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Pd nanosized particles supported on chitosan and 6-deoxy-6-amino chitosan as recyclable catalysts for Suzuki–Miyaura and Heck cross-coupling reactions

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ABSTRACT

Several chitosan and 6-deoxy-6-amino chitosan-Schiff base ligands (1–4) were prepared by condensation of either 2-pyridinecarboxaldehyde or 2-(diphenylphosphino)benzaldehyde with the amino group(s) on chitosan and its derivative (6-deoxy-6-amino chitosan). The supported ligands were reacted with $[PdCl_2(COD)]$ to form chitosan-supported Pd^{II} catalysts (5–8). All the supported catalysts were air- and moisture-stable and have been characterized using elemental analysis, ICP-MS, UV-vis, FT-IR, PXRD, TGA, ³¹P solid state NMR and TEM. As models for the heterogenized catalysts (5 and 6), monouclear Pd^{II} complexes (9 and 10) were also prepared *via* the Schiff-base condensation reaction of 1,3,4,6-tetra-O-acetyl- β -D-glucos-2-(diphenylphosphino)imine which were subsequently reacted with [PdCl_2(COD)]. Complexes (9 and 10) and their precursors were characterized by ¹H and ³¹P NMR, UV-vis, FT-IR spectroscopy and elemental analysis.

Catalytic Suzuki–Miyaura and Heck carbon–carbon cross-coupling reactions were carried out using the supported Pd catalysts and their mononuclear analogues. The immobilized and homogeneous catalysts showed high activity for both the Suzuki–Miyaura and Heck cross-coupling reactions in organic and aqueous media. Homogeneous catalysts (9 and 10) decomposed during the first run, while the supported catalysts could be recycled and reused up to five times.

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1. Introduction

Palladium-catalyzed cross coupling reactions of organo-halides with olefins (Heck) and organo-boronic acids (Suzuki) for carbon–carbon bond formation are extremely useful to the chemical industry and in research. Since their discovery they have evolved into a general technique in preparing biologically active functionalized biphenyls which are important intermediates or products in drug discovery, pharmaceuticals and agricultural compounds [1,2].

Historically, palladium complexes such as $[Pd(OAc)_2]$ and $[Pd(PPh_3)_2Cl_2]$ have been widely used as homogeneous catalyst systems in cross coupling reactions [1]. However, these homogeneous catalytic systems suffer from problems associated with the separation and recovery of the active catalyst as well as instability at high temperatures. These drawbacks have so far precluded their industrial exploitation [3]. Also from the perspective of process development, homogeneous catalysts require expensive phosphine ligands (to generate the active catalyst) which are often not available in bulk. Metal contamination of the products is inevitable when using homogeneous catalysts, an undesirable

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result especially in the pharmaceutical industry [1,2]. Therefore, there is a need to develop improved and practical strategies for recycling active catalysts for economical and environmental stewardship reasons [3].

Most of the problems related to homogeneous catalysts can be solved by immobilizing the catalyst or catalyst precursor on polymer supports with good solvation attributes [4–6]. For example, supporting transition metal catalysts on insoluble polymer supports can improve their stability without compromise in the activity and selectivity of the homogeneous catalyst. Supported catalysts also allow simplified recovery and reuse of the catalyst as well as physical separation of the active site, thus minimizing catalyst self-destruction [6a–b].

Due to the inherent advantages of heterogenizing homogeneous catalysts through immobilization on solid supports, a great deal of effort has been devoted to these developments [4–6]. However, the majority of these reported catalysts are based on synthetic organic polymer supports (polystyrene, poly(ethylene)glycol, etc.) and inorganic supports (silica, alumina or other metal oxides). Some of these supported catalysts, such as [Pd(PPh₃)₄]-crosslinked polystyrene-bound and Pd⁰ on alumina, are commercially available [5a–c]. Recent efforts in the development of cleaner and sustainable chemistry have lead to the use of biopolymers as catalyst supports. Biopolymers are readily available in nature and can be used

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Fig. 1. Idealized structures of chitin and chitosan. (Chitosan is rarely 100% deacetylated, so it is more accurately described as a copolymer intermediate between chitin and chitosan.).

as suitable supports for many reagents and catalysts, offering the advantages of being renewable, biodegradable and non-toxic. As such, biopolymers such as cellulose, gelatine and starch have been investigated as catalyst supports [6].

Chitosan is produced by deacetylation of the abundant biopolymer chitin, a key constituent of the exoskeletons of crustaceans and the cell walls of algae (Fig. 1) [4,6,7]. It has been shown to exhibit interesting biopesticidal, antifungal and anticancer properties and has been used successfully in food and water treatment [6a,7a–e].

Chitosan can be readily transformed into films or fibres and has found applications as adsorbents for metals, in medicine and in drug delivery [4,6,7]. Its chirality, insolubility (in many organic solvents) and capability of being cast into films and fibres from dilute acid makes chitosan an excellent candidate as a support for catalysts. In this respect, several catalytic systems using chitosan as a support are known [6,8]. Functionalization of chitosan to provide coordination sites has been carried out and this has provided catalysts for oxidation, cyclopropanation of olefins, Suzuki and Heck cross coupling reactions [4,7,9].

We now present our work on the synthesis, characterization and evaluation of chitosan- and 6-deoxy-6-amino chitosan-supported Schiff base Pd^{II} complexes and mononuclear Pd^{II} complexes in the catalytic Suzuki-Miyaura and Heck cross coupling reactions. Our aim was to use chitosan and 6-deoxy-6-amino chitosan-supports to aid catalyst recovery, reuse and stability. Chitosan-supported Pd^{II} iminopyridyl catalysts, were reported to catalyze Heck and Suzuki cross-coupling reactions [4b,9f]. This work has expanded on this by preparing new iminophosphine and iminopyridyl Pd^{II} supported catalysts for Suzuki and Heck cross-coupling reactions. Chitosan has been modified to 6-deoxy-6-amino chitosan for increased solubility purposes and application as a gene carrier [10d]. Furthermore, the synthetic methodology for this has been improved to obtain higher amine loading [10a]. Increased solubility and metal loading was expected of the modified chitosan, therefore the activity and efficiency of catalysts (7 and 8) were compared to (5 and 6) and these in turn to homogeneous catalysts (9 and 10).

2. Experimental

Low molecular weight chitosan (Cat. No. 44,886-9, deacetylation 75–85%), 1,5-cyclooctadiene (COD), 2-pyridinecarboxaldehyde and 2(diphenylphosphino)benzaldehyde were purchased from Sigma–Aldrich and used as received. 6-Deoxy-6-amino chitosan [10a] and 1,3,4,6-tetra-O-acetyl- β -D-glucosamine hydrochloride [11a] were prepared according to reported procedures. All solvents were obtained commercially and distilled under N₂ prior to use. Methanol, ethanol, dichloromethane and acetone were dried over calcium hydride. PdCl₂ was obtained from Johnson Matthey and [PdCl₂(COD)] [11b], was prepared according to a literature procedure.

UV–vis spectra were obtained at ambient temperature using a Varian Cary 50 Conc. UV–vis spectrophotometer as glycerol mulls. Powder X-ray diffraction (PXRD) data was collected on a Bruker D8 Advanced diffractometer. IR spectra were recorded as KBr disks on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Elemental analyses were conducted with a Thermo Flash 1112 Series CHNS-O Analyzer. Inductively coupled plasma-mass spectrometry was obtained using a Perkin-Elmer Elan600 quadrupole ICP-MS with a Cetax LSX-200 UV laser module. TEM imaging was done on a JEOL 1200EXII CRYO TEM. Catalysis products were analysed using a Varian 3900 GC. ¹H and ³¹P NMR spectra were recorded on a Varian XR400 MHz spectrometer using tetramethylsilane (TMS) as the internal standard (for ¹H) and H₃PO₄ as the external standard (for ³¹P).

2.1. General procedure for the synthesis of 6-deoxy-6-amino chitosan- and chitosan-Schiff base ligands (1–4)

Chitosan and the corresponding aldehydes (30 mmol) were refluxed in methanol (30 ml) and acetic acid (3 ml) for 10 h. After completion of the reaction, the chitosan-Schiff base ligands were collected by filtration and washed thoroughly with distilled water, ethanol then acetone (50 ml each), respectively. The product was then dried under vacuum at $60 \,^{\circ}$ C for 8 h.

6-Deoxy-6-amino chitosan-Schiff base ligands (**3**) and (**4**) were prepared by a similar procedure as above.

2.1.1. Preparation of chitosan-2-pyridylimine (1)

Compound (1) was prepared using chitosan (1.90 g) and 2pyridinecarboxaldehyde (2.87 ml, 30.08 mmol). The product was obtained as a light brown solid. Yield by mass (1.60 g, 84%). *FT-IR* (KBr): 3422 ν (OH), 2881 ν (C–H), 1649, ν (C=N), 1590 ν (pyridyl C=N), 1569 ν (C=C), 1153–1070 ν (pyranose), 776 cm⁻¹ ν (aromatic C–H). Elemental analysis, Found: C, 54.79; H, 6.02; N, 10.39.

2.1.2. Preparation of chitosan-2(diphenylphosphino)imine (2)

Compound (2) was prepared using chitosan (0.500 g) and 2-(diphenylphosphino)benzaldehyde (0.160 g, 0.56 mmol). The product was obtained as a light brown solid. Yield by mass (0.725 g, 69%). *FT-IR* (KBr): 3429 ν (OH), 2917 ν (C–H), 1642, ν (C=N), 1577 ν (aromatic C=C), 1158–1024 ν (pyranose), 665 cm⁻¹ ν (aromatic C–H). Elemental analysis, Found: C, 44.63; H, 6.92; N, 7.03.

2.1.3. Preparation of 6-deoxy-6-amino chitosan-2muriduliming (2)

pyridylimine (**3**)

Compound (**3**) was prepared using 6-deoxy-6-amino chitosan (400 mg) and 2-pyridinecarboxaldehyde (1.20 ml, 12.53 mmol). The product was obtained as a brown solid. Yield by mass (241 mg, 60%). *FT-IR* (KBr): 3434 ν (OH), 2919 ν (C–H), 1648 ν (C=N), 1591 ν (pyridyl C=N), 1569 ν (aromatic C=C), 1154–1069 ν (pyranose), 777 cm⁻¹ ν (aromatic C–H). Elemental analysis, Found: C, 50.08; H, 5.89; N, 9.10.

2.1.4. Preparation of 6-deoxy-6-amino 2(diphenylphosphino) imine (**4**)

Compound (**4**) was prepared using 6-deoxy-6-amino chitosan (500 mg) and 2-(diphenylphosphino)benzaldehyde (142 mg, 0.490 mmol). The product was obtained as an orange solid.

Yield by mass (324 mg, 65%). *FT-IR* (KBr): 3436 ν (OH), 2913 ν (C–H), 1639 ν (C=N), 1154–1023 ν (pyranose), 697 cm⁻¹ ν (aromatic C–H). Elemental analysis, Found: C, 45.66; H, 6.22; N, 7.28.

2.2. General procedure for the synthesis of 6-deoxy-6-amino chitosan- and chitosan-Schiff base Pd^{II} catalysts (**5–8**)

The 6-deoxy-6-amino chitosan- and chitosan-Schiff base ligands were stirred with a solution of $[PdCl_2(COD)]$ in acetone, at room temperature over 48 h. After the reaction, the supported Schiff base catalysts were collected by filtration, washed with distilled water, ethanol then acetone (50 ml each), respectively then dried under vacuum at 60 °C for 8 h.

2.2.1. Preparation of chitosan–2-pyridylimine–Pd catalyst (5)

Catalyst (**5**) was prepared using chitosan-Schiff base (**1**)(500 mg, 0.025 mmol) and [PdCl₂(COD)] (21 mg, 0.075 mmol). The product was obtained as a yellow solid. Yield by mass (482 mg, 96%). *FT-IR* (KBr): 3418 ν (OH), 2881 ν (C–H), 1651 ν (C=N), 1591 ν (pyridyl C=N), 1569 ν (aromatic C=C), 1152–1068 ν (pyranose), 776 cm⁻¹ ν (aromatic C–H). Elemental analysis, Found: C, 48.82; H, 5.92; N, 9.05. *ICP-MS* (Pd, mmol g⁻¹): 0.044.

2.2.2. Preparation of chitosan–2(diphenylphosphino)imine–Pd catalyst (**6**)

Catalyst (**6**) was prepared using chitosan-Schiff base (**2**) (350 mg, 0.035 mmol) and [PdCl₂(COD)] (30 mg, 0.105 mmol). The product was obtained as a pale yellow solid. Yield by mass (310 mg, 88%). *FT-IR* (KBr): 3429 ν (OH), 2920 ν (C–H), 1639 ν (C=N), 1576 ν (aromatic C=C), 1154–1023 ν (pyranose), 669 cm⁻¹ ν (aromatic C–H). Elemental analysis, Found: C, 44.54; H, 5.65; N, 5.10. *ICP-MS* (Pd): 0.054 mmol g⁻¹.

2.2.3. Preparation of 6-deoxy-6-amino chitosan-2-pyridylimine-Pd catalyst (**7**)

Catalyst (**7**) was prepared using 6-deoxy-6-amino chitosan-Schiff base (**3**) (200 mg, 0.02 mmol) and [PdCl₂(COD)] (17 mg, 0.06 mmol). The product was obtained as a dark yellow solid. Yield by mass (218 mg, 91%). *FT-IR* (KBr): 3419 ν (OH), 2918 ν (C–H), 1639 ν (C=N), 1595 ν (pyridyl C=N), 1566 ν (aromatic C=C), 1152–1066 ν (pyranose), 775 cm⁻¹ ν (aromatic C–H). Elemental analysis, Found: C, 44.08; H, 5.70; N, 7.42. *ICP-MS* (Pd): 0.121 mmol g⁻¹.

2.2.4. Preparation of 6-deoxy-6-amino chitosan–2 (diphenylphosphino)imine–Pd catalyst (**8**)

Catalyst (8) was prepared using 6-deoxy-6-amino chitosan-Schiff base (4) (350 mg, 0.035 mmol) and [PdCl₂(COD)] (15 mg, 0.052 mmol). The product was obtained as a dark orange solid. Yield by mass (100 mg, 67%). *FT-IR* (KBr): 3428 ν (OH), 2920 ν (C–H), 1638 ν (C=N), 1576 ν (aromatic C=C), 1152–1021 ν (pyranose), 667 cm⁻¹ ν (aromatic C–H). Elemental analysis, Found: C, 42.08; H, 6.50; N, 4.12. *ICP-MS* (Pd): 0.123 mmol g⁻¹.

2.2.5. Preparation of 1,3,4,6-tetra-O-acetyl- β -D-glucosyl-2-pyridyliminepalladium(II) complex (**9**)

1,3,4,6-tetra-O-acetyl-β-D-glucosamine hydrochloride (500 mg, 1.440 mmol) was treated with Et₃N (218 mg, 2.160 mmol) in dry CH₂Cl₂ (30 ml) for 15 min. 2-Pyridinecarboxaldehyde (154 mg, 1.440 mmol) was then added to the solution and the contents were stirred for 24 h at room temperature. Anhydrous magnesium sulphate was transferred to the stirred solution and the mixture was filtered, the solvent was removed by rotary evaporation to give a white solid of the 1,3,4,6-tetra-O-acetyl-β-D-glucosyl-2-pyridylimine ligand. Yield (243 mg, 90%). Mp.: 49–52 °C. *FT-IR* (KBr): 2960 (s) ν(C–H), 1754 (vs) ν(C=O), 1650 (s) ν(C=N), 1588

(m) ν (pyridyl C=N), 1569 (m) ν (aromatic C=C), 1220–1206 (vs) ν (pyranose), 779 cm⁻¹ (s) ν (aromatic C–H). ¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ (ppm) = 8.66 (d, 1H, *J* = 4.8 Hz, Ar_{pyr}), 8.36 (s, 1H, imine), 8.00 (m, 1H, Ar_{pyr}), 7.76 (m, 1H, Ar_{pyr}), 7.36 (m, 1H, Ar_{pyr}), 6.00 (d, 1H, *J*_{1,2} = 9.5 Hz, H-1), 5.48 (t, 1H, *J*_{3,4} = 9.7 Hz, H-3), 5.18 (t, 1H, *J*_{2,3} = 8.37 Hz, H-2), 4.16 (dd, 2H, *J*_{5,6} = 1.9, 12.4 Hz, H-6), 4.00 (m, 1H, H-4), 3.60 (dd, 1H, *J*_{4,5} = 9.5 Hz, H-5), 1.98–2.21 (4s, 12H, OAc).

[PdCl₂(COD)] (131 mg, 0.459 mmol) was added to the 1,3,4,6tetra-O-acetyl-β-D-glucosyl-2-pyridylimine ligand (200 mg, 0.459 mmol) in dry CH₂Cl₂ (25 ml) and this stirred at room temperature. After 12 h, the solvent was removed by rotary evaporation to afford an orange solid which was washed with *n*-hexane $(3 \times 25 \text{ ml})$ and dried under vacuum for 2 h. Compound (9); Yield (180 mg, 90%). Mp.: decomp. without melting at 248 °C. FT-IR (KBr): 2957 (s) v(C-H), 1754 (vs) v(C=O), 1624 (s) ν (C=N), 1593 (m) ν (pyridyl C=N), 1569 (m) ν (aromatic C=C), 1224–1214 (vs) ν (pyranose), 770 cm⁻¹ (s) ν (aromatic C–H). ¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ (ppm)=9.03 (d, 1H, J=5.3 Hz, Ar_{pyr}), 8.80 (s, 1H, imine), 8.36 (m, 1H, Ar_{pyr}), 8.17 (m, 1H, Ar_{pyr}), 7.91 (m, 1H, Ar_{pyr}), 6.44 (d, 1H, $J_{1,2}$ = 8.37 Hz, H-1), 5.44 (m, 1H, H-3), 5.21 (t, 1H, J_{2,3} = 9.1 Hz, H-2), 4.24 (dd, 2H, J_{4.5} = 4.1, 12.6 Hz, H-6), 4.12 (m, 1H, H-4), 3.99 (m, 1H, H-5, 1.92-2.29 (4s, 12H, OAc). Elemental analysis calculated for C₂₀H₂₄Cl₂N₂O₉Pd: C, 39,14; H, 3.94, N, 4.56, Found: C, 39.33; H, 3.10; N, 4.77.

2.2.6. Preparation of 1,3,4,6-tetra-O-acetyl-β-D-glucosyl-2 (diphenylphosphino)imine palladium(II) complex (**10**)

1,3,4,6-Tetra-O-acetyl-β-D-glucosamine hydrochloride (280 mg, 0.806 mmol) was treated with Et₃N (122 mg,1.209 mmol) in dry CH_2Cl_2 (25 ml) for 15 min. 2-(Diphenylphosphino)benzaldehyde (233 mg, 0.806 mmol) was then added to the solution and the contents were stirred for 24 h at room temperature. Anhydrous magnesium sulphate was transferred to the stirred solution and the mixture was filtered, the solvent was removed by rotary evaporation to give a yellow solid of the 1,3,4,6-tetra-O-acetyl-β-D-glucosyl-2(diphenylphosphino)imine ligand which was dried under vacuum for 2 h. Yield (218 mg, 78%). Mp.: 109-111 °C. FT-IR (KBr): 2977 (s) v(C-H), 1755 (vs) v(C=O), 1697 (s) v(C=N), 1674 (s) v(aromatic C=C), 1254–1228 (vs) v(pyranose), 700 cm⁻¹ (s) v(aromatic C–H). ¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ (ppm)=7.97 (s, 1H, imine), 6.98-7.52 (br m, 14H, Arpyr, Ph), 5.46 (d, 1H, J_{1.2} = 8.5 Hz, H-1), 5.03 (m, 1H, H-3), 4.11 (m, 1H, H-2), 4.08 (d, 2H, J_{5.6} = 2.0 Hz, H-6), 3.82 (m, 1H, H-4), 3.03 (m, 1H, H-5), 2.03–2.17 (4s, 12H, OAc). ${}^{31}P{}^{1}H{}$ NMR (121 MHz, DMSO-d₆, 25 °C): δ (ppm) = -13.01, (s).

[PdCl₂(COD)] (184 mg, 0.646 mmol) was added to the 1,3,4,6tetra-O-acetyl-β-D-glucosyl-2(diphenylphosphino)imine ligand (400 mg, 0.646 mmol) in dry CH₂Cl₂ (30 ml) and this stirred at room temperature. After 12 h, the solvent was removed by rotary evaporation to afford a yellow solid which was washed with *n*-hexane $(3 \times 25 \text{ ml})$ and dried under vacuum for 2 h. Yield (401 mg, 92%). Mp.: 146–147 °C. FT-IR (KBr): 2946 (s) ν(C-H), 1747 (vs) ν (C=O), 1676 (s) ν (C=N), 1573 (m) ν (aromatic C=C), 1242–1211 (vs) v(pyranose), 693 cm⁻¹ (s) v(aromatic C–H). ¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ (ppm)=8.61 (s, 1H, imine), 7.36–7.52 (br m, 14H, Ar_{pyr}, Ph), 5.93 (d, 1H, J_{1,2} = 8.20 Hz, H-1), 5.39 (m, 1H, H-3), 5.21 (t, 1H, J_{2,3} = 9.7 Hz, H-2), 4.17 (dd, 2H, $J_{4,5}$ = 4.1, 12.0 Hz, H-6), 4.00 (m, 1H, H-4), 3.54 (m, 1H, H-5), 1.92-2.05 (4s, 12H, OAc). ³¹P{¹H} NMR (121 MHz, DMSO-d₆, 25 °C): δ (ppm)=35.99, (s). Elemental analysis calculated for C₃₃H₃₄Cl₂NO_{9P}Pd: C, 49,74; H, 4.30, N, 1.76, Found: C, 49.18; H, 4.58; N, 1.77.

2.3. General procedure for the Suzuki-Miyaura reaction

The general procedure used for the Suzuki–Miyaura crosscoupling reactions was as follows:

A quantity equivalent to $(4.47 \times 10^{-4} \text{ mmol})$ of either one of the Pd catalyst (5-10) was suspended in the corresponding solvent (xylene or EtOH:H₂O, 50:50) (20 ml) and the arylhalide (5.1 mmol), phenyl boronic acid (7.5 mmol), base (10 mmol) and *n*-decane (4.4 mmol) were added. The reaction mixture was then heated at the appropriate temperature and followed by GC using *n*-decane as the internal standard. The conversion was calculated relative to arylhalide, the limiting reagent of the reaction.

In the case of the Pd leaching tests, 4 molar equivalents of mercury was also added to the reaction mixture. For catalyst recycling experiments, the recovered catalysts was washed with water, ethanol and acetone (80 ml each), respectively, oven dried at $80 \degree C$ for 8 h and reused in the subsequent run.

2.4. General procedure for the Heck reaction

A quantity equivalent to (0.00437 mmol, 0.00044 mol%) of either one of the Pd catalysts (**5–8**) was suspended in DMF (20 ml) and arylhalide (5.3 mmol), methyl acrylate or styrene (5.3 mmol), triethylamine (10 mmol) and *n*-decane (4.4 mmol) were added. The reaction mixture was then heated at 130 °C and followed by GC using *n*-decane as the internal standard. The conversion was calculated relative to arylhalide.

3. Results and discussion

3.1. Catalyst characterization

Stirring chitosan Schiff base ligands (1–4) with [PdCl₂(COD)] precursor complex in acetone over 48 h (Schemes 1 and 2) resulted in the respective formation of several chitosan-supported Pd^{II} catalysts (5–8). The chitosan catalysts (5–8) were obtained in good to moderate yields. The yellow to dark yellow supported-catalysts proved to be air- and moisture-stable and have been stored on the bench-top for up to 12 months without disintegration. The catalysts were characterized using elemental analysis, ICP-MS, UV-vis, FT-IR, TGA, PXRD and TEM.

Comparison of the elemental analyses results of the supported Schiff base ligands (1-4) (Schemes 1 and 2) with the corresponding

catalysts (**5–8**) evidenced partial complexation of the Pd, through decreases in the percentage of CHN content in the materials (Tables 1 and 2). Approximately 20% of the nitrogens in the low molecular weight chitosan used in these experiments were acety-lated. Therefore, 2.10 mmol g⁻¹ are present as free NH₂ units [4b]. Of these supported ligands, 7% (**1**) and 6% (**2**), have been functionalized with Schiff base groups. This corresponds to 0.150 mmol g⁻¹ (**1**) and 0.120 mmol g⁻¹ (**2**), final loading of the ligand sites (Table 1).

The free NH₂ functionalities in 6-deoxy-6-amino chitosan amounts to 2.99 mmol g⁻¹. Of these 7% (**3**) and 6% (**4**) were functionalized with 2-pyridylimine and 2(diphenylphosphino)imine groups, respectively. Loading of the imine ligands in (**3**) and (**4**) was higher than that of (**1**) and (**2**), this was expected due to the presence of more NH₂ sites in 6-deoxy-6-amino chitosan (Table 1). From the analyses, it can be seen that not all NH₂ sites have reacted to form imines, suggesting that many are inaccessible given that chitosan is a weakly swelling polymer at pH 3–4.5 in methanol, as 15% of the polymer is still acetylated.

In addition to elemental analysis, the loading of ligand sites was also determined using UV spectrophotometry, by measuring the absorbance of increasing amounts $(0.5-11.0 \times 10^{-6} \text{ M}, \text{ in methanol})$ of the aldehydes (2-pyridinecarboxaldehyde and 2(diphenylphosphino)benzaldehyde) which gave linear (*R* = 0.995) calibration curves. Thus, the absorbances of the supported imines, once cleaved with dilute HCl were measured and used to determine the imine loading (Table 1) [10b].

The degree of substitution (DS) was calculated from the elemental analyses results using Eq. (1) [12]. This equation slightly overestimates the values obtained by UV analysis, potentially due to the residual water molecules in the biopolymer (Table 1).

$$DS = \frac{\Delta_{C/N}}{\{M_{C/N}(1 - DA)\}},$$
(1)

where $\Delta_{C/N}$ is the C/N percentage ratio differences of these elements in the derivatives and in the original starting material (chitosan or 6-deoxy-6-amino chitosan), $M_{C/N}$ is the ratio of C to N molar mass and DA is the degree of acetylation of the starting material [12].

The metal loading was determined using ICP-MS, and the results showed Pd loadings of 0.044 (**5**), 0.054 (**6**), 0.121 (**7**) and 0.123 mmol g^{-1} (**8**) (Table 2). Thus for the supported Pd catalysts approximately 27% (**5**), 45% (**6**), 60% (**7**) and 62% (**8**) of the ligands are occupied by metal. Generally, the Pd loading levels on the sup-



Scheme 1. Outline for the preparation of supported Schiff base ligands (1 and 2) and supported catalysts (5 and 6).



Scheme 2. Outline for the preparation of supported Schiff base ligands (3 and 4) and supported catalysts (7 and 8).

Table 1 Microanalyses, yields and degree of substitution (DS) of chitosan-Schiff base ligands.

Biopolymer/chitosan-ligand	Elemental analysis EA (%)				$Loading(DS)(mmol g^{-1})$		Yield (%)
	С	Н	Ν	C/N	EA	UV ^a	
Chitosan	40.92	6.89	7.85	5.21	2.10 ^b	-	-
6-Deoxy-6-amino chitosan	44.35	7.04	8.14	5.45	2.99 ^c	-	-
1	54.79	6.02	10.39	5.27	0.15	0.13	84
2	44.63	6.92	7.03	6.34	0.12	0.12	69
3	50.08	5.89	9.10	5.50	0.20	0.18	60
4	45.66	6.22	7.28	6.27	0.18	0.14	65

^a Absorbance is dependent on conc, solvent and pH [10b].

^b Free NH₂ determined using literature [4b].

^c Loading of NH₂ in 6-deoxy-6-amino chitosan previously determined by a fluorescamine assay [10a].

ported catalysts are comparable to similar catalysts in literature [4a-c].

UV-vis studies were conducted on complexes (9) and (10), in order to confirm the molecular Pd^{II} loading onto catalysts (5) and (6). Similar to complexes (9) and (10) (absorbance peaks at 360 nm and 330 nm, respectively), catalysts (5) and (6) displayed absorbance peaks at 358 nm and 332 nm, respectively (Fig. 2(a)-(d)). The presence of similar, though weak absorbance peaks for catalysts (5) and (6), suggests that a low loading of Pd complexes on the chitosan structure has been attained [4a].

The IR spectral data for the chitosan-Schiff base derivatives (1-4) showed characteristic imine (C=N) stretching vibrations in the range of 1631–1648 cm⁻¹. There were also new bands in the

range of 1559–1590 and $695-817 \, \text{cm}^{-1}$ which were not present in the starting materials (chitosan or 6-deoxy-6-amino chitosan). They were attributed to the C=C and C-H stretching vibrations in the aromatic ring of the Schiff-base ligands.

Upon complexation of the chitosan-Schiff bases with Pd, subtle shifts in the imine stretching vibrations were observed. This is possibly due to low degree of incorporation of the Pd. Also, overlapping of the imine bands coordinated to Pd with those that are uncoordinated may occur since most of the imine sites were left unaltered during complexation.

The chitosan-based catalysts and their corresponding chitosan-Schiff base ligands proved to be insoluble in most common solvents including THF, EtOH, MeOH, acetone and water, but showed slight swelling in DMSO.

Table 2
Microanalyses, yields and Pd content of chitosan-Schiff base catalysts.

Chitosan-catalyst	Metal	Elemental a	Elemental analysis EA (%)			Pd loading (mmol g^{-1})	Yield (%)
		С	Н	N	C/N	ICP value	
5	Pd	48.82	5.92	9.05	5.39	0.044	96
6	Pd	44.54	5.65	5.10	8.73	0.054	88
7	Pd	44.08	5.70	7.42	5.94	0.121	91
8	Pd	42.08	6.50	4.12	10.21	0.123	67



Fig. 2. UV-vis spectra showing absorbance peaks of supported catalysts: 5 (a) and 6 (b) and complexes 9 (c) and 10 (d).

TEM images of catalysts (**5**) and (**6**) taken at 1000 nm showed that these catalysts formed evenly dispersed nano-sized Pd particles across the biopolymer (Fig. 3(a) and (b)). The majority of these particles lie in the 15–20 nm range. Catalysts (**7**) and (**8**) formed nano-sized Pd particles of average size 80–120 nm (Fig. 3(c) and (d)). The existence of Pd particles visible through TEM imaging may imply intermolecular interactions between angstrom size molecular Pd^{II} sites on the biopolymer resulting in nanosized particles. Willocq et al. have also seen Pd and Ru particles of size range 2–6 nm on phosphine modified active carbon, in which surface coordination of Pd and Ru organometallic complexes was achieved through the phosphines on the active carbon [13a–b].

Characteristic Pd⁰ peaks $(2\theta = 40^{\circ}, 45^{\circ}, 68^{\circ} \text{ and } 80^{\circ})$ were not observed in the diffractograms of catalysts (**5–8**), implying that Pd exists in an amorphous state on the chitosan structure (Fig. 4(a)–(d)) [6f]. It was interesting to see that the crystallinity of chitosan was of fairly good quality showing well resolved specific peaks at $2\theta = 10^{\circ}$ and 20° [6e–f, 9e]. As expected the 6-deoxy-6amino chitosan has lower crystallinity, due to the reaction steps involved in introducing the second amino group (Fig. 4(c) and (d)).

The supported-Pd catalysts (**5–8**) were analysed thermally by thermal gravimetric analysis (TGA) in air. Thermal analysis of the catalysts showed that the catalysts are stable up to 240 °C, following which a significant weight loss due to degradation of the



Fig. 3. TEM images of supported catalysts 5 (a), 6 (b), 7 (c) and 8 (d).



Fig. 4. Powder X-ray diffraction diagrams of catalysts (5-8) (patterns a-d, respectively).

biopolymer was observed. Thus the catalysts would be capable of withstanding high reaction temperatures up to slightly below 240 °C. A weight loss of 3.5-5.0% occurs before degradation and is attributed to the desorption of water [9c–d]. These thermal analysis results were the same for all the supported catalysts (**5–8**).

Solid state ³¹P NMR spectroscopy of the precursor chitosan-iminophosphine ligand (2) showed a signal at δ -18.5 ppm (Fig. 5(a)) This further indicates that the ligand has been successfully anchored to the chitosan support as this shift corresponds with the chemical shift obtained for the soluble ligand seen at δ –13.0 ppm. A resonance due to phosphine oxide was also present at δ 35.0 ppm [14a]. The complex [PdCl₂(COD)] was reacted with the chitosan-iminophosphine and the solid state ³¹P NMR spectrum of the resulting chitosan-supported complex (6) showed a decrease in intensity of the peak at δ –18.5 ppm, and the appearance of a resonance at $ca \delta 20.0 \text{ ppm}$ assigned to the Pd complex (Fig. 5(b)). This effect was previously observed in phosphine-Rh complexes attached to a peptide synthesis resin [14b]. These NMR experiments indicated that there are changes on the chitosan structure upon the formation of the chitosan-supported Schiff base ligand (2) and subsequent complex formation. To this effect, we have reason to believe molecular Pd^{II} complexes do exist on the chitosan and 6-deoxy-6-amino chitosan supports, and it would thus be fair to assume the same for the chitosan-supported iminopyridyl catalyst (5 and 7).

3.2. Catalytic studies

3.2.1. Suzuki-Miyaura cross-coupling reactions

The activities of catalysts (**5–8**) were examined in the Suzuki–Miyaura reaction of aryl halides with phenylboronic acid (Scheme 3).

Under conditions similar to those reported in literature (143 °C) [4b], catalysts (**5**) and (**7**) gave yields of 87% and 85%, respectively (Table 3, entries 5 and 6), while catalyst (**6**) afforded 65% of the biphenyl. On varying the reaction temperature (143 °C, 130 °C and 95 °C), it was observed that the optimal temperature for Suzuki–Miyaura cross-coupling using catalysts (**6** and **8**) was 130 °C. Subsequently, all other reactions were performed at this temperature, resulting in good catalytic activities (4.4×10^{-4} mol% Pd used) as evidenced by moderate to high TONs (Table 3). Our cat-



Fig. 5. Solid state ³¹P NMR spectra of (a) chitosan-iminophosphine ligand (**2**) and (b) chitosan-supported Pd complex (**6**): ³¹P one-pulse experiments were performed at a ³¹P frequency of 15 kHz at room temperature. Chemical shifts were referenced to Na₂ HPO₄ at δ = 0 ppm. Signals arising from side bands are marked with an asterisk (*).

S11711/21_M1W3111	ra cross coupling reaction	c catalyzed by cupp	orted Vd catalysts (5-8)
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Entry	Catalyst ^a	R	Х	Base	Conversion (%) ^b	TON $[(mol_{Prod.})/(mol_{Pd})]^c$	Selectivity (%)
1	6	Н	Br	K ₂ CO ₃	98	1144	>99
2	8	Н	Br	K ₂ CO ₃	96	1116	>99
3	5	Н	Br	K ₂ CO ₃	82	959	99
4 ^d	6	Н	Br	K ₂ CO ₃	48	558	98
5 ^e	5	Н	Br	K ₂ CO ₃	87	1016	99
6 ^e	7	Н	Br	K ₂ CO ₃	85	1144	99
7 ^e	6	Н	Br	K ₂ CO ₃	65	763	98
8	6	$p-NO_2$	Br	K ₂ CO ₃	76	904	99
9	6	p-OMe	Br	K ₂ CO ₃	26	320	97
10	6	p-Ac	Br	K ₂ CO ₃	19	221	97
11	8	p-Bu ⁿ	Br	K ₂ CO ₃	75	879	98
12	6	Н	Cl	K ₂ CO ₃	5	56	97
13	7	Н	Cl	K ₂ CO ₃	1	12	97
14	8	Н	Cl	K ₂ CO ₃	8	88	97
15	6	Н	Ι	K ₂ CO ₃	34	397	97
16	7	Н	Ι	K ₂ CO ₃	29	342	98
17	13	Н	Ι	K ₂ CO ₃	71	823	99
18	6	Н	Br	Na_2CO_3	21	249	98
19	5	Н	Br	Na_2CO_3	32	346	99
20	8	Н	Br	Na_2CO_3	26	309	99
21	7	Н	Br	Na_2CO_3	34	405	99
22 ^f	6	Н	Br	K ₂ CO ₃	100	1167	>99
23 ^f	6	p-Ac	Br	K ₂ CO ₃	99	1160	>99
24 ^f	7	$p-NO_2$	Br	K ₂ CO ₃	87	1015	>99
25	9	Н	Br	K ₂ CO ₃	84	1010	99
26	10	Н	Br	K ₂ CO ₃	100	1167	>99

^a Reactions carried out in xylene (20 ml) over 6 h, with 5.1 mmol of arylhalide, 7.5 mmol of phenylboronic acid, 10 mmol of base and 4.47×10^{-4} mmol Pd catalyst (loading = 0.044 (5); 0.054 (6); (7) 0.121 and (8) 0.123 mmol g⁻¹) at 130 °C unless stated otherwise.

^b GC conversions obtained using *n*-decane as an internal standard and are based on the amount of arylhalide employed in relation to authentic standard biphenyl or substituted biphenyl.

^c Maximum TON from reaction at 4 h.

 $^{\rm d}\,$ Reaction carried out at 95 $^\circ\text{C}.$

e Reaction carried out at 143 °C.

^f Reaction carried out in EtOH:H₂O (1:1, 20 ml).

alysts' TON values are comparably higher than those reported in literature, that reported the use of more catalyst (by mol%) [4b,15]. Generally, the iminophosphine supported catalysts afforded better yields than their iminopyridyl counterparts and this can be attributed to the better stabilizing nature of phosphorus donor ligands as compared to nitrogen donor ligands. When substituted bromobenzenes were employed (entries 8-11) a good yield of the coupled product was obtained for the substrate containing p-NO₂ and *p*-Bu^{*n*} substituents (TONs 904 and 879, respectively). The *p*-OMe and p-Ac containing substrates gave low yields as the catalysts decomposed to a black species, possibly Pd⁰ particles. As shown in Table 3 (entries 12-17), the arylbromide gave good yields followed by aryliodide while the less reactive arylchloride gave the poorest product yield. Thus, unexpectedly the order of reactivity follows: Br>I>Cl. In addition to the bond dissociation energies, we suspect as possible halide size contribution to this different result, however further extensive experiments involving the effect of halide would be necessary to confirm this. When sodium carbonate was used as the base, conversions dropped by approximately 60% under these reaction conditions (entries 18-21). Reactions performed in EtOH:H₂O (1:1 ratio) drastically improved product yields to as high as 100% (entries 22-24), indicating that the



R = H, 4-Buⁿ, 4-Ac, 4-OMe or 4-NO₂ X = Cl, Br or I

Scheme 3. Outline for the Suzuki–Miyaura reactions carried out using catalysts (**5–8**).

chitosan-supported catalyst works well in aqueous conditions. The homogeneous complexes (**9** and **10**, Fig. 6) displayed good activity (TONs 1010 and 1167, respectively) for the Suzuki reactions (entries **25–26**), but showed decomposition to a black species minutes into the reaction. This suggests that the chitosan support plays a crucial stabilizing role in the supported Schiff-base catalysts in these reactions.

On following the yields to biphenyl over time, it was observed that the reaction is almost complete in the first 15 min when using supported catalysts (**5**) and (**6**) (Fig. 7). Catalysts (**7**) and (**8**) exhibited lower activity and required longer time for near completion. The homogeneous catalysts (**9** and **10**) showed similar activity as the chitosan-supported ones, with the iminophosphine complex being slightly more active than its iminopyridyl counterpart. This phenomenon is also evident when comparing the activities of catalysts (**5**–**8**).

3.2.2. Reusability of catalysts

Catalysts (**5–8**) were recovered by simple filtration and washed with water, ethanol then acetone and oven dried. The catalysts



Fig. 6. Structure of homogeneous catalysts: samples 9 and 10.



Fig. 7. Variation of the biphenyl formation with time on stream achieved over catalysts (**5–10**): Reactions carried out in xylene (20 ml) over 6 h, with 5.1 mmol of arylhalide, 7.5 mmol of phenylboronic acid, 10 mmol of base and 4.47×10^{-4} mmol Pd catalyst (loading = 0.044(**5**); 0.054(**6**); (**7**) 0.121 and (**8**) 0.123 mmol g⁻¹) at 130 °C unless stated otherwise. Similar considerations were taken for reactions involving catalysts (**9** and **10**). GC conversions obtained using *n*-decane as an internal standard biphenyl or substituted biphenyl.



Fig. 8. Variation of conversion with the number of runs achieved for catalysts (**5–8**): Reactions carried out in xylene (20 ml) over 6 h, with 5.1 mmol of arylhalide, 7.5 mmol of phenylboronic acid, 10 mmol of base and 4.47×10^{-4} mmol Pd catalyst (loading =0.044 (**5**); 0.054 (**6**); (**7**) 0.121 and (**8**) 0.123 mmol g⁻¹) at 130 °C unless stated otherwise. GC conversions obtained using *n*-decane as an internal standard and are based on the amount of arylhalide employed in relation to authentic standard dard biphenyl or substituted biphenyl.

could be reused at least five times without significant loss of activity (Fig. 8). Loss of activity in the 6th run may be due to poisoning or fouling of the catalysts by waste inorganics and unreacted reagents therefore blocking the active Pd sites. Sintering of the nanosized Pd particles (thus decreasing the catalyst surface area) also occurs as evidenced by TEM images of catalyst (**5** and **6**) after five cycles (Fig. 9(a) and (b)). This is possibly induced by the fairly high temperature at which the reactions were carried out.



Fig. 10. Effect of removing Pd catalyst (**6**) from reaction (hot filtration test catalyst (**6**) removed after 5 min): Reactions carried out in xylene (20 ml) over 6 h, with 5.1 mmol of arythalide, 7.5 mmol of phenylboronic acid, 10 mmol of base and 4.47×10^{-4} mmol Pd catalyst (loading = 0.054 (**6**) mmol g⁻¹) at 130 °C unless stated otherwise. GC conversions obtained using *n*-decane as an internal standard and are based on the amount of arythalide employed in relation to authentic standard biphenyl or substituted biphenyl.

3.2.3. Pd leaching tests

A hot filtration test, whereby the catalyst was filtered 5 min after the reaction started, followed by the filtrate taken back to the reaction temperature, stopped the catalytic reaction. This, effectively proves the heterogeneous nature of the supported catalyst and without a measurable homogeneous contribution (Fig. 10). Furthermore, no Pd was detected in the filtrate by ICP-MS analysis in this mixture together with samples from entries 1, 3 and 6 (Table 3). Coordination of Pd to the biopolymer-supported Schiff-base ligands has shown no evidence of Pd leaching into the products. This provides evidence of chitosan acting as a good scaffold for Pd^{II} catalyst precursors [1,2,4].

A test was performed to establish whether the reactions were catalyzed by Pd^0 or Pd^{II} species. A reaction using catalyst (**6**) in the presence of mercury resulted in no inhibition of catalytic activity (94% yield). This result suggested predominantly heterogeneous catalysis.

3.2.4. Heck cross-coupling reactions

Heck reactions were also investigated under similar temperature conditions as utilised for the Suzuki–Miyaura reactions (Scheme 4). The reactions using catalysts (**5** and **7**) with iodobenzene and methyl acrylate produced 98% and 99% *trans*methylcinnamate, respectively, in 4 h at 130 °C (Table 4, entries 1 and 3). Coupling of styrene and iodobenzene was also accomplished, giving 99% and 90% of *trans*-stilbene, respectively, with good TONs of 1209 and 1086 (entries 2 and 4). Thus, the aforementioned catalytic reactions lead to the regiospecific formation



Fig. 9. TEM images of used supported catalysts: 5 (a) and 6 (b).

240 Table 4

Tuble 4
Heck cross coupling reactions catalyzed by supported Pd catalysts (5-8).

Entry	Catalyst ^a	Х	Y	R	Conversion (%) ^b	TON [(mol _{Product})/(mol _{Pd})]	Selectivity (%)
1	5	I	Н	CO ₂ Me	98	1110	>98
2	6	Ι	Н	Ph	99	1150	>99
3	7	Ι	Н	CO_2Me	99	1209	>99
4	8	Ι	Н	Ph	90	1086	>99
5	8	Ι	OMe	Ph	20	237	>99
6	7	Ι	OMe	CO_2Me	62	757	>99
7	5	Br	Н	CO ₂ Me	8	93	>99

^a Reactions carried out in DMF (20 ml) over 4 h, with 5.3 mmol of iodobenzene, 5.3 mmol of methyl acrylate or styrene, 10 mmol of triethylamine and 4.47 × 10⁻⁴ mmol Pd catalyst (loading = 0.044 (**5**); 0.054 (**6**); (**7**) 0.121 and (**8**) 0.123 mmol g⁻¹) at 130 °C unless stated otherwise.

^b GC conversions obtained using *n*-decane as an internal standard and is based on the amount of iodobenzene employed in relation to authentic standard *trans*-methyl cinnamate or *trans*-stilbene.



 $P = CO M_{0} \text{ or } P$

 $R = CO_2 Me \text{ or } Ph$

Scheme 4. Outline for the Heck reactions carried out using catalysts (5-8).

of the *trans* isomers as products. This was confirmed by GC analysis and NMR spectroscopy. With 2-iodobenzene, poor yields of the coupling products were obtained (entries 5 and 6), which was also the case for the bromobenzene substrate (entry 7). Furthermore, catalysts (**5–8**) gave better yields of the coupled product when compared to a commercial polystyrene-supported catalyst for unsubstituted iodobenzene under similar reaction conditions [5c].

4. Conclusions

In summary, several new chitosan- and 6-deoxy-6-amino chitosan-supported Pd^{II} catalysts and their precursors have been successfully prepared in a stable form. These materials were characterized using a variety of complementary techniques including elemental analysis, UV–vis, FT-IR, ICP-MS, PXRD, TEM, ³¹P solid state NMR and TGA. Stable mononuclear model Pd^{II} complexes of the chitosan-supported catalyst were also prepared and characterized using ¹H and ³¹P NMR, UV–vis and FT-IR spectroscopy and elemental analysis.

The supported-Pd catalysts exhibited high activity in the Suzuki-Miyaura and Heck cross-coupling reactions in xylene and aqueous ethanol solvents, with no Pd detected in the reaction products. The supported catalysts displayed good activity at low Pd loading $(4.4 \times 10^{-4} \text{ mol}\%)$ and in aqueous media. Though the mononuclear model catalysts also showed good activity for Suzuki-Miyaura cross-coupling, they could not be recycled and reused, thus the chitosan environment plays an essential stabilizing role for the supported catalysts in the coupling reactions. The supported catalysts could be easily separated and recovered from the reaction mixture (by filtration) and reused several times. The combination of advantages displayed by the supported catalysts such as: ease of preparation, high catalytic activity, stability, reusability, versatility (organic or aqueous solvent catalysis) and no measurable Pd leaching, prove that these catalysts should be considered as a viable alternative in cross-coupling reactions on efficiency, environmental stewardship and economical grounds.

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