# Preparation and catalytic studies of palladium nanoparticles stabilized by dendritic phosphine ligand-functionalized silica

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## ABSTRACT

Silica is a prominently utilized heterogeneous metal catalyst support. Functionalization of the silica with poly(ether imine) based dendritic phosphine ligand was conducted, in order to assess the efficacy of the dendritic phosphine in reactions facilitated by a silica supported metal catalyst. The phosphinated poly(ether imine) (PETIM) dendritic ligand was bound covalently to the functionalized silica. For this purpose, the phosphinated dendritic ligand containing an amine at the focal point was synthesized initially. Complexation of the dendritic phosphine functionalized silica with Pd(COD)Cl$_2$ yielded Pd(II) complex, which was reduced subsequently to Pd(0), by conditioning with EtOH. The Pd metal nanoparticle thus formed was characterized by physical methods, and the spherical nanoparticles were found to have >85% size distribution between 2 nm and 4 nm. The metal nanoparticle was tested as a hydrogenation catalyst of olefins. The catalyst could be recovered and recycled more than 10 times, without a loss in the catalytic efficiency.

## 1. Introduction

Studies on solid supports present a significant importance in heterogeneous organometallic catalysis [1,2]. Alumina, silica, carbon and MCM types are the most commonly adopted solid supports, in order to impregnate or immobilize metal catalysts. Traditionally, solid supports are known to facilitate the catalyst recovery and recycling. Many developments further have shown that solid supported catalysts mediate reactions resulting in higher selectivities in the products formed. Functionalization of the solid supports with suitable chelating ligands is emerging as a viable strategy to circumvent not only the pertinent metal catalyst deterioration and leaching limitations, but also to stabilize the metal particles and to adjust their catalytic efficiencies. Various types of functionalization of the silica with ligands are reported previously. Few pertinent examples are: (i) phosphino ferrocene [3]; (ii) phosphino phenoxazine [4]; (iii) Schiff-bases from 3-amino propyl silica and pyridine, thiophene, furan, pyrrole and acetophenone derivatives [5–7]; (iv) amino propyl moieties [8]; (v) urea-cross-linked imidazolium derivative [9–11] and (vi) (P, N) ligands constituted with bis-phosphinoamino moiety, diphenylphosphino pyridine moiety and Schiff-base from 3-aminopropyl silica and a diphenylphosphine derivative of phenyl ethanone [12,13]. Each of these ligands, functionalizing the silica, was used to form the palladium metal catalyst.

The resulting silica bound catalysts were found to exhibit considerable increases in the catalytic efficiencies and selectivities in chosen reactions, as well as, their recoverabilities and reusabilities. Functionalization of silica with the newly emerged dendritic ligands has been demonstrated in recent years. In a series of pioneering work, Alper and co-workers reported not only the facile synthesis of poly(amido amine) series of dendrimers on the silica support, but also further functionalization of the dendritic moieties with phosphine ligands and palladium metal complexes [14–16]. These dendritic metal complexes on silica support were shown to lead higher product selectivities and recyclabilities. In continuing our work in the area of poly(propyl ether imine) (PETIM) dendrimers [17–22], we tested the functionalization of silica with a phosphinated PETIM dendrimer, followed by the formation of a palladium metal catalyst and studies of the catalytic reactions. In the event, we identify that the functionalization of silica with a phosphinated PETIM dendrimer provides an ability to form smaller size distribution of metal particles and their subsequent profound catalytic efficiencies. Functionalization of the silica support with diphenylphosphinomethyl-derivatized dendritic amine, palladium nanoparticle formation and the catalytic studies are described herein.

## 2. Experimental

### 2.1. General

Solvents were dried and distilled according to the literature procedures [23]. The amine functionalized dendrimer 1 [17] and

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PdCODCl$_2$ [24] were synthesized according to known procedures. The olefin substrates were used as received or treated through a short column of activated alumina. In case of phosphine compounds, the experiments were performed under an inert gas atmosphere. FT-IR spectra were recorded as the KBr sample. $^{13}$C, $^{29}$Si and $^{31}$P solid state NMR spectral analyses were performed on a spectrometer operating at 75.4 MHz, 59.6 MHz and 121.4 MHz, respectively. The following abbreviations are used to explain the multiplicities: s, singlet; m, multiplet; band, several overlapping signals; b, broad. Elemental analysis was performed using an automated CHNS analyzer. For ICP-OES analysis, samples were digested in HCl:HNO$_3$ = 3:1 and heated for 1 h, diluted with H$_2$O and analyzed for Pd content. ICP-OES measurements were performed at 340.98 nm, with Pd standard. XPS was recorded using Al Kα radiation (1486.6 eV). Binding energies were calibrated with respect to C(1s) at 284.5 eV, with a precision of 0.2 eV. For TEM analysis, an acetone dispersion was drop-cast onto a carbon coated copper grid, and TEM observations were performed. Gas chromatographic analyses were performed by flame ionization gas chromatography (FID).

**2**. To a solution of G1 amine **1** [17] (1.5 g, 2.53 mmol) in H$_2$O (40 mL), a solution of Boc$_2$O (0.14 g, 0.63 mmol) in H$_2$O:THF (2:1, 15 mL) was added dropwise, at room temperature, stirred for 24 h. The reaction mixture was extracted first with Et$_2$O (2× 30 mL), then separately with CH$_2$Cl$_2$ (2× 30 mL) and CHCl$_3$ (2× 30 mL). The combined CH$_2$Cl$_2$ and CHCl$_3$ portions were concentrated, diluted with CHCl$_3$ (30 mL), washed with water (10 mL), dried (Na$_2$SO$_4$), solvents evaporated *in vacuo* and dried to afford **2**, as an oil. Yield: 0.33 g (75%); FT-IR (neat) $\nu$: 3365, 3297, 2935, 2859, 2801, 1712, 1469, 1367, 1171, 1115; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 5.11 (b s, 1H), 3.50–3.38 (m, 20H), 3.24–3.18 (m, 2H), 2.83–2.79 (m, 6H), 2.49–2.45 (m, 18H), 1.76–1.64 (m, 20H), 1.44 (s, 9H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ 156.0, 78.9, 69.2, 69.0, 50.7, 39.6, 38.6, 33.3, 33.1, 33.0, 29.8, 29.6, 28.4, 27.4; HRMS $m/z$: 693.5859 [M+H]$^+$; calcd for C$_{35}$H$_{77}$N$_6$O$_7$: 693.5854.

**3**. A mixture of diphenylphosphine (1.02 g, 5.45 mmol) and paraformaldehyde (0.17 g, 5.32 mmol) in MeOH (10 mL) was heated at 70 °C for 10 min. The reaction mixture was cooled to room temperature and treated with a solution of **2** (0.6 g, 0.87 mmol) in MeOH (10 mL). After 0.5 h, PhMe (20 mL) was added and the solution heated at 65 °C for 0.5 h, and then stirred at room temperature for 12 h. The reaction mixture was concentrated *in vacuo* and hexane (20 mL) was added. The product precipitated, which was collected and dried at 60–65 °C for 10 h, to afford Boc-protected **3**, as a colorless foamy solid. Yield: 1.43 g (88%); FT-IR (neat) $\nu$: 3316, 3053, 2942, 2861, 2803, 1708, 1482, 1437, 1174, 1119, 742, 696; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.40–7.36 (m, 24H) 7.27 (band, 36H), 5.05 (b s, 1H), 3.54 (s, 8H), 3.47–3.38 (m, 12H), 3.26–3.09 (m, 14H), 2.94–2.86 (m, 6H), 2.64 (band, 12H), 1.76–1.54 (m, 20H), 1.42 (s, 9H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ 156.0, 138.2, 138.0, 133.1, 132.9, 130.7, 130.6, 78.6, 68.8, 68.7, 68.5, 58.8, 58.7, 52.9, 50.6, 29.8, 28.4, 26.8, 26.5, 26.3–25.8; $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ −28.4; ESI-MS $m/z$: 1919.1692 [M+O+Na]$^+$; calcd for C$_{113}$H$_{142}$N$_6$O$_8$P$_6$Na: 1919.9213.

To a solution of the above Boc-protected **3** (1.2 g, 0.64 mmol) in CH$_2$Cl$_2$ (70 mL), TFA (2.8 mL, 38.3 mmol) was added and the solution stirred at room temperature for 4 h. The reaction mixture was washed with saturated aq. NaHCO$_3$ (2× 30 mL), brine (2× 30 mL), the organic portion dried (Na$_2$SO$_4$) and concentrated to afford **3**, as a colorless gum. Yield: 1.05 g (92%); FT-IR (neat) $\nu$: 3402, 3052, 2942, 2861, 2803, 1482, 1437, 1174, 1119, 741, 695. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.42–7.35 (m, 24H), 7.27 (band, 36H), 3.54 (d, $J$ = 3 Hz, 8H), 3.48–3.39 (m, 16H), 3.26–3.19 (m, 12H), 2.91 (band, 6H), 2.66 (b, 12H), 1.77–1.59 (m, 20H), 1.61 (band, 4H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ 138.1, 137.9, 133.0, 132.8, 130.6, 130.4, 128.3, 128.2, 68.7, 68.3, 58.7, 50.6, 29.5, 26.7, 26.5, 26.0; $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ −28.4.

**4**. A mixture of silica (3 g, 9.5–11 μm, pore volume 50–76 Å, surface area 475–560 m$^2$ g$^{-1}$) and (MeO)$_3$Si(CH$_2$)$_3$Cl (6.5 g, 32.6 mmol)

in PhMe (100 mL) was refluxed for 8 h. The solvents were removed *in vacuo* and the residue was admixed again with (MeO)$_3$Si(CH$_2$)$_3$Cl (6.5 g, 32.6 mmol) and PhMe (100 mL) refluxed for 8 h and the solvents removed *in vacuo*. Treatment with (MeO)$_3$Si(CH$_2$)$_3$Cl was repeated once more the reaction mixture was refluxed for 8 h and then solvents removed *in vacuo*. The resulting residue was washed with CH$_2$Cl$_2$ (5× 15 mL) and dried at 60 °C for ∼10 h, to afford **4** (3.5 g). $^{13}$C NMR: $\delta$ 50.7 (OCH$_3$), 47.7 (CH$_2$Cl), 27.6 (CH$_2$CH$_2$CH$_2$), 8.8 (SiCH$_2$); $^{29}$Si NMR: $\delta$ −112.3; Anal. found: C 5.55, H 1.78. Loading of methoxychloropropyl group onto silica was estimated to be 1.16 mmol/g of silica, calculated on the basis of elemental analysis.

**5**. A mixture of **3** (1.0 g, 67.6 mmol) and **4** (1.5 g) in CHCl$_3$ (60 mL) was refluxed for 24 h, solvents were then removed *in vacuo*. The residue was washed with CHCl$_3$ (5× 10 mL), MeOH (3× 10 mL), and dried to afford **5** (1.6 g). FT-IR (KBr): $\nu$ 3437, 2948, 1482, 1436, 1100, 804, 742, 696; $^{13}$C NMR: $\delta$ 128.8 (PPh$_2$), 68.7 (CH$_2$O), 51.3 (CH$_2$N), 27.2 (CH$_2$CH$_2$CH$_2$), 9.6 (SiCH$_2$); $^{31}$P NMR: $\delta$ −28.4; $^{29}$Si NMR: $\delta$ −112.3; Anal. found: C 7.50, H 1.82, N 2.02. Loading of phosphinated dendritic amine onto silica was 0.24 mmol/g of silica, calculated on the basis of elemental analysis.

**5-Pd(II) complex** A suspension of **5** (0.74 g) in THF (20 mL) was admixed with Pd(COD)Cl$_2$ (0.17 g, 0.59 mmol) and stirred at room temperature for 24 h. The reaction mixture filtered, washed with THF (6× 10 mL), CH$_2$Cl$_2$ (6× 10 mL) and dried for ∼6 h at 50 °C, to afford **5**-Pd(II) complex (0.74 g). $^{13}$C NMR: $\delta$ 130.2 (PdCl$_2$PPh$_2$), 68.1 (CH$_2$O), 51.5 (CH$_2$N), 26.5 (CH$_2$CH$_2$CH$_2$), 9.9 (SiCH$_2$); $^{29}$Si NMR: $\delta$ −110.6; $^{31}$P NMR: $\delta$ 13.9. Loading of Pd by ICP-OES analysis: 0.43 mmol/g of silica; XPS: 337.6 eV (Pd 3d$_{5/2}$), 342.9 eV (Pd 3d$_{3/2}$).

**6**. A mixture of **5**-Pd(II) complex (0.74 g) and EtOH (100 mL) was refluxed for 24 h, filtered and the residue washed with EtOH (5× 20 mL), dried for 8 h, at 60 °C, to afford the metal nanoparticle-silica composite **6** (0.71 g). $^{13}$C NMR: $\delta$ 9.2 (SiCH$_2$), 25.4 (CH$_2$CH$_2$CH$_2$), 50.5 (CH$_2$N), 66.6 (CH$_2$O), 129.9 (OPPh$_2$); $^{29}$Si NMR: $\delta$ −111.7; $^{31}$P NMR: $\delta$ 12.9, 29.6. Loading of Pd by ICP-OES: 0.40 mmol/g of silica; XPS: 335.6 eV (Pd 3d$_{5/2}$), 340.7 eV (Pd 3d$_{3/2}$) and 337.5 eV (Pd 3d$_{5/2}$), 342.6 eV (Pd 3d$_{3/2}$).

## 2.2. General procedure of hydrogenation

A stainless steel reactor (50 mL) was charged with the olefin substrate (1 mmol), **6** (0.5 mol %) and EtOAc (5 mL). The autoclave was closed and maintained at H$_2$ (g) pressure of 1 atm. The mixture was stirred at 25 °C and the progress of the reaction was monitored by GC. Upon completion of the reaction, the mixture was centrifuged, the precipitate washed with EtOAc (5× 5 mL), dried at 50 °C, and used again in the recycling experiments.

## 3. Results and discussion

Functionalization of silica with a first generation phosphinated dendritic amine was desired, as the dendritic amine is pre-formed, requiring a protection and a deprotection step, before its attachment to the solid support. A nucleophilic substitution is a commonly adopted reaction for the functionalization of amines onto silica [25,26]. The phosphinated dendritic amine ligand was prepared according to Scheme 1.

The amine terminated first generation PETIM dendrimer **1** was synthesized by following the reported procedure [17]. The mono-protection of an amine group in **1** was conducted using di-*tert*-butyl dicarbonate (Boc$_2$O), in water:THF solution for 24 h. The reaction afforded the mono-protected dendrimer **2**, in 75% yield. Double phosphinomethylation of **2** was performed using *in situ* formed PPh$_2$CH$_2$OH, which was prepared from HPPh$_2$ and HCHO [27,28], to afford the phosphinated dendron, in 88% yield. The protecting group was removed subsequently to afford **3**, in 92% yield. The IR spectrum of **3** exhibited disappearance of the vibrational peak, corresponding
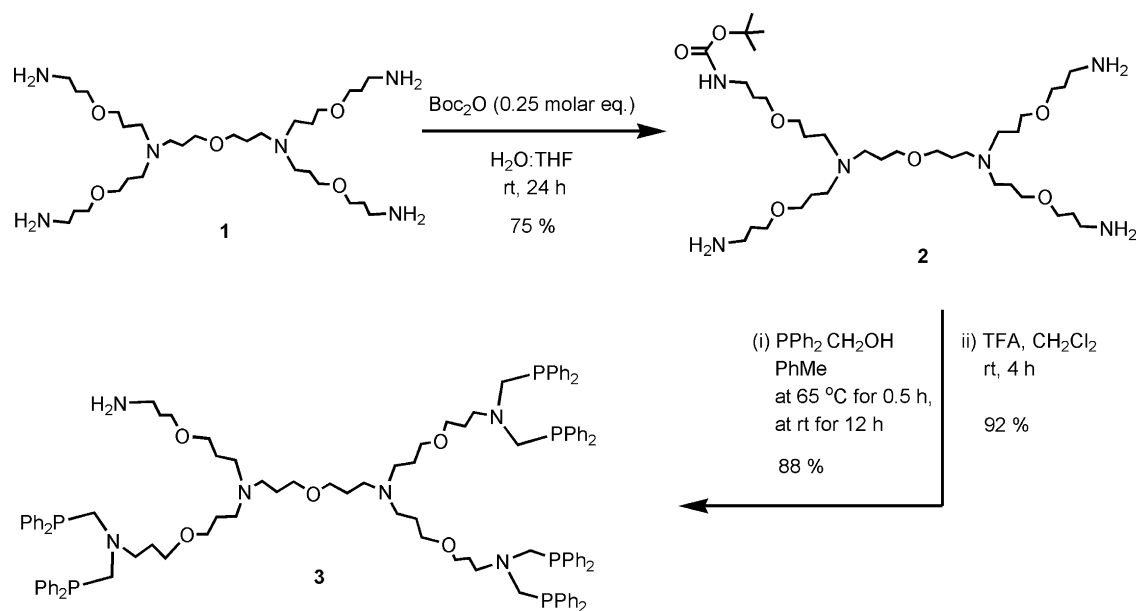
**Scheme 1.** Synthesis of the phosphinated dendrimer **3**.

to tert-butoxy carbonyl group at 1708 cm$^{-1}$. In $^1$H NMR spectrum, the absence of tert-butyl group at $\delta$ 1.42 confirmed the removal the protecting group and the presence of aromatic and methylene resonances confirmed the phosphination of the dendrimer backbone.

Phosphinated dendritic amine **3** was reacted, in the subsequent step, with chloropropylated silica **4** (Scheme 2). The chloropropylated silica **4**, in turn, was prepared [29] upon reaction of silica (9.5–11 μm; pore volume 50–76 Å, surface area 475–560 m$^2$ g$^{-1}$) with chloropropyl trimethoxysilane in PhMe. The silanization process was repeated twice, and the loading of the chloropropyl group was estimated to be 1.16 mmol per gram of silica, calculated on the basis of the elemental analyses results. The presence of a methoxy group in **4** was adjudged from the $^{13}$C NMR spectrum (50.7 ppm). The reaction of the chloropropylated silica **4** with amine **3** was con-

ducted in CHCl$_3$, under reflux, for 24 h. After the reaction, silica was washed with CHCl$_3$ and MeOH, to remove the physisorbed and the unreacted dendritic amine, which is soluble in both these solvents, to afford the phosphinated dendritic amine attached silica **5**.

Solid state $^{29}$Si NMR confirmed the silica matrix and $^{31}$P NMR showed resonance at −28.4 ppm, corresponding to the –PPh$_2$ group (Fig. 1a). Solid state $^{13}$C NMR spectrum exhibited resonances at (i) 128.8 ppm, corresponding to PPh$_2$ nuclei and (ii) 68.7, 51.3, 27.2 and 9.6, corresponding to the skeletal carbon nuclei of **5** (Fig. 2).

These resonances confirmed the presence of the dendritic moiety and the diphenylphosphinomethyl moieties in **5**. Elemental analysis of the resulting silica was performed and from this analysis, the loading of the amine was calculated to be 0.24 mmol per gram of silica.
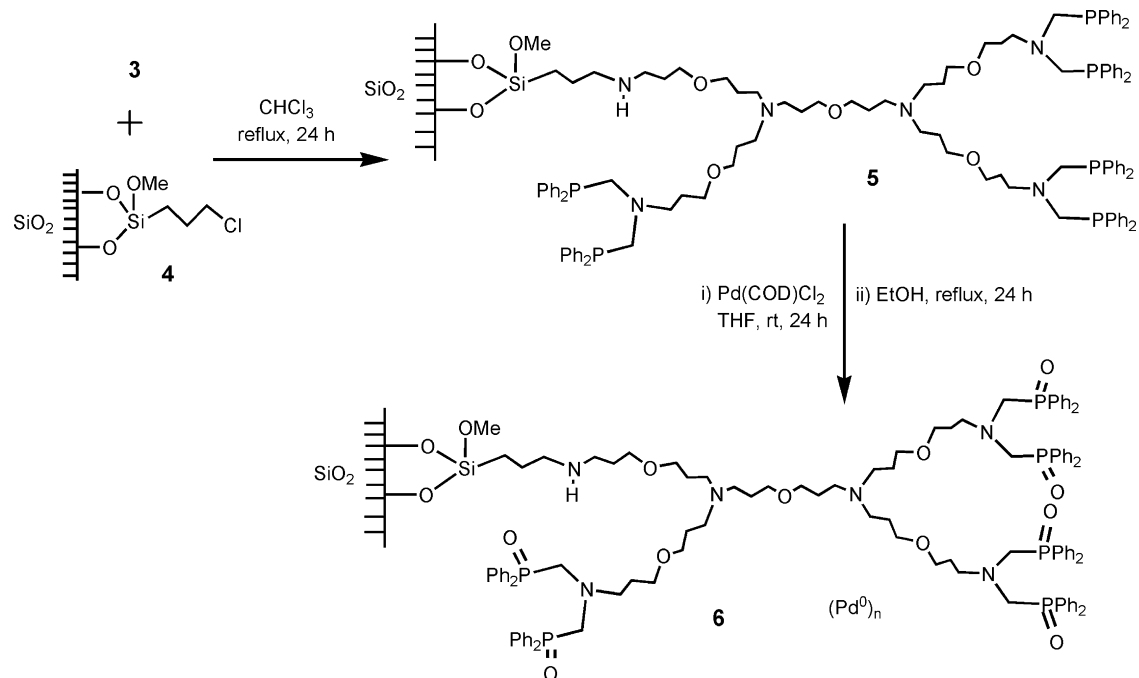


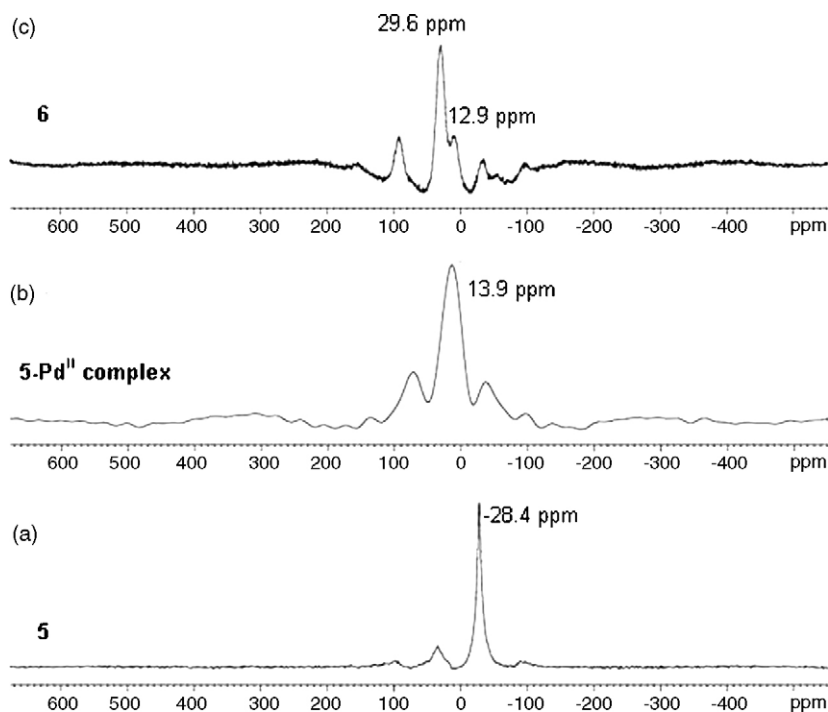**Scheme 2.** Synthesis of Pd nanoparticles on dendritic phosphine functionalized silica.

**Fig. 1.** Solid state $^{31}$P NMR spectra of (a) **5**; (b) **5**-Pd(II) complex and (c) **6**.

Complexation of the functionalized silica **5** with Pd(COD)Cl$_2$ was conducted subsequently. The reaction was conducted in THF for 24 h, followed by removal of the solvent and washing the residue with THF and CH$_2$Cl$_2$ repeatedly (Scheme 2). $^{31}$P NMR spectrum of the residue, on first examination, showed the absence of resonance at −28.4 ppm, whereas, a resonance emerged at 13.9 ppm, denoting the complexation of phosphine ligand with Pd (Fig. 1b). ICP-OES analysis showed that the Pd loading onto the functionalized silica was 0.43 mmol *per* gram of silica. The loading of Pd onto the functionalized silica was anticipated to be 0.72 mmol *per* gram of silica, resulting from a bidendate binding of phosphine ligand to Pd metal. The observed ICP-OES result indicated that all phosphine ligands did not chelate the metal.

With the desire to secure the metal nanoparticles, the complex was subjected to a reduction, which was performed by conditioning **5**-Pd(II) complex in EtOH. This method is known previously [30,31] to obtain metal nanoparticles. The Pd(II)-dendritic phosphine impregnated on silica was refluxed in EtOH. During this process, the yellow color of the silica turned brown, suggesting the formation of Pd particles. After 24 h of conditioning, the mixture was filtered, washed with EtOH repeatedly, and dried to afford the conditioned catalyst **6**. The solid state $^{13}$C NMR spectrum appeared similar to **5**. Solid state $^{31}$P NMR spectrum of **6** exhibited a peak at 29.6 ppm, in addition to a small peak at 12.9 ppm (Fig. 1c). These peaks referred to the presence of phosphine oxide and metal bound phosphine, respectively. The presence of a smaller peak at 12.9 ppm showed that the reduction of Pd(II), impregnated onto functionalized silica **5** was not complete.

X-ray photoelectron spectroscopic (XPS) analysis was performed on **5** and **6**. The metal 3d$_{5/2}$ and 3d$_{3/2}$ electronic states for **5**-Pd(II) complex were observed at 337.6 eV and 342.9 eV, respectively (Fig. 3a). On the other hand, **6** showed photoelectron peaks, corresponding to both Pd(II) and Pd(0) species (Fig. 3b). The metal 3d$_{5/2}$ and 3d$_{3/2}$ electronic states for Pd(0) were observed at 335.6 eV and 340.7 eV, respectively. It also showed peaks at 337.5 eV and 342.6 eV, that corresponded to 3d$_{5/2}$ and 3d$_{3/2}$ electronic states of Pd(II) species, in about 60% [32–34]. The presence of Pd(II) species correlated with the observation of $^{31}$P NMR spectrum (Fig. 1c), due to phosphine-Pd(II) complex.

The efficacy of the conditioned metal nanoparticle **6** to mediate a selected reaction was studied. A catalytic hydrogenation of olefin was chosen, in order to evaluate the efficiencies of the Pd metal impregnated silica. The substrates tested and the observed results are presented in Table 1. It was observed that while the terminal olefins underwent hydrogenation in less than 2 h, the reaction with 1-octene required 4 h for complete conversion. Internal olefins also required longer duration for the hydrogenation. The catalytic activity of the catalyst for hydrogenation of styrene to ethyl benzene was determined to be 1205 mol$^{-1}$ h$^{-1}$, expressed as the turn-over-frequency (TOF). The catalyst was recovered quantitatively after the reaction.

The catalyst recycling experiments were conducted more than 10 times, and no loss in catalytic activities was observed (Table 2). In practice, the recycling was observed to increase the catalytic efficiencies of the catalyst, which was presumed to be due to the complete conversion of Pd(II) to Pd(0), after the hydrogenation reaction. The absence of the peaks at 337.5 eV and 342.6 eV in the XPS spectrum clearly indicated the complete conversion of Pd(0).
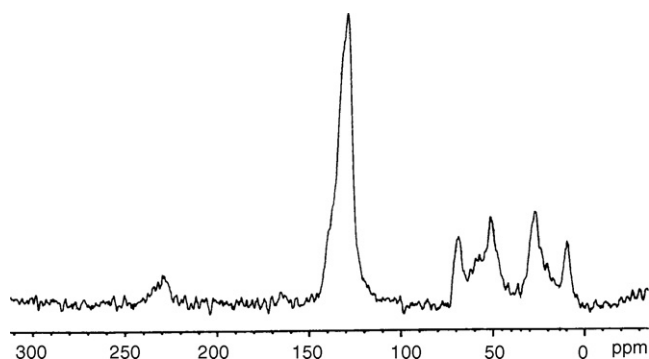


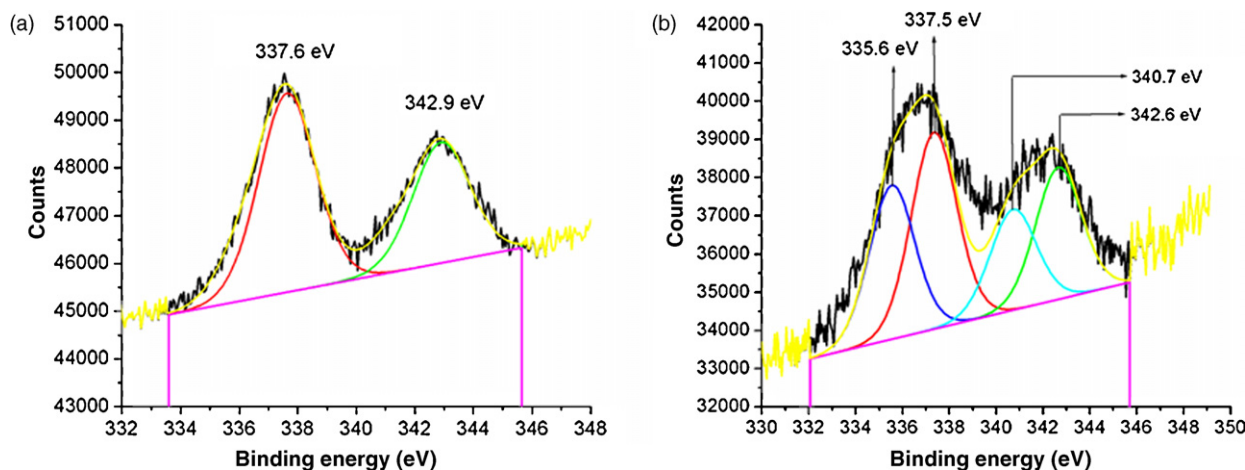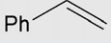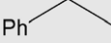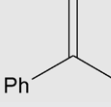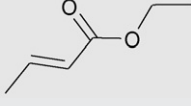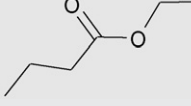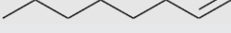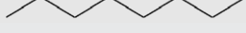**Fig. 2.** Solid state $^{13}$C NMR spectrum of **5**.
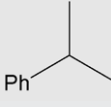
**Fig. 3.** X-ray photoelectron spectra of (a) **5**-Pd(II) complex and (b) **6**.

**Table 1**
Hydrogenation of various olefins[a,b].

| Entry | Substrate | Product | Time (h) | Yield (%) |
|---|---|---|---|---|
| 1 | Ph (styrene) | Ph (ethylbenzene) | 1.5 | 100 |
| 2 | Ph (α-methylstyrene) | Ph (cumene) | 2 | 100 |
| 3 | ethyl acrylate | ethyl propanoate | 5 | 100 |
| 4 | 1-octene | octane | 4 | 100 |

[a] 0.5 mol% of fresh catalyst **6**, in EtOAc (5 mL), H$_2$ (1 atm), 25 °C.
[b] Yields determined based on the GC analyses.

Fig. 4 shows the XPS spectrum of the recycled catalyst. It showed the absence of peaks at 337.5 eV and 342.6 eV, corresponding to Pd(II) moiety and the presence of peaks at 335.6 eV and 340.7 eV, corresponding to 3d$_{5/2}$ and 3d$_{3/2}$ respectively, of Pd(0) species.

Further characterization of the Pd impregnated functionalized silica **6** was conducted by transmission electron microscopy (TEM). TEM image of the conditioned catalyst before the catalysis reaction showed spherical particles and the size distribution for >85% was found to be between 2 nm and 4 nm (Fig. 5a). Such a smaller size range suggested that the metal nanoparticles did not agglomerate, as a result of prior complexation with dendritic phosphine ligands, functionalizing the silica. This narrow size distribution, in turn, led to higher catalytic activity, which was retained even after more than 10 times of recycling. Also, it was found that the catalyst retained its activity after storage for several months, at room temperature.

The effect of the hydrogenation reaction conditions on the catalyst morphology was also examined by TEM on the recycled catalyst (Fig. 5b). The spherical size of the nanoparticle with size distribu-

tion remained nearly the same as that of the fresh catalyst. Loss in the metal composition as a result of recycling was examined by ICP-OES analysis. The metal content was identified to be 0.38 mmol of Pd *per* gram of silica, which compared closely with the metal content value of 0.40 mmol of Pd *per* gram of silica determined for the fresh catalyst.
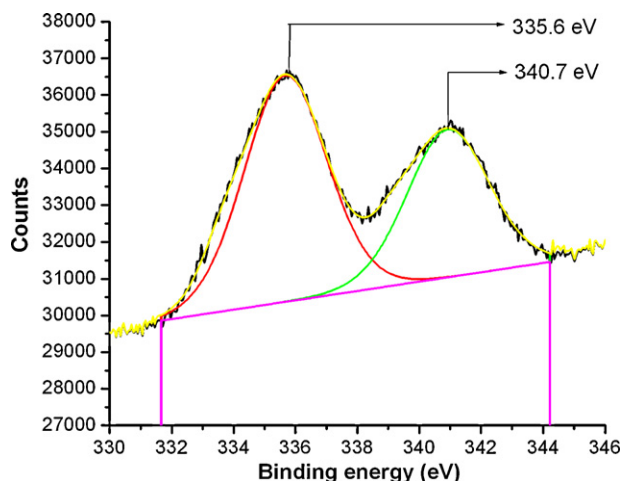
**Table 2**
Recycling of **6**, in the hydrogenation of styrene[a].

| Cycles | 1 | 2 | 3 | 4 | 5 | 6–10 |
|---|---|---|---|---|---|---|
| % Conversion[b] | 94.4 | 100 | 100 | 99 | 100 | 100 |

[a] 0.5 mol% of **6**; in EtOAc (5 mL), H$_2$ (1 atm), 25 °C, 1 h.
[b] Yields determined based on the GC analyses.



**Fig. 4.** X-ray photoelectron spectrum of the fifth time recycled catalyst **6**.
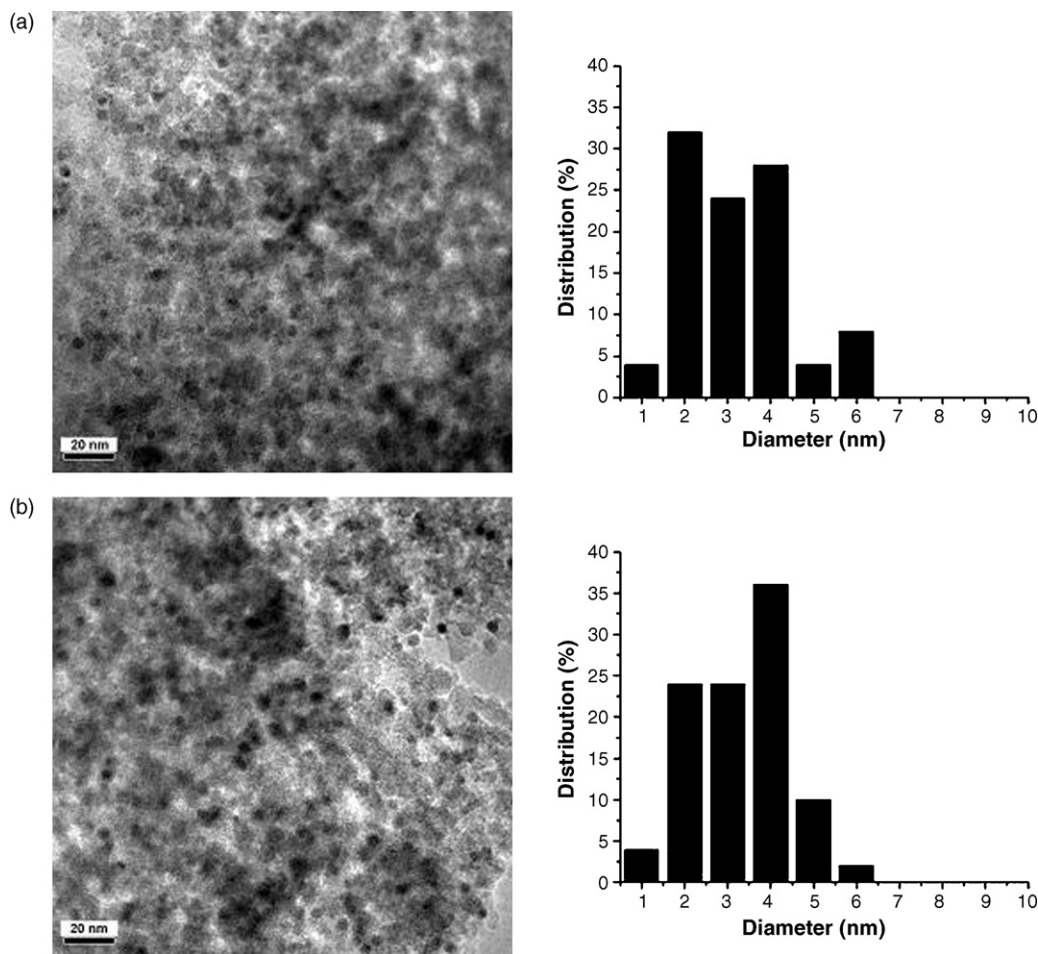
**Fig. 5.** Transmission electron micrographs and histograms of **6**: (a) obtained after treatment with EtOH and (b) fifth time recycled catalyst **6**.

It is pertinent to compare the silica supported dendritic catalysts prepared herein with that known previously. The catalytically active moiety, namely (bis(diphenyl) phosphinomethyl)amino-moiety has been studied previously, upon incorporation to PAMAM dendrimers [16], as well as, resins, such as Wang resin [36]. An early report of the use of the above catalytic moiety in a heterogeneous dendrimer-silica framework is the report of Reynhardt and Alper [35], wherein, the PAMAM dendritic wedges of generations 0–4 were attached with (bis(diphenyl)phosphinomethyl)amino-groups. Upon metallation with Pd(0), the catalysts were used in hydroesterification reactions. The catalysts were recovered and reused several times. Selective hydrogenation of dienes to mono-olefins was also demonstrated using silica supported Pd-based dendrimers. In addition, polystyrene-supported dendritic bidentate phosphine ligands, complexed with Pd(0), were utilized as the catalysts for the Heck and the carbonylation reactions [36]. This study of Portnoy and co-workers demonstrated that dendronisation of the polystyrene matrix influenced the catalytic performances to varying degrees, ranging from improvement in catalysis to negative impact on the catalytic profiles, depending on the type of the reaction which the catalyst mediates. A non-supported, dendritic phosphine-Pd(II) catalyst was also studied in the hydrogenation of dienes to mono-olefins by Kaneda and co-workers [37]. This study demonstrated higher catalytic activities and recyclabilities for the dendritic catalysts, when compared to the monomeric catalysts. Unlike the previous reports, wherein the phosphination of the dendritic amines was performed after attaching the dendritic amines to the solid support, in the present study the phosphination of the dendritic amines was conducted before the dendrimer was bound to the silica matrix. This approach allowed a facile phosphination of the available primary amines in the dendrimer scaffold. Further, the attachment of the phosphinated dendrimer to silica matrix was accomplished, unlike the previous reports, wherein both the dendrimer synthesis and the phosphination were performed on the solid support. An advantage of our approach is the absence of a truncation during phosphination, as the reaction was performed in the homogeneous solution phase. Secondly, we find that the functionalization of silica with phosphinated dendrimer prevents larger sizes of Pd(0) nanoparticles. The presence of the phosphine ligand was found to be important for preventing the large particle formation, as the sizes of the metal particles were observed to be at least ∼20 times larger for the silica functionalized with non-phosphinated dendrimer. The fine dispersion of the metal nanoparticles, with narrow sizes of 2–4 nm, in the functionalized silica matrix and the ligand-promoted stability of the resulting metal nanoparticle could be the reasons for the high catalytic activities, as well as, the multiple reusabilities, without the loss in the catalytic efficacies, of the catalysts prepared herein.

Metal leaching is an impediment in many heterogeneous metal catalysts. A significant reduction in leaching of the metal catalyst studied herein could be attributed to the influence exerted by the dendritic phosphine ligands that facilitated the uptake of the metal. Clearly, a significant reduction in leaching could also contribute to the consistent catalytic activity of the recycled catalyst. The role of the dendritic amine can be summarized as: (i) to functionalize the surfaces of silica matrix; (ii) to covalently link the high affinity metal chelating phosphine ligands; (iii) to facilitate uniform metal uptake by the ligands and (iv) to reduce metal particle

aggregation and the leaching of the metal particles during catalytic reactions.

## 4. Conclusion

A phosphinated PETIM dendrimer was immobilized onto chloropropylated silica, through an amination reaction. The dendritic phosphine moieties immobilized silica were complexed with Pd(II) initially, followed by conversion of Pd(II) to Pd(0) metal nanoparticles, through a conditioning process. It was found that the conditioning process led to only a partial reduction of Pd(II) to Pd(0). A hydrogenation of olefins was studied, in order to assess the efficacies of the Pd nanoparticles, stabilized by dendritic phosphine functionalized silica. The metal nanoparticles mediated the reduction efficiently, and the efficiencies of the reductions were found to be better in the recycling experiments. Complete reduction of Pd(II) to Pd(0) was observed in the recycled catalysts, after the hydrogenation reaction. The functionalized silica-metal nanoparticles were characterized by solid state $^{13}$C, $^{31}$P and $^{29}$Si NMR spectroscopies, elemental, ICP-OES analyses, TEM and XPS analyses. Functionalization of silica with the phosphinated PETIM dendrimer was observed to provide not only uniformly distributed, small metal nanoparticles, but also, higher catalytic activities of the metal nanoparticles, in repeated catalytic cycles. These advantages will be explored further in varied types of organic transformations.

## References

[1] P. Laszlo, Preparative Chemistry Using Supported Reagents, Academic Press, San Diego, 1987.
[2] G. Ertl, H. Knötzinger, J. Weit Kamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 5, Verlag Chemie, Weinheim, 1997.
[3] B.F.G. Johnson, S.A. Raynor, D.S. Shephard, T. Mashmeyer, J.M. Thomas, G. Sankar, S. Bromley, R. Oldroyd, L. Gladden, M.D. Mantle, Chem. Commun. (1999) 1167–1168.
[4] N.J. Meehan, A.J. Sandee, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, M. Poliakoff, Chem. Commun. (2000) 1497–1498.
[5] K.S. Morley, P. Licence, C. Patricia, J.R. Hyde, P.D. Brown, R. Mokaya, Y. Xia, S.M. Howdle, J. Mater. Chem. 14 (2004) 1212–1217.
[6] E.B. Mubofu, J.H. Clark, D.J. Macquarrie, Green Chem. 3 (2001) 23–25.
[7] R.V.S. Alfaya, S.T. Fujiwara, Y. Gushikem, Y.V. Kholin, J. Colloid Interface Sci. 269 (2004) 32–36.
[8] J.-W. Park, Y.-M. Chung, Y.-W. Suh, H.-K. Rhee, Catal. Today 93–95 (2004) 445–450.
[9] J.Y. Shin, B.S. Lee, Y. Jung, S.J. Kim, S.-G. Lee, Chem. Commun. (2007) 5238–5240.
[10] N. Erathodiyil, S. Ooi, A.M. Seayad, Y. Han, S.S. Lee, J.Y. Ying, Chem. Eur. J. 14 (2008) 3118–3125.
[11] M. Trilla, R. Pleixats, M.W.C. Man, C. Bied, J.E. Moreau, Adv. Synth. Catal. 350 (2008) 577–590.
[12] R.B. Bedford, U.G. Singh, R.I. Walton, R.T. Williams, S.A. Davis, Chem. Mater. 17 (2005) 701–707.
[13] G. Singh, S. Bali, A.K. Singh, Polyhedron 26 (2007) 897–903.
[14] S. Antebi, P. Arya, L.E. Manzer, H. Alper, J. Org. Chem. 67 (2002) 6623–6631.
[15] M.K. Richmond, S.L. Scott, H. Alper, J. Am. Chem. Soc. 123 (2001) 10521–10525.
[16] P.P. Zweni, H. Alper, Adv. Synth. Catal. 348 (2006) 725–731 (and references cited therein).
[17] T.R. Krishna, N. Jayaraman, J. Org. Chem. 68 (2003) 9694–9704.
[18] T.R. Krishna, S. Jain, U.S. Tatu, N. Jayaraman, Tetrahedron 61 (2005) 4281–4288.
[19] T.R. Krishna, N. Jayaraman, Tetrahedron 60 (2004) 10325–10334.
[20] G. Jayamurugan, N. Jayaraman, Tetrahedron 62 (2006) 9582–9588.
[21] G. Jayamurugan, C.P. Umesh, N. Jayaraman, Org. Lett. 10 (2008) 9–12.
[22] C. Jana, G. Jayamurugan, R. Ganapathy, P.K. Maiti, N. Jayaraman, A.K. Sood, J. Chem. Phys. 124 (2006) (204719/1-204719/10).
[23] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd ed., Pergamon, Oxford, 1988.
[24] D. Drew, J.R. Doyle, Inorg. Synth. 13 (1972) 52–55.
[25] U. Deschler, P. Kleinschmit, P. Panster, Angew. Chem. Int. Ed. Engl. 25 (1986) 237–252.
[26] C. Airoldi, M.R.M.C. Santos, J. Mater. Chem. 4 (1994) 1479–1485.
[27] S.O. Grim, L.J. Matienzo, Tetrahedron Lett. 14 (1973) 2951–2953.
[28] M.T. Reetz, G. Lohmer, R. Schwickardi, Angew. Chem. Int. Ed. Engl. 36 (1997) 1526–1529.
[29] T.M. Jyothi, M.L. Kaliya, M.V. Landau, Angew. Chem. Int. Ed. 40 (2001) 2881–2884.
[30] T. Teranishi, M. Miyake, Chem. Mater. 10 (1998) 594–600.
[31] A.W. Bosman, R. Vestberg, A. Heumann, J.M.J. Fréchet, C.J. Hawker, J. Am. Chem. Soc. 125 (2003) 715–728.
[32] V. Calo, A. Nacci, A. Monopoli, A. Fornaro, L. Sabbatini, N. Cioffi, N. Ditaranto, Organometallics 23 (2004) 5154–5158.
[33] T. Mizugaki, M. Murata, M. Ooe, K. Ebitani, K. Kaneda, Chem. Commun. (2002) 52–53.
[34] M. Terasawa, K. Kaneda, T. Imanaka, S. Teranishi, J. Organomet. Chem. 162 (1978) 403–414.
[35] J.P.K. Reynhardt, H. Alper, J. Org. Chem. 68 (2003) 8353–8360.
[36] A. Mansour, T. Kehat, M. Portnoy, Org. Biomol. Chem. 6 (2008) 3382–3387.
[37] T. Mizugaki, M. Ooe, K. Ebitani, K. Kaneda, J. Mol. Catal. A: Chem. 145 (1999) 329–333.