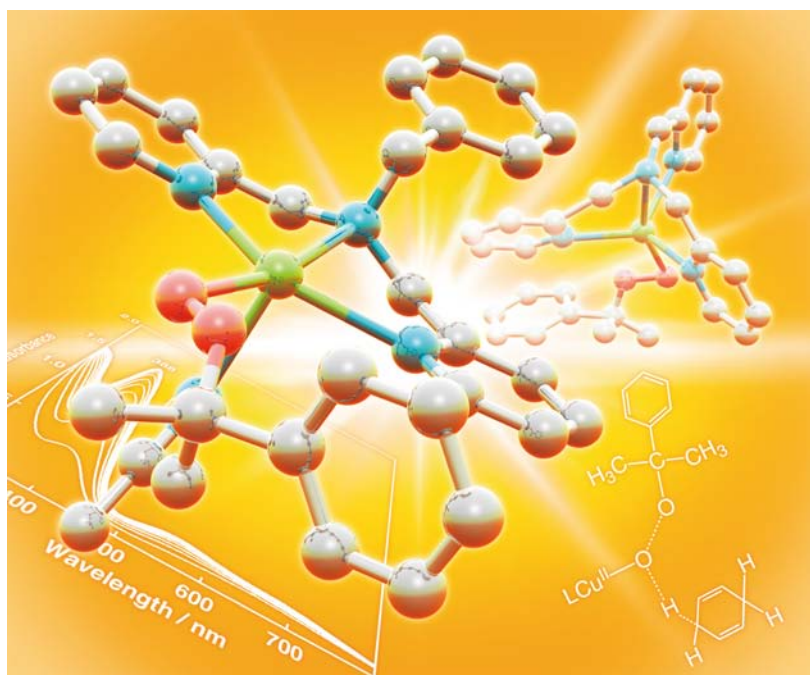


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# Mesoporous silicabis(ethylsulfanyl)propane palladium catalysts for hydrogenation and one-pot two-step Suzuki cross-coupling followed by hydrogenation†

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The solid phase catalytic activity of mesoporous silicabis(ethylsulfanyl)propane palladium catalysts for hydrogenation and novel one-pot two-step Suzuki cross-coupling followed by hydrogenation is described. The efficiency of catalytic hydrogenation was measured for substrate nitrobenzene with 5, 7 and 14 nm average pore diameter materials. The 5 nm pore material performed best and was also very effective in the catalytic hydrogenation of alkene, nitrile and imine substrates. Novel one-pot two-step Suzuki cross-coupling and hydrogenation was demonstrated using bromonitro- and bromodinitrobenzene and phenylboronic acid as substrates with conversion to the corresponding coupled amino compounds. As a consequence of the high affinity of the sulfur ligands for palladium, none was detected in leaching tests and the catalyst is easily separated and recycled.

## Introduction

Hydrogenation is a very important transformation for pharmaceutical and fine chemical synthesis and solid phase catalysts are desirable in that they can be easily recycled and separated from the product.<sup>1</sup> Leaching of catalytic metal is a significant issue in many cases that can result in product contamination as well as catalyst deactivation.<sup>2</sup> Catalysts with high affinity for the active metal are therefore required. Of particular interest in the context of this report is hydrogenation catalysed by silica supported Pd catalysts. For example, Pd-SBA-15 where the Pd source was Pd(acac)<sub>2</sub> is an effective catalyst for hydrogenation of 3-hexyne<sup>3</sup> with reported turnover frequencies, TOFs 2538–111 s<sup>−1</sup>. Using Pd(dibenzylideneacetone)<sub>2</sub> as the Pd source, a derived Pd–SiO<sub>2</sub> catalyst was very effective for hydrogenation of the substrates, 1-hexene, cyclohexene, benzene, 2-hexanone, cyclohexanone and benzonitrile.<sup>4</sup> These reports did not discuss catalyst stability to leaching. Hydrogenation of olefins was investigated using Pd-MCM-48,<sup>5</sup> Pd-MCM-41 and Pd–SiO<sub>2</sub><sup>6</sup> where all three were effective catalysts. The authors<sup>6</sup> indicated that some metal leaching occurs. Other metals apart from palladium have been reported in this context. For example, materials derived from the ion exchange of the Pt cluster anion [Pt<sub>12</sub>(CO)<sub>24</sub>]<sup>2−</sup> using alkyl ammonium modified MCM-41, were demonstrated as catalysts for the hydrogenation of different substrates including methyl pyruvate, acetophenone, nitrobenzene, benzonitrile, ethyl-

lactate, 4-nitrotoluene, cyclohexanone, allyl alcohol, and styrene.<sup>7</sup> Hydrogenation of cyclohexene with Rh(I) alkylphosphine modified MCM-41 was accomplished<sup>8</sup> with minimal leaching and a TOF of 2 s<sup>−1</sup>. MCM-41 modified with pincer-ligated Au and Rh complexes have proven to be highly effective catalysts for the hydrogenation of alkenes with high enantiomeric excess.<sup>9</sup>

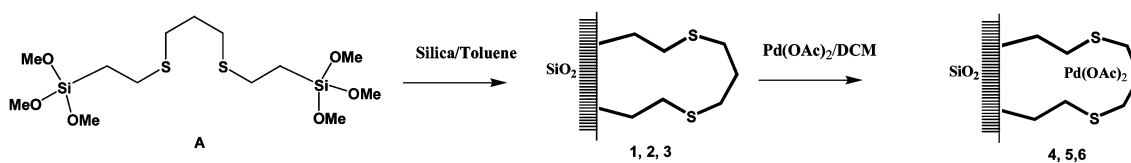
We have previously reported on silica immobilised sulfanyl ligated Pd catalysts in Suzuki cross-coupling chemistry<sup>10</sup> where we observed excellent catalytic activity. The covalently attached sulfanyl ligand resulted in very high affinity for palladium and there was no detectable metal leaching. In this paper we report the use of this catalyst system for hydrogenation reactions and also for novel one-pot Suzuki cross-coupling followed by hydrogenation reactions. For this purpose the catalyst was prepared and characterised from silica with three nominal average pore sizes and hydrogenation activity initially evaluated with nitrobenzene as substrate. Subsequently, the substrates benzonitrile, 1-octene and the imine (4-methoxyphenylimino)phenylacetic acid methyl ester were evaluated. Finally one-pot Suzuki cross-coupling and hydrogenation using bromonitrobenzenes and phenylboronic acid was explored. Studies describing heterogeneous catalysis of one-pot two-step and multistep reactions were recently reviewed.<sup>11</sup> Such reactions are viewed as an important means of achieving greater efficiency in the drive towards sustainable chemical processing.

## Results and discussion

The silica supported materials **1**, **2**, **3** were formed by grafting the compound **A**, bis(trimethoxysilanylethylsulfanyl)propane, to silica with nominal pore sizes 60, 90 and 150 Å. Post modification of **1–3** with palladium acetate gave deep orange coloured materials

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Scheme 1

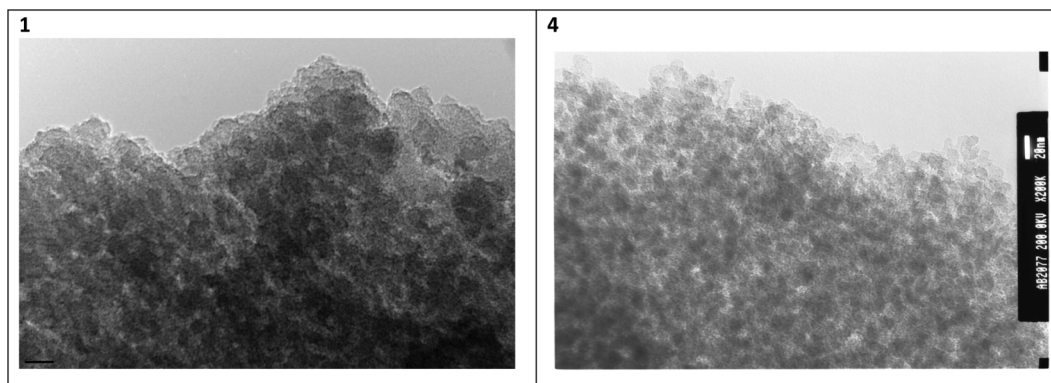


Fig. 1 TEM images of 1 and 4.

4–6. The process is represented schematically (Scheme 1). We have previously reported on materials 1 and 4.<sup>10</sup>

Modification of the silica with A and subsequently with palladium acetate was confirmed by proton NMR on materials dispersed in NaOD/D<sub>2</sub>O, solid state <sup>13</sup>C CPMAS NMR, IR, and sulfur and palladium analysis. The palladium loading (mmol g<sup>-1</sup>) showed some variation between the materials 0.41(4), 0.59(5) and 0.54(6). The precise coordination of palladium in 4–6 was not defined however the Cambridge crystallographic database contains a large number of palladium complexes with sulfur ligation in fragments of the type PdS<sub>2</sub>C<sub>3</sub>.<sup>12</sup> XPS for Pd 3d<sub>5/2</sub> in 4 gave binding energies at 335 eV (5.2%), Pd(0), 336.2 eV (37.2%) Pd(II) and 337.4 eV (57.6%) Pd(II). The binding energy of Pd 3d<sub>5/2</sub> in palladium acetate is 336.6 eV.<sup>13</sup> Clearly there was a small amount of reduction to Pd(0) on immobilisation of the palladium acetate and more than one type of Pd(II) environment. Acetate vibrational modes<sup>14</sup> were observed close to 1600 and 1435 cm<sup>-1</sup> in 4–6 (e.g. Supplementary Fig. A†). For a 1 : 1 sulfur ligand to palladium coordination, the percentage of free sulfur ligand sites in the materials would be 20%(4), 21%(5) and 18%(6).

TEM images of 1 and 4 (Fig. 1) are shown and no evidence of palladium nanoparticles or agglomerates was observed in 4.

TGA analysis of the materials carried out under nitrogen displayed some residual solvent or water loss up to 100 °C and a single weight loss (approx. 6–8%) between 300–500 °C for 1–3. Materials 4–6 had weight loss steps between 125–250 °C (approx. 2%) and 350–500 °C (approx. 3%). (e.g. Supplementary Fig. B†). The higher temperature weight loss event was common to both palladium loaded and palladium free materials and may therefore be attributed to decomposition of the sulfanyl ligand. The onset temperature of this event was slightly higher in 4 in keeping with some modification of the sulfanyl environment by palladium. The lower temperature event was only seen in the palladium loaded materials and may therefore be attributed to acetate decomposition. Thermal decomposition

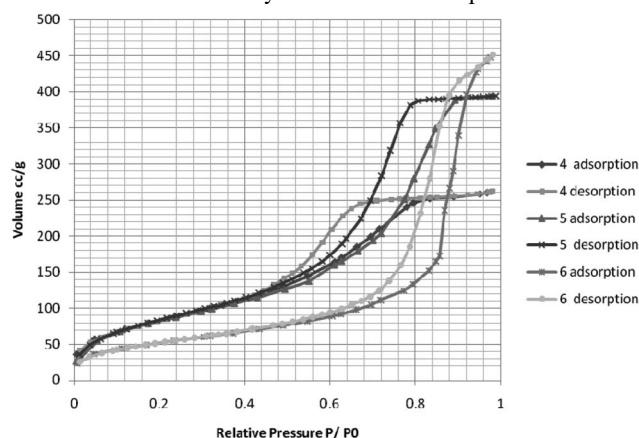
Table 1 Porosimetry parameters for 1–3 and 4–6

Materials	1 4	2 5	3 6
Surface area/m <sup>2</sup> g <sup>-1</sup>	445.6 319.9	379 278.1	497 238.2
Average pore volume/cc g <sup>-1</sup>	0.51 0.39	0.63 0.47	1.47 0.71
Average pore diameter/Å	54.5 51.3	79.3 72.4	120 137.0

of palladium acetate trimer, [Pd(OAc)<sub>2</sub>]<sub>3</sub> occurs between 200–300 °C.<sup>15</sup>

### Porosimetry of 1–6

Porosimetry data for the materials 1–6 is summarised in Table 1 and nitrogen sorption isotherms and pore size distributions are shown in Fig. 2 and 3 for 4–6. The isotherms suggest slit shaped mesoporosity according to IUPAC designations.<sup>16</sup> The pore size distribution is considerably broader in 6 compared to 4 or 5 a

Fig. 2 N<sub>2</sub> sorption isotherms 4, 5 and 6.

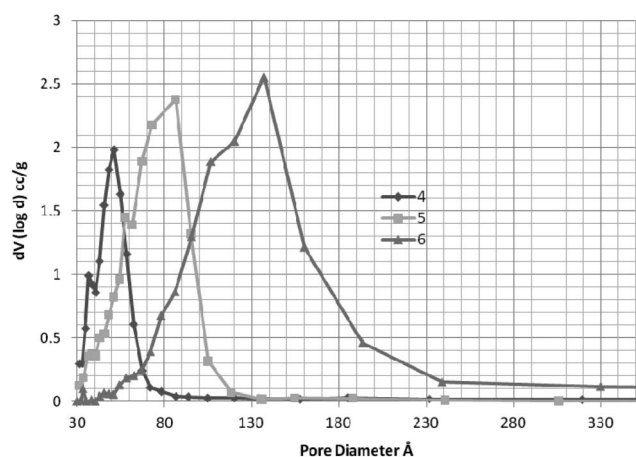


Fig. 3 BJH Pore size distribution of 4–6.

trend that was also seen in the precursor silica materials 1–3. Generally there is a decrease in surface area and pore volume following the modification with palladium acetate. The change in the average pore diameter observed from 3 to 6 is reversed relative to the other pairs with an increase in average pore size observed instead. This indicates that some small-pore blocking has occurred in this case. Overall however the textural properties after modification remained consistent with those required for heterogeneous catalysis.

To explore the effect of material texture on catalytic activity, the three materials 4, 5 and 6 were initially tested for the hydrogenation of nitrobenzene. Subsequently the hydrogenation of benzonitrile, 1-octene and the imine (4-methoxyphenylimino)phenylacetic acid methyl ester was examined using 4. Conditions for complete or near conversion were identified within the ranges, ambient temperature to 50 °C, 1–20 bar hydrogen, 1–24 h reaction time and using single substrate: Pd molar ratios between 1000 and 250 depending on the reaction. No attempt was made to optimise turnover frequency outside these conditions.

#### Comparative evaluation of 4, 5 and 6 for the hydrogenation of nitrobenzene

Nitro aromatics are an important class of intermediates for agrochemicals, pharmaceuticals, dyestuffs and other industrially important products.<sup>17</sup> Reaction conditions giving complete conversion of the nitrobenzene to aniline (Table 2) were first identified

Table 2 Hydrogenation of nitrobenzene

Catalyst <sup>a</sup>	Pd mol % <sup>a</sup>	% Conversion <sup>b</sup>
4	0.10	99, 99, 99, 99, 99
5	0.12	87
6	0.12	79
none	none	0

<sup>a</sup> Conditions, 10 mmol nitrobenzene, in MeOH (30 mL), and 4 (25 mg) or 5 (22 mg) or 6 (20 mg), H<sub>2</sub> 10 bar, 50 °C, 1 h; <sup>b</sup> % conversion as determined by GC and NMR

using catalyst 4 and then applied to 5 and 6. The conversion was assessed at a number of time points in each case and the reaction appeared to go cleanly to aniline without by-products. A detailed analysis of surface mechanisms for nitrobenzene hydrogenation with Pd/C catalysts has been reported.<sup>18</sup> The final conversion results for 4–6 at 60 min are shown in Table 2 and the conversion profile for each catalyst is shown in Fig. 4.

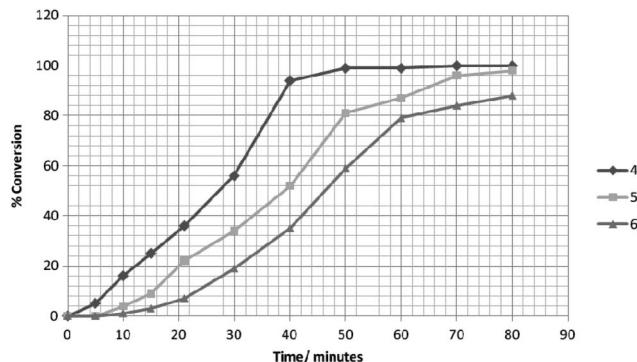


Fig. 4 Conversion profiles for the hydrogenation of nitrobenzene catalysed by 4, 5 and 6.

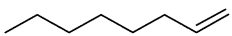
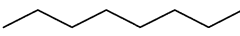
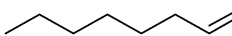
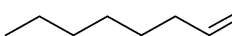
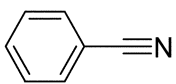
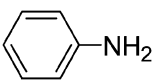
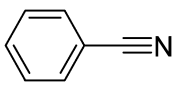
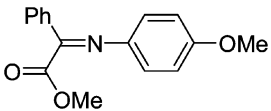
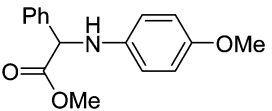
It is clear from the profiles that conversion efficiency decreased as average pore size and average pore size distribution increased, which is counter to expectations based on diffusion. On the other hand conversion efficiency increased with specific surface area. Material 4 with the smallest average pore size and narrowest pore size distribution and highest surface area displayed the best kinetic profile, going to completion within 1 h under these conditions. Complete conversion with 5 and 6 was however achieved in 80 and 120 min respectively. The palladium specific areas (mmol m<sup>-2</sup>) 4 (1.3), 5 (2.1) and 6 (2.3) indicate a greater degree of site isolation in 4 which could be an important factor in the observed relative conversion efficiency. Catalyst 4 was recycled five times without loss of activity. For the selected fixed substrate: catalyst ratios employed in this work the single batch turnover frequencies, TOF (mol<sub>sub</sub> mol<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup>) were 4 1200 h<sup>-1</sup>, 5 625 h<sup>-1</sup>, 6 416 h<sup>-1</sup>. For comparison Wilkinson's catalyst, RhCl(PPh<sub>3</sub>)<sub>3</sub>, was immobilised on 1 by the method<sup>10</sup> described for palladium acetate and the 1-Rh material obtained was employed as a catalyst under the reaction conditions used for 4 at 0.1 mol% Rh. Conversion to aniline was only 56% after 1 h, corresponding to a TOF of 560 h<sup>-1</sup>. Leaching tests were negative in all cases as measured by standard hot filtration tests and filtrate analysis for Pd (details given in experimental section). In comparison we found that hydrogenation of nitrobenzene catalysed by a sample of commercially sourced Pd/C (10%) resulted in complete conversion to aniline at 5 bar H<sub>2</sub> and ambient temperature but in leaching tests ICP-OES analysis of the filtrate solution revealed that 24% of the Pd had leached.

#### Hydrogenation of alkene, nitrile, imine with 4

An assessment of catalyst 4 for hydrogenation of other functional groups, using a single fixed 10 mmol substrate to 0.4 mol% Pd ratio, was subsequently carried out and the results are indicative of broad substrate activity as shown in Table 3. Substrates including 1-octene, benzonitrile and a more complex multifunctional amino acid precursor, (4-methoxyphenylimino)phenylacetic acid methyl



**Table 3** Hydrogenation of alkene, nitrile and imine with catalyst **4**

Entry	H <sub>2</sub> /bar	Temp/°C	Substrate	Product	% Conversion <sup>c,f</sup> (time/h)
1 <sup>a</sup>	1	50			99, 99, 99, 99, 99, 99 (1)
2 <sup>b</sup>	1	RT		—	0 (1)
3 <sup>b</sup>	1–10	50		—	0 (4)
4 <sup>d</sup>	15	50			99, 98, 97(6)
5 <sup>b</sup>	20	50		—	0(6)
6 <sup>e</sup>	20	50			99 (24)  0(24) <sup>b</sup>

<sup>a</sup> Conditions, 10 mmol 1-octene, 30 mL methanol, 100 mg **4**, 0.4 mol % Pd. <sup>b</sup> No catalyst employed. <sup>c</sup> % conversion determined by GC. <sup>d</sup> 10 mmol benzonitrile, 30 mL methanol and 100 mg **4**, 0.4 mol% Pd. <sup>e</sup> 10 mmol  $\alpha$ -iminoester, 30 mL trifluoroethanol, 20 mg **4**, 0.08 mol% Pd. <sup>f</sup> Hot filtration and palladium analysis of filtrates indicated that **4** was stable towards leaching.

ester<sup>19</sup> were used. Thus, 1-octene converted at 50 °C and 1 bar hydrogen without loss in activity during 6 cycles with a TOF of 250 h<sup>-1</sup>.

Benzonitrile converted at >96% under relatively mild conditions without significant loss over three cycles and with a TOF of 250 h<sup>-1</sup>. Hydrogenation of the more complex multifunctional  $\alpha$ -iminoester required higher pressure and a longer time to reach complete conversion to the corresponding amine. The methoxy and methyl ester groups remained intact under these conditions. With NaBH<sub>4</sub> as reducing agent the aminoalcohol was obtained. Others reported 65% conversion (64% *e.e.*) to the amine using a chiral homogeneous iridium catalyst at 5 mol%.<sup>20</sup>

The catalyst **4** appeared stable to leaching under the conditions employed as determined by both hot filtration tests and ICP Pd analysis of filtrates after 24 h.

The catalyst colour changed from bright orange prior to use to dark brown after use. The TGA of catalyst **4** immediately after use for hydrogenation of nitrobenzene showed solvent loss below 100 °C and weight loss (approx. 2%) between 125–250 °C with further almost continuous weight loss (approx. 6%) up to 500 °C (Supplementary Fig. C†). This profile was consistent with loss of some residual aniline product as well as catalyst decomposition.

### One-pot cross-coupling and hydrogenation with **4**

We had previously reported on the very effective activity of catalyst **4** for cross-coupling of Suzuki substrates and in the light of the hydrogenation results reported here showing effective catalytic hydrogenation of nitrobenzene, this catalyst was further explored in one-pot 2-step Suzuki and hydrogenation reactions using phenylboronic acid and bromonitrobenzenes as substrates. There do not appear to be other reports of a similar one-pot single catalyst 2-step reaction combination, although many other

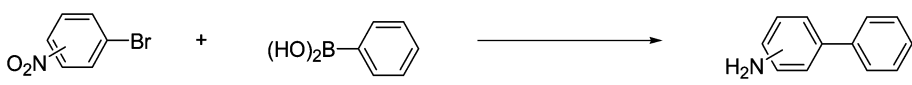
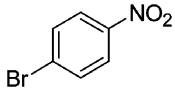
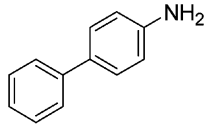
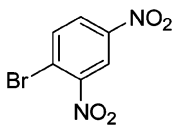
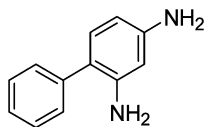
combinations including examples of Heck coupling followed by hydrogenation have been reported.<sup>11</sup> In this case the reaction mixture for the Suzuki coupling including, a boronic acid, an aryl halide, the base NaO<sup>t</sup>Bu, catalyst **4** and the solvent isopropanol were placed under 10 bar H<sub>2</sub> at room temperature from the outset. Apart from the hydrogen other conditions were selected in accordance with those we previously used for the cross-coupling reaction where 3 mol% Pd was employed.<sup>10</sup> The results are summarised in Table 4. The reaction was run at room temperature and gave complete conversion to the corresponding aminobiphenyl products after 6h. The catalyst was recycled three times in the case of 1,4-bromonitrobenzene with a small loss in activity on the third cycle.

Aminobiphenyl products were obtained and no nitrobiphenyl intermediates were detected. Residual nitroaryl bromide (but not aminoaryl bromide) was detected (third recycle Entry 1 and Entry 2). This suggests that the coupling step precedes hydrogenation.

### Conclusion

We have demonstrated that palladium acetate immobilised on silicabis(ethylsulfanyl)propane is a very effective solid phase catalyst for catalytic hydrogenation of a range of substrates and that the catalyst resists palladium leaching under the conditions applied. Conversion efficiency for hydrogenation of nitrobenzene increased with surface area of the catalyst but showed an inverse correlation with average pore size and palladium specific area. It may be that palladium site isolation is an important factor influencing the relative conversion efficiency observed. In addition we have demonstrated a novel one-pot two-step Suzuki cross-coupling followed by hydrogenation using nitroaryl substrates catalysed by our mesoporous silicabis(ethylsulfanyl)propane palladium system without leaching or loss of activity over several runs. Further work

**Table 4** One pot, single catalyst, 2-step Suzuki coupling and hydrogenation reactions catalysed by **4**

			
Entry <sup>a</sup>	Aryl halide	Products	% Conversion
1			99, 99, 95 (TOF 5.8 h <sup>-1</sup> )
2			94 (TOF 5.3 h <sup>-1</sup> )

<sup>a</sup> Conditions: 1.5 mmol boronic acid, 1.0 mmol aryl halide, 1.2 mmol NaO<sup>t</sup>Bu, 70 mg **4** (3.4mol%Pd), 5 mL isopropanol, 10 bar H<sub>2</sub>, room temperature, 6 h. % conversion was determined by <sup>1</sup>H NMR and GC.

will focus on establishing the nature of the active palladium species and in addition the broader scope for the use of this catalyst in one-pot multistep processes.

## Experimental

Chemicals used were purchased from Aldrich, Avocado, Lancaster, Zeo Chem (90 Å silica) and Grace Davison (60 Å and 150 Å silica) and were used without further purification. Hydrogen was supplied by BOC. Proton NMR spectra were recorded on a JEOL 270 MHz instrument; solid state NMR were measured on a Bruker AMX 600 MHz spectrometer: <sup>29</sup>Si HPDec MAS-frequency 119.2 MHz, spinning speed 12 KHz; 1 min recycle delay with a 2 μs, ~45° pulse; <sup>13</sup>C CP MAS-frequency 150.9 MHz, spinning speed 10 KHz, 1 ms contact time, 5 s delay, 90° pulse for 3.5 μs. Porosimetry measurements were obtained from a Quantachrome Nova instrument and data processed in Novawin<sup>TM</sup> software. Sulfur analysis was obtained from Medac Ltd. Infrared spectra were recorded on the neat powders using a Perkin Elmer Spectrum 65 FT-IR with Universal ATR sampling accessory. Pd analysis was performed on a Spectro Genesis ICP-OES. Gas chromatography (GC) was performed on Hewlett Packard 5890A. Thermal gravimetric analysis was performed on a Universal V4.7A TA Instrument. (4-methoxyphenylimino)phenylacetic acid methyl ester was prepared as previously described.<sup>19</sup> The compound trimethoxysilanylethylsulfanylpropane **A**, the silica immobilised materials **1–3**, and palladium acetate derivatives **4–6** were prepared by the methods previously described for **1** and **4**.

### Synthesis of **A**

To trimethoxyvinylsilane (67 mL, 0.44 mol) was added 1,3-dimercaptopropane (20 mL, 0.22 mol) and di-*tert*-butyl peroxide (10 drops). The mixture was stirred at room temperature for 1 h. The crude product was evaporated under reduced pressure (0.01 mm Hg) at 100 °C to remove any starting material. The cooled residue was a colourless oil (79 g, 99%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub>: 0.77 (4H, t, *J* = 8.1, SiCH<sub>2</sub>), 1.63–1.69 (2H, m, CH<sub>2</sub>), 2.45 (8H, m, CH<sub>2</sub>), 3.38 (18H, s, OMe); <sup>13</sup>C NMR

(CDCl<sub>3</sub>) δ<sub>C</sub>: 10.5 (SiCH<sub>2</sub>), 25.9 (CH<sub>2</sub>S), 29.1 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S), 30.6 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S), 50.4 (OMe); <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ<sub>Si</sub>: -45.04; FAB-MS (*m/z*): [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>32</sub>O<sub>6</sub>S<sub>2</sub>Si<sub>2</sub>, 422.1517, Found. 422.1515; *m/z* (%): 422 (M<sup>+</sup>, 100), 274.1 (22), 138.1 (49).

### General procedure for synthesis of **1–3**

To **A** (6 g, 14.8 mmol) was added silica, average pore diameter 60 Å or 90 Å or 150 Å (20 g) and toluene (70 mL). The resulting mixture was stirred at reflux for 8 h. After cooling, the mixture was filtered, washed with methanol and then dried to give white powders.

**1**: <sup>1</sup>H NMR (NaOD/D<sub>2</sub>O, 270 MHz) δ<sub>H</sub>: 0.38 (4H, m, SiCH<sub>2</sub>), 1.54 (2H, m, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S) and 2.31–2.36 (8H, m, CH<sub>2</sub>S); <sup>13</sup>C NMR (CP MAS) δ<sub>C</sub>: 13 (SiCH<sub>2</sub>), 26.1 (CH<sub>2</sub>S), 29.5 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S); <sup>29</sup>Si NMR (MAS) δ<sub>Si</sub> -76, -108 and -117; IR ν/cm<sup>-1</sup>: 1073 brs, 994 m, 808 m, 696 w; sulfur 3.29%. Ligand loading 0.51 mmol g<sup>-1</sup>. (DTG profile Supplementary Info. Fig. B(a)†).

**2**: <sup>1</sup>H NMR (NaOD/D<sub>2</sub>O, 270 MHz) δ<sub>H</sub>: 0.39 (4H, m, SiCH<sub>2</sub>), 1.52 ppm (2H, m, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S) and 2.30–2.34 (8H, m, CH<sub>2</sub>S); <sup>13</sup>C NMR (CP MAS) δ<sub>C</sub>: 14.4 (SiCH<sub>2</sub>), 26.3 (CH<sub>2</sub>S) and 32.2 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S); <sup>29</sup>Si NMR (MAS) δ<sub>Si</sub> -75, -108 and -116; IR ν/cm<sup>-1</sup>: 1050 brs, 916 m, 814 m; sulfur 4.83%; ligand loading 0.75 mmol g<sup>-1</sup>.

**3**: <sup>1</sup>H NMR (NaOD/D<sub>2</sub>O, 270 MHz) δ<sub>H</sub>: 0.38 (4H, m, SiCH<sub>2</sub>), 1.53 ppm (2H, m, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S) and 2.28–2.33 (8H, m, CH<sub>2</sub>S); <sup>13</sup>C NMR (CP MAS) δ<sub>C</sub>: 14 (SiCH<sub>2</sub>), 26 (CH<sub>2</sub>S) and 32 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S); IR ν/cm<sup>-1</sup>: 1064 brs, 957 m, 791 m, 671 w; sulfur 4.20%; ligand loading 0.66 mmol g<sup>-1</sup>.

### General procedure for **4–6**

To a solution of Pd(OAc)<sub>2</sub> (0.32 g, 1.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added **1**, **2** or **3** (2 g). The mixture was stirred at room temperature for 24 h and then filtered, washed with CH<sub>2</sub>Cl<sub>2</sub> until the washings were clear and the orange material formed was then dried under reduced pressure.

**4:** IR  $\nu/\text{cm}^{-1}$ : 1603 brw, 1437 w, 1077 brs, 987 m, 814 m, 726 w; specific surface area  $319.9 \text{ m}^2 \text{ g}^{-1}$ ; average pore volume  $0.39 \text{ cc g}^{-1}$ ; average pore diameter  $51.3 \text{ \AA}$ ; Pd loading  $0.41 \text{ mmol g}^{-1}$ ; (DTG profile Supplementary Info. Fig. B(b)†).

**5:** IR  $\nu/\text{cm}^{-1}$ : 1612 w, 1448 w, 1074 brs, 993 m, 813 m; specific surface area  $278.1 \text{ m}^2 \text{ g}^{-1}$ ; average pore volume  $0.47 \text{ cc g}^{-1}$ ; average pore diameter  $72.4 \text{ \AA}$ ; Pd loading  $0.59 \text{ mmol g}^{-1}$ .

**6:** IR  $\nu/\text{cm}^{-1}$ : 1601 brw, 1435 w, 1070 brs, 972 m, 810 m, 694 w. Specific surface area  $238.2 \text{ m}^2 \text{ g}^{-1}$ ; average pore volume  $0.71 \text{ cc g}^{-1}$ ; average pore diameter  $137.0 \text{ \AA}$ ; Pd loading  $0.54 \text{ mmol g}^{-1}$ .

### Procedure for hydrogenation

The substrate (10 mmol) and methanol (30 mL) were combined with stirring in a vial and catalyst added. A glass cup was used to partially cover the vial which was then transferred to a 250 mL autoclave reactor. The vessel was purged with nitrogen three times and then purged with hydrogen before being charged at the desired pressure. The reaction mixtures were stirred and external heating was applied as appropriate. After the given reaction time the catalyst was filtered off, the solvent removed and the residue analysed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) and GC.

Recycles were carried out with filtered catalyst after washing with methanol.

### Procedure for one-pot cross-coupling and hydrogenation catalysed by **4**

The substrates, nitro-substituted aryl bromide (1 mmol), phenyl boronic acid (1.5 mmol), base  $\text{NaO}^t\text{Bu}$  (0.12 g, 1.2 mmol), catalyst **4** (70 mg, 0.029 mmol, 2.9 mol % Pd) and isopropanol (4 mL) were combined with stirring in a vial. A glass cup was used to partially cover the vial which was then transferred to a 250 mL PTFE lined autoclave reactor. The vessel was purged with nitrogen three times, hydrogen twice and the mixture was stirred at room temperature for 6 h under 10 bar hydrogen. The catalyst was filtered off, solvent removed and the residue analysed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) and GC.

Recycles were carried out with filtered catalyst washed with isopropanol.

### Leaching tests

Reactions were interrupted at partial conversion (20 min for nitrobenzene, 1 h for 1-octene and benzonitrile) and using a 0.2 micron filter, the catalyst was separated from the reaction solution. Samples of the filtrates were taken and the partial conversion to amine was measured. The hydrogenation reaction was allowed to continue with the remaining filtrate and conversion measured again after the required reaction time. No further conversion was

observed in the filtered samples. Furthermore, no palladium could be detected by ICP-OES analysis of the filtrates.

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