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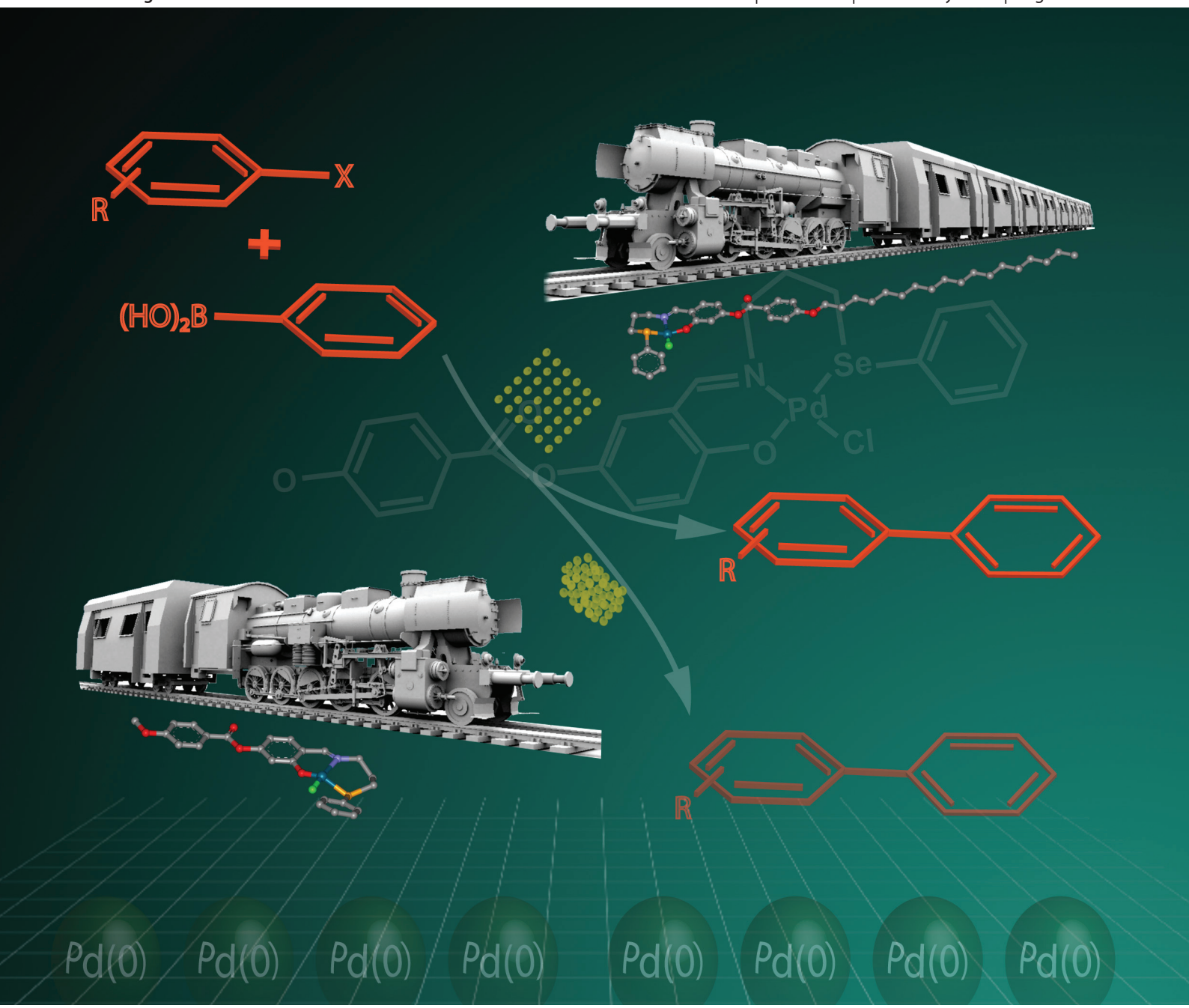

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PAPER

Palladium(II)-selenated Schiff base complex catalyzed Suzuki–Miyaura coupling: Dependence of efficiency on alkyl chain length of ligand†

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The new selenated Schiff bases **L1–L4** which differ in the chain lengths (longest in **L4**) of non-coordinating substituents and their square planar complexes [Pd(**L**–H)Cl] (**1–4**) [**L** = **L1–L4**, behaving as (Se, N, O^-) ligand] have been synthesized and characterized by multinuclei NMR. The molecular structure of **1** has been elucidated by X-ray diffraction on its single crystal [Pd–Se = 2.3965(9) Å]. All the complexes **1–4** (0.5 mol%) have been found suitable to catalyze Suzuki–Miyaura coupling reactions under mild conditions. The activity of **4** which has ligand **L4** has been found highest. The formation of palladium(0) nano-particles (NPs) stablilized by organoselenium species appears to be the catalytic pathway. The length of the pendent alkyl chain present in the complex molecule unprecedentedly controls the dispersion and composition of these particles and consequently the catalytic activity.

1. Introduction

The palladium-catalyzed carbon–carbon coupling reactions are essential tools for organic synthesis.[1] One of the most important among them is the Suzuki–Miyaura cross-coupling of aryl halides with organoboronic acids.[2] Palladium complexes of a large number of phosphorus,[3] carbene,[4] oxime,[5] imine[6,7] and other ligands[8] have been reported as catalysts for such coupling. Palladium species having dendritic macromolecular structure[9,10] have been explored for Suzuki–Miyaura coupling and it has been found that the catalytic activity increases with the generation of dendrimer.[10] This is a very significant observation implying that branching of the macromolecule controls the activity of the catalytic system. As parallel to this the length of the pendent/non-coordinating arm of a ligand may influence the catalytic properties of its palladium complex. However, it is little known how on increasing the bulkiness of a multi-dentate ligand while keeping the dentate character the same, the catalytic efficiency of its complex changes, and therefore it is worth studying. The chalcogenated Schiff bases having S, Se or Te in their frame-work at an appropriate position so that they can act as donor atom have been thought worthwhile for such a study because of two reasons. First, the chalcogenated ligands[4a,7,11] have been found attractive recently for designing Pd-complexes which are efficient as catalysts for C–C coupling reactions even under aerobic conditions. Second, Schiff bases themselves are versatile ligands widely used for designing several types of catalysts due to their capability of fine tuning the properties of the metal center by varying its immediate and distant surroundings. Thus the influence of alkyl chains (differing in lengths and numbers) present on the framework of selenated Schiff base (**L1–L4**: Scheme 1) on Suzuki–Miyaura coupling reactions (eqn (1)) has been studied by catalyzing such reactions with Pd(II) complexes, [Pd(**L**–H)Cl] (**1–4**) (**L** = **L1–L4**) which are pre-catalysts giving palladium(0) nano-particles (appearing to be protected by organoselenium species) that are responsible for the activity. Further, our experiments suggest that the chain lengths influence the dispersion of these nanoparticles (NPs) generated *in situ* during catalysis, which in turn affects the efficiency. This novel observation has been made for the first time for molecular complexes which are single source palladium catalysts. These results are presented in this paper.

$$\text{Aryl Bromide} + \text{PhB(OH)}_2 \rightarrow \text{Ar–Ph} \qquad (1)$$

2. Experimental

2.1. Materials and instruments

Diphenyldiselenide, $NaBH_4$, 3-chloropropylaminehydrochloride, alkyl halides, 2,4-dihydroxybenzaldehyde, sodium tetrachloropalladate, potassium carbonate and all aryl halides *viz*. 1-bromo-4-nitrobenzene, 4-bromobenzonitrile, 4-bromobenzaldehyde, 4-bromobenzoic acid, bromobenzene, 4-bromotoluene, 4-bromoanisol, 2-bromopyridine, 5-bromopyrimidine were procured from Aldrich (USA). Precursor amine $H_2N(CH_2)_3SePh$ was synthesized according the previously published procedure.[12] The benzoate esters of 2,4-dihydroxybenzaldehyde were prepared

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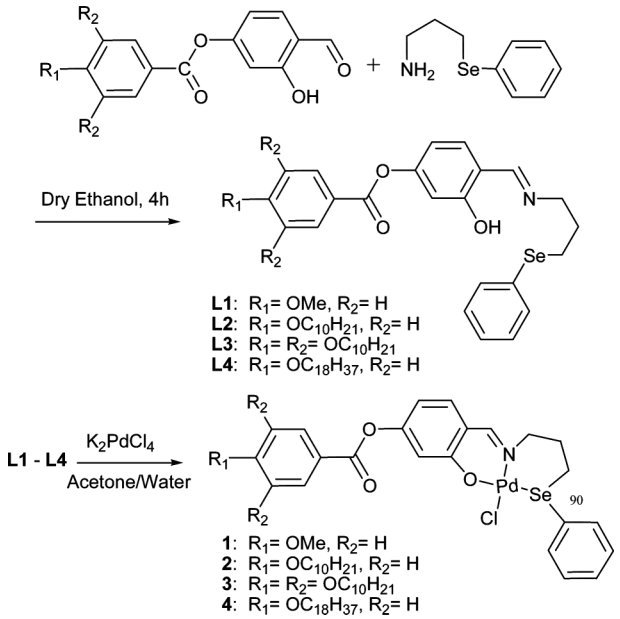
† Electronic supplementary information (ESI) available: NMR data of ligands and complexes **1–4**; data for X-ray structure of **1**, SEM, SEM-EDX and TEM-EDX of Pd nano-particles stabilised by organoselenium species. CCDC reference number 823568. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11695a



Scheme 1 Syntheses of ligands **L1–L4** and complexes **1–4**.

by literature methods.[13] Other commercially available reagents were used as received without further purification. The solvents *viz*. chloroform, DMF, MeOH and EtOH were dried by the standard methods.

^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H} and ^{15}N{^{1}H} NMR spectra were recorded on a Bruker Spectrospin DPX 300 NMR spectrometer at 300.13, 75.47, 57.24 and 30.41 MHz respectively. ^{13}C DEPT NMR was used routinely to determine the number of hydrogen atoms linked to carbon atoms. Assignments of proton and carbon were done on the basis of 2D COSY and 2D HMQC experiments. Elemental analyses were carried out with a Perkin-Elmer 2400 Series II C, H, N analyzer. Estimation of the palladium in the nanoparticles was carried out with an AA7000 Series atomic absorption spectrophotometer (Lab India).

TEM studies were carried out with a Technai G^2 20 electron microscope operated at 200 kV. The specimens for TEM were prepared by dispersing the powder in chloroform by ultrasonic treatment, dropping slurry onto a porous carbon film supported on a copper grid, and then drying in air. The phase morphologies of the samples were observed by using a Carl Zeiss EVO5O scanning electron microscope (SEM). Samples were mounted on a circular metallic sample holder with a sticky carbon tape. Elemental composition of nano-particles at SEM were analyzed by EDX system, model Quan Tax 200 which is based on the SDD technology and provides an energy resolution of 127 eV at Mn Kα. The samples were scanned in different regions in order to minimize the error in the analysis for evaluating the morphological parameters.

Melting points were determined in an open capillary and reported as such. The progress of the ligand's synthesis was monitored by a TLC plate coated with an appropriate grade silica gel. Iodine was used for visualizing the spots. The products of Suzuki reactions were separated and purified (if required) by column chromatography using silica gel (60–120 mesh) as the solid support. *n*-Hexane and its mixtures with chloroform/ethyl acetate in variable proportions were used as eluent. They were authenticated by matching their spectroscopic data with those reported in the literature. All reactions were carried out in glassware dried in an oven, under ambient conditions. The commercial nitrogen gas was used after passing it successively through traps containing solutions of alkaline anthraquinone-sodium dithionite, alkaline pyrogallol, conc. H_2SO_4 and KOH pellets. Nitrogen atmosphere if required was created using the Schlenk technique.

X-ray diffraction data for crystals of **1**, obtained by slow evaporation of its solution made in chloroform-hexane mixture (10 : 1), were collected on a BRUKER AXS SMART-APEX diffractometer equipped with a CCD area detector (Kα = 0.71073 Å; monochromator, graphite). Frames were collected at T = 298(2)K by ω, φ, and 2θ-rotations with full quadrant data collection strategy (four domains each with 600 frames) at 10 s per frame with SMART. The measured intensities were reduced to F^2 and corrected for absorption with SADABS. Structure solution, refinement, and data output were carried out with the SHELXTL package by direct methods. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in idealized positions, and a riding model was used for the refinement. Images were created with the program Diamond.

2.2. Syntheses of L1 to L4

2-(Phenylseleno) propylamine (0.428 g, 2.0 mmol) was stirred in dry ethanol (5 mL) at room temperature for 0.5 h. 4-Methoxy benzoate ester of 2,4-dihydroxybenzaldehyde (0.544 g, 2.0 mmol)/4-decyloxy benzoate ester of 2,4-dihydroxybenzaldehyde (0.796 g, 2.0 mmol)/2,3,4-trisdecyloxy benzoate ester of 2,4-dihydroxybenzaldehyde (1.422 g, 2.0 mmol)/4-octadecyloxy benzoate ester of 2,4-dihydroxybenzaldehyde (1.022 g, 2.0 mmol)[13] dissolved in dry ethanol (5 mL), was added drop wise with stirring. The mixture was stirred further at room temperature for 4 h. The precipitate was filtered off. All ligands **L1** to **L4** were finally dried in *vacuo* (See ESI for numbering of C and H).

L1: Yield: (0.851 g) 91%; m.p. 79 °C. Anal. Found: C, 61.43; H, 4.87; N, 3.04%. Calc. for $C_{24}H_{23}NO_4Se$: C, 61.54; H, 4.95; N, 2.99%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 2.063–2.130 (m, 2H, H_6), 2.966 (t, J = 7.2 Hz, 2H, H_5), 3.674 (t, J = 6.3 Hz, 2H, H_7), 3.873 (s, 3H, H_{20}), 6.728 (dd, J = 8.1 & 1.8 Hz, 1H, H_{13}), 6.806 (d, J = 1.8 Hz, 1H, H_{11}), 6.970 (d, J = 8.7 Hz, 2H, H_{18}), 7.209–7.257 (m, 4H, H_1, H_2, H_{14}), 7.484–7.509 (m, 2H, H_3), 8.132 (d, J = 8.7 Hz, 2H, H_{17}), 8.253 (s, 1H, H_8), 13.773 (bs, 1H, -OH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 24.99 (C_5), 30.86 (C_6), 55.44 (C_7), 58.25 (C_{20}), 110.41 (C_{11}), 112.32 (C_{13}), 113.79 (C_{18}), 116.46(C_9), 121.48 (C_{16}), 126.91 (C_1), 129.07 (C_2), 129.75 (C_4), 132.07 (C_{14}), 132.27 (C_{17}), 132.66 (C_3), 154.08 (C_{10}), 162.86 (C_{12}), 163.91 (C_{19}), 164.31 (C_{15}), 164.72 (C_8). ^{77}Se{^{1}H} NMR (57 MHz, $CDCl_3$, 25 °C, Me_2Se): δ (ppm): 285.87.

L2: Yield: (1.012 g) 85%; m.p. 71 °C. Anal. Found: C, 66.59; H, 6.91; N, 2.41%. Calc. for $C_{33}H_{41}NO_4Se$: C, 66.66; H, 6.95; N, 2.36%. NMR: ^{1}H (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 0.886 (t, J = 6.9 Hz, 3H, H_{22}), 1.279–1.490 (m, 14H, H_Y), 1.790–1.838 (m, 2H, H_{21}), 2.071–2.116 (m, 2H, H_6), 2.973 (t, J = 7.2 Hz, 2H, H_5), 3.686 (t, J = 6.3 Hz, 2H, H_7), 4.032 (t, J = 6.6 Hz, 2H, H_{20}), 6.731 (dd, J = 8.4 & 2.1 Hz, 1H, H_{13}), 6.802 (d, J = 2.1 Hz, 1H, H_{11}), 6.961 (d, J = 9.0 Hz, 2H, H_{18}), 7.216–7.278 (m, 4H, H_1, H_2, H_{14}), 7.484–7.515 (m, 2H, H_3), 8.121 (d, J = 9.0 Hz, 2H, H_{17}), 8.265 (s, 1H, H_8), 13.787 (bs, 1H, -OH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$,

25 °C, TMS): δ (ppm): 14.09 (C_{22}), 22.64, 25.06 (C_5), 25.94, 29.28, 29.32, 29.51, 31.86, 29.05 (C_{21}), 30.93 (C_6), 58.34 (C_7), 68.31 (C_{20}), 110.47 (C_{11}), 112.38 (C_{13}), 114.29 (C_{18}), 116.50 (C_9), 121.27 (C_{16}), 126.96 (C_1), 129.11 (C_2), 129.80 (C_4), 132.08 (C_{14}), 132.30 (C_{17}), 132.75 (C_3), 154.18 (C_{10}), 162.88 (C_{12}), 163.61 (C_{19}), 164.40 (C_{15}), 164.76 (C_8). ^{77}Se{^{1}H} NMR (57 MHz, $CDCl_3$, 25 °C, Me_2Se): δ (ppm): 285.91.

L3: Yield: (1.34 g) 76%; m.p. < room temperature. Anal. Found: C, 70.13; H, 9.08; N, 1.60%. Calc. for $C_{53}H_{81}NO_6Se$: C, 70.18; H, 9.00; N, 1.54%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 0.880 (t, J = 6.6 Hz, 9H, H_{22}), 1.272–1.486 (m, 42H, H_Y), 1.715–1.878 (m, 6H, H_{21}), 2.085–2.130 (m, 2H, H_6), 2.986 (t, J = 7.2 Hz, 2H, H_5), 3.707 (t, J = 6.3 Hz, 2H, H_7), 4.022–4.077 (m, 6H, H_{20}), 6.724 (dd, J = 8.1 & 1.8 Hz, 1H, H_{13}), 6.792 (d, J = 2.1 Hz, 1H, H_{11}), 7.239–7.264 (m, 4H, H_1, H_2, H_{14}), 7.386 (s, 2H, H_{17}), 7.499–7.524 (m, 2H, H_3), 8.286 (s, 1H, H_8), 13.831 (bs, 1H, -OH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 14.08 (C_{22}), 22.65, 25.04 (C_5), 26.04, 29.26–29.69, 30.31 (C_6), 30.90 (C_{21}), 31.87, 58.31 (C_7), 69.22 (C_{20b}), 73.54 (C_{20a}), 108.54 (C_{17}), 110.50 (C_{11}), 112.31 (C_{13}), 116.58 (C_9), 123.61 (C_{16}), 126.96 (C_1), 129.11 (C_2), 129.77 (C_4), 132.12 (C_{14}), 132.74 (C_3), 143.05 (C_{19}), 152.92 (C_{18}), 154.10 (C_{10}), 162.93 (C_{12}), 164.51 (C_{15}), 164.74 (C_8). ^{77}Se{^{1}H} NMR (57 MHz, $CDCl_3$, 25 °C, Me_2Se): δ (ppm): 285.69.

L4: Yield (1.144 g) 81%; m.p. 89 °C. Anal. Found: C, 69.61; H, 8.11; N, 2.03%. Calc. for $C_{41}H_{57}NO_4Se$: C, 69.67; H, 8.13; N, 1.98%. NMR: ^{1}H (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 0.880 (t, J = 6.6 Hz, 3H, H_{22}), 1.265–1.473 (m, 30H, H_Y), 1.773–1.842 (m, 2H, H_{21}), 2.058–2.147 (m, 2H, H_6), 2.981 (t, J = 7.2 Hz, 2H, H_5), 3.696 (t, J = 6.3 Hz, 2H, H_7), 4.040 (t, J = 6.6 Hz, 2H, H_{20}), 6.739 (dd, J = 8.4 & 2.1 Hz, 1H, H_{13}), 6.803 (d, J = 2.1 Hz, 1H, H_{11}), 6.963 (d, J = 8.7 Hz, 2H, H_{18}), 7.220–7.291 (m, 4H, H_1, H_2, H_{14}), 7.494–7.519 (m, 2H, H_3), 8.121 (d, J = 8.7 Hz, 2H, H_{17}), 8.277 (s, 1H, H_8), 13.718 (bs, 1H, -OH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 14.10 (C_{22}), 22.66, 25.06 (C_5), 25.94, 29.06–29.67, 30.91 (C_{21}), 31.89 (C_6), 58.32 (C_7), 68.30 (C_{20}), 110.47 (C_{11}), 112.39 (C_{13}), 114.28 (C_{18}), 116.49 (C_9), 121.24 (C_{16}), 126.96 (C_1), 129.11 (C_2), 129.79 (C_4), 132.09 (C_{14}), 132.30 (C_{17}), 132.74 (C_3), 154.17 (C_{10}), 162.90 (C_{12}), 163.60 (C_{19}), 164.41 (C_{15}), 164.75 (C_8). ^{77}Se{^{1}H} NMR (57 MHz, $CDCl_3$, 25 °C, Me_2Se): δ (ppm): 286.41.

2.3. Syntheses of palladium complexes 1 to 4

$Na_2[PdCl_4]$ (0.294 g, 1.0 mmol) was dissolved in 5 mL of water. The solution of a ligand from **L1** to **L4** (1.0 mmol) made in 10 mL of acetone was added to it with vigorous stirring. The mixture was further stirred for 2 h. The orange red solution was extracted with chloroform. The chloroform layer was washed with water, dried with anhydrous Na_2SO_4, reduced in volume (~5 mL) under *vacuo* and mixed with excess hexane to obtain **1** to **4** as an orange colored powder. Single crystals of **1** were grown from chloroform (containing a few drops of hexane per 5 mL). See ESI for numbering of C and H.

1 [Pd(**L1**–H)Cl]: Yield (0.542 g) 89%; m.p. 148 °C (d). Anal. Found: C, 47.35; H, 3.67; N, 2.34%. Calc. for $C_{24}H_{22}ClNO_4PdSe$: C, 47.32; H, 3.64; N, 2.30%. NMR: ^{1}H (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 2.016–2.178 (m, 1H, H_6), 2.553–2.587 (m, 2H, H_5, H_6), 3.420–3.483 (m, 2H, H_5, H_7), 3.899 (s, 3H, H_{20}), 4.174–4.254 (m, 1H, H_7), 6.244 (dd, J = 8.4 & 1.5 Hz, 1H, H_{13}), 6.682 (d, J = 1.5 Hz, 1H, H_{11}), 6.840 (d, J = 8.7 Hz, 1H, H_{14}), 6.990 (d, J = 8.7 Hz, 2H, H_{18}), 7.294 (s, 1H, H_8), 7.412–7.428 (m, 3H, H_1, H_2), 8.140 (d, J = 8.7 Hz, 2H, H_{17}), 8.346–8.374 (m, 2H, H_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 27.92 (C_6), 32.56 (C_5), 55.53 (C_{20}), 62.15 (C_7), 109.76 (C_{13}), 111.63 (C_{11}), 113.89 (C_{18}), 117.01(C_9), 121.83 (C_{16}), 129.58 (C_1 & C_2), 131.23 (C_4), 132.34 (C_{17}), 133.93 (C_3), 136.67 (C_{14}), 156.68 (C_{10}), 161.15 (C_8), 164.00 (C_{12}), 164.08 (C_{19}), 164.83 (C_{15}). ^{77}Se{^{1}H} NMR (57 MHz, $CDCl_3$, 25 °C, Me_2Se): δ (ppm): 332.72.

2 [Pd(**L2**–H)Cl]: Yield (0.588 g) 80%; m.p. 184 °C (d). Anal. Found: C, 53.93; H, 5.46; N, 1.94%. Calc. for $C_{33}H_{40}ClNO_4PdSe$: C, 53.90; H, 5.48; N, 1.90%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 0.884 (t, J = 6.6 Hz, 3H, H_{22}), 1.280–1.473 (m, 14H, H_Y), 1.771–1.863 (m, 2H, H_{21}), 2.198–2.290 (m, 1H, H_6), 2.543–2.590 (m, 2H, H_5, H_6), 3.422–3.488 (m, 2H, H_5, H_7), 4.042 (t, J = 6.6 Hz, 2H, H_{20}), 4.182–4.261 (m, 1H, H_7), 6.226 (dd, J = 8.4 & 2.1 Hz, 1H, H_{13}), 6.665 (d, J = 2.1 Hz, 1H, H_{11}), 6.818 (d, J = 8.7 Hz, 1H, H_{14}), 6.971 (d, J = 9.0 Hz, 2H, H_{18}), 7.276 (s, 1H, H_8), 7.405–7.426 (m, 3H, H_1, H_2), 8.121 (d, J = 9.0 Hz, 2H, H_{17}), 8.346–8.377 (m, 2H, H_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 14.07 (C_{22}), 22.63, 25.93, 27.80, 29.04, 29.26, 29.31, 29.50, 31.84, 32.69 (C_5), 62.08 (C_7), 68.33 (C_{20}), 109.65 (C_{13}), 111.45 (C_{11}), 114.31 (C_{18}), 117.01(C_9), 121.41 (C_{16}), 129.48 (C_1 & C_2), 131.39 (C_4), 132.27 (C_{17}), 133.94 (C_3), 136.83 (C_{14}), 156.56 (C_{10}), 161.07 (C_8), 163.58 (C_{12}), 163.75 (C_{19}), 164.92 (C_{15}). ^{77}Se{^{1}H} NMR (57 MHz, $CDCl_3$, 25 °C, Me_2Se): δ (ppm): 333.83.

3 [Pd(**L3**–H)Cl]: Yield (0.692 g) 66%; m.p. < room temperature. Anal. Found: C, 60.71; H, 7.71; N, 1.39%. Calc. for $C_{53}H_{80}ClNO_6PdSe$: C, 60.74; H, 7.69; N, 1.34%. NMR: ^{1}H (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 0.797–0.902 (m, 9H, H_{22}), 1.274–1.639 (m, 42H, H_Y), 1.746–1.866 (m, 6H, H_{21}), 2.128–2.169 (m, 1H, H_6), 2.555–2.614 (m, 2H, H_5, H_6), 3.401–3.476 (m, 2H, H_5, H_7), 4.196–4.277 (m, 6H, H_{20}), 6.214 (dd, J = 8.4 Hz & 1.8 Hz, 1H, H_{13}), 6.659 (d, J = 1.8 Hz 1H, H_{11}), 6.828 (d, J = 8.7 Hz, 1H, H_{14}), 7.294 (s, 2H, H_{17}), 7.385–7.429 (m, 3H, H_1, H_2), 8.356–8.388 (m, 2H, H_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 14.01 (C_{22}), 22.60, 26.02 (C_6), 29.26–30.28, 31.83, 31.86 (C_5), 62.07 (C_7), 69.26 (C_{20a}), 73.53 (C_{20b}),109.46 (C_{13}), 111.43 (C_{11}), 117.13 (C_9), 123.74 (C_{16}), 129.44 (C_1 & C_2), 131.38 (C_4), 133.86 (C_3), 136.89 (C_{14}), 143.11 (C_{19}), 152.96 (C_{18}), 156.46 (C_{10}), 161.05 (C_8), 163.76 (C_{12}), 165.04 (C_{15}). ^{77}Se{^{1}H} NMR (57 MHz, $CDCl_3$, 25 °C, Me_2Se): δ (ppm): 335.62.

4 [Pd(**L4**–H)Cl]: Yield (0.626 g) 74%; m.p. 185 °C (d). Anal. Found: C, 58.13; H, 6.68; N, 1.64%. Calc. for $C_{41}H_{56}ClNO_4PdSe$: C, 58.10; H, 6.66; N, 1.65%. NMR: ^{1}H (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 0.878 (t, J = 6.6 Hz, 3H, H_{22}), 1.259–1.472 (m, 30H, H_Y), 1.795–1.842 (m, 2H, H_{21}), 2.108–2.143 (m, 1H, H_6), 2.554–2.588 (m, 2H, H_5, H_6), 3.407–3.473 (m, 2H, H_5, H_7), 4.042 (t, J = 6.3 Hz, 2H, H_{20}), 4.149–4.226 (m, 1H, H_7), 6.242 (d, J = 8.4 Hz, 1H, H_{13}), 6.684 (s, 1H, H_{11}), 6.832 (d, J = 8.7 Hz, 1H, H_{14}), 6.969 (d, J = 8.7 Hz, 2H, H_{18}), 7.285 (s, 1H, H_8), 7.421–7.427 (m, 3H, H_1, H_2), 8.118 (d, J = 8.7 Hz, 2H, H_{17}), 8.352–8.364 (m, 2H, H_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 14.09 (C_{22}), 22.06, 25.94, 27.81 (C_6), 29.06–29.66, 31.59, 32.70 (C_5), 62.07 (C_7), 68.33 (C_{20}), 109.68 (C_{13}), 111.47 (C_{11}), 114.30 (C_{18}), 117.00(C_9), 121.38 (C_{16}), 129.49 (C_1 & C_2), 131.37 (C_4), 132.28 (C_{17}), 133.94 (C_3), 136.81 (C_{14}), 156.56 (C_{10}), 161.07 (C_8), 163.58 (C_{12}), 163.74 (C_{19}), 164.93 (C_{15}). ^{77}Se{^{1}H} NMR (57 MHz, $CDCl_3$, 25 °C, Me_2Se): δ (ppm): 334.97.

2.4. General procedure for Suzuki–Miyaura C–C coupling reaction

An oven-dried flask was charged with aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), DMF (2.0 mL) and H_2O (1.0 mL). A solution of complex of **1–4** in DMF (5×10^{-3} mmol, 1 mL, 0.5 mol %) was then added *via* syringe. The flask was placed on an oil bath at 100 °C for 12 h. The mixture was extracted with diethyl ether. The extract was washed with water and dried over anhydrous Na_2SO_4. The solvent of the extract was removed with rotary evaporator and the resulting residue was purified by column chromatography on silica gel.

2.5. General procedure for the Suzuki Reaction of aryl bromides with phenylboronic acid catalyzed by nanoparticles

An oven-dried flask was charged with aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), DMF (2.0 mL) and H_2O (1.0 mL). Nanoparticles resulting from **1** or **4** (Pd ~ 2 mol %) were added. The flask was heated on an oil bath at 100 °C with stirring of the reaction mixture for 8 h. The mixture was extracted with diethyl ether. The extract was washed with water and dried over anhydrous Na_2SO_4. The solvent of the extract was evaporated off with a rotary evaporator and the resulting residue was purified by column chromatography using silica gel.

2.6. Isolation of nanoparticles generated from 1 and 4 during catalytic reactions

A mixture of Pd(II) complex **1/4** (0.5 mmol), phenylboronic acid (1.0 mmol), 1-bromo-4-nitrobenzene (1.0 mmol) and K_2CO_3 (2.0 mmol) in DMF (4.0 mL) and water (4.0 mL) was heated at 100 °C for 1.5 h and then cooled to room temperature. The solvent was decanted and the black residues were thoroughly washed with water-acetone(1 : 3) and subjected to various analytical measurements for their characterization.

2.7. Hot filtration test

The reaction with catalyst **4** was subjected to a hot filtration test. The reaction mixture of the Suzuki coupling reaction of phenylboronic acid (1.2 mmol) with 4-bromobenzaldehyde (1.0 mmol) catalyzed with 1 mol % of **4** under optimal reaction conditions was filtered hot through a G-4 crucible containing 1 g celite, when 26% conversion (monitored by ^{1}H NMR spectroscopy) occurred (after ~1 h of reaction). The conversion was monitored in the filtrate with time, continued and reached a maximum (72%) after 15 h.

2.8. Hg poisoning test

For the mercury poisoning test an excess of Hg (Hg:Pd: 400 : 1) was taken in the reaction flask before the addition of reactants. Thereafter the coupling reaction of 4-bromobenzaldehyde (1.0 mmol) with phenylboronic acid (1.2 mmol) using **4** (2 mol%) and nanoparticles isolated from **4** during Suzuki–Miyaura coupling (4 mol%) as catalyst under optimum conditions was carried out in the flask. The product biphenyl-4-carboxyldehyde was obtained in ~100% yield after 24 h even in the presence of excess of Hg.

2.9. PPh_3 poisoning test

To the coupling reaction of 4-bromobenzaldehyde with phenylboronic acid using **4** (2 mol%) as a catalyst, PPh_3 (1 mol%) was added under optimal conditions. After 24 h of reaction cross coupling the product 4-biphenylcarboxyldehyde (~100% conversion) was obtained.

3. Results and discussion

The syntheses of **L1–L4** and **1–4** have been summarized in Scheme 1. In the complexation reaction on varying metal:ligand ratio the products did not change. The ligands and complexes have been characterized by ^{1}H, ^{13}C{^{1}H} and ^{77}Se{^{1}H} NMR spectroscopy (ESI†). In the ^{77}Se{^{1}H} NMR spectra of **L1–L4** the signals appear almost at the same position (285.8, 285.9, 285.7 and 286.4 ppm respectively). The assignments in the ^{1}H and ^{13}C{^{1}H} spectra are based on correlations with COSY and HMQC experiments (ESI†) and are consistent with their structures depicted in Scheme 1. The absence of a signal of the phenolic (-OH) proton in ^{1}H NMR spectra of complexes **1–4** supports the involvement of O^- in the coordination which is also supported by the crystal structure of **1** (Fig. 1). ^{77}Se{^{1}H} NMR signals of **1–4** are at higher frequency (47–50 ppm) with respect to those of the corresponding free ligands indicating the involvement of Se in coordination with Pd. In the ^{15}N{^{1}H} NMR spectra of **L1** and **L4** signals appear at 290.52 and 290.97 ppm respectively.

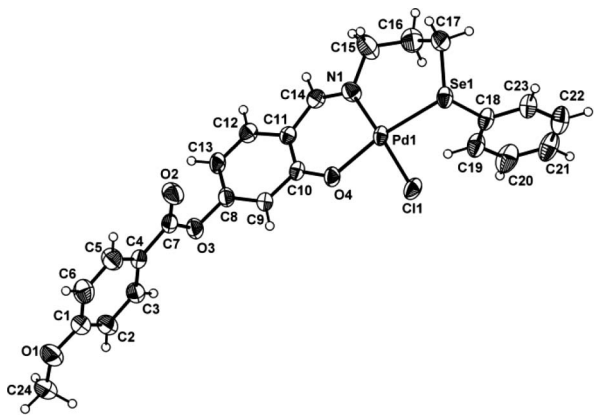


Fig. 1 ORTEP diagram of **1** with ellipsoids at the 30% probability level. The solvent molecule ($CHCl_3$) has been omitted for clarity. Selected bond lengths (Å): Pd(1)–O(4) 2.000(5); Pd(1)–N(1) 2.018(6); Pd(1)–Cl(1) 2.305(2); Pd(1)–Se(1) 2.3965(9); Se(1)–C(18) 1.928(7); Se(1)–C(17) 1.951(9). Selected bond angles (°): O(4)–Pd(1)–Se(1) 167.97(14); O(4)–Pd(1)–N(1) 92.5(2); O(4)–Pd(1)–Cl(1) 84.95(15); N(1)–Pd(1)–Cl(1) 176.48(19); N(1)–Pd(1)–Se(1) 99.51(19).

3.1. Crystal structure

The structure of **1** has been elucidated by X-ray diffraction on its single crystals (Fig. 1). The molecular structure of **1** with its selected bond distances and angles is shown in Fig. 1. The coordination geometry around Pd is almost square planar. The ligand is coordinated with Pd in a monoanionic tridentate (Se, N, O^-) mode and forms two six membered chelate rings, one *via* O^- and N and the other *via* Se and N. The Pd–N bond

length 2.018(6) in **1** is almost similar to the reported value of 2.010(4) Å for [PdCl{$C_6H_5(C_6H_4$–2—O^-)C═N–$(CH_2)_2$SePh}][7a] and is longer than 1.986(6) Å reported[7a] for [PdCl{$C_6H_5(C_6H_4$–2–O^-)C═N $(CH_2)_3$SePh}]. The Pd–O distance 2.000(5) in **1** is consistent with values 1.993(3) and 1.995(6) Å[7a] reported for Pd–O of the Pd(II)-selenated Schiff base complex. The bond distances of Pd–Se 2.3965(9) Å and Pd–Cl 2.305(2) Å of **1** are found to be longer than those of [PdCl{$C_6H_5(C_6H_4$–2–O^-)C═N$(CH_2)_3$ SePh}],[7a] where the ligand is also a tridentate selenated Schiff base. The Cl···H (aromatic), Cl···H (-OCH_3) and C–H···π secondary interactions in the crystal of **1** result in the formation of a three dimensional chain structure shown in Fig. 2 and the ESI† (Fig. S2.1 to Fig. S2.8).

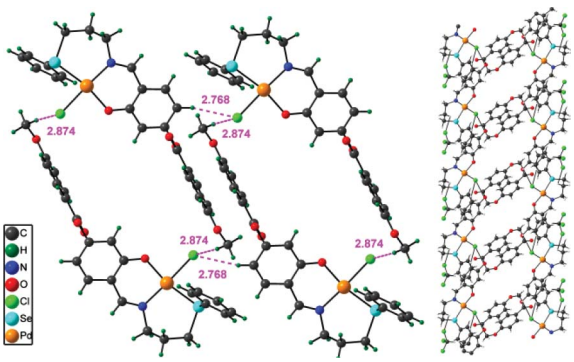


Fig. 2 Molecular packing of **1** showing Cl···H (aromatic) and Cl···H (OMe) interactions.

3.2. Suzuki-Miyaura C–C coupling reaction catalyzed by 1–4

1–4 have been explored as catalysts for Suzuki–Miyaura C–C coupling reactions (Table 1) of several aryl bromides. K_2CO_3 has been found the most appropriate base as with the alternatives *viz*. Cs_2CO_3, CH_3COONa, Et_3N or Na_2CO_3, a longer reaction time was necessary for reasonable conversions. Among the various solvents explored the best results were obtained in a DMF–H_2O mixture. The optimum concentration of **1–4** for catalysis was found to be 0.5 mol%. The reaction time was optimized as 12 h. The catalytic efficiency of **4** was found to be highest whereas **1** showed significantly lower efficiency than **2–4**. The enhanced efficiency of **4** can also be gauged from the fact that it can give more than 84% conversions in only 6 h (Table 1: Entry No. 3, 5 and 6). One of the reasons for this variation in catalytic activities of these Pd-complexes may be the electronic properties of Se and N in **L1–L4**. As mentioned earlier the $^{77}Se\{^1H\}$ NMR signals of all the four ligands appear at almost the same position (from 285.41 to 286.87 ppm), implying that the lengths of alkyl chains present on the ligand framework do not affect significantly the electronic property of the selenium donor site. The signals in $^{15}N\{^1H\}$ NMR spectra of ligands **L1** and **L4** appear at 290.52 and 290.97 ppm respectively (Fig. S4.1 and S4.2 in ESI†) and indicate that the electronic environment of nitrogen is also almost unaffected by alkyl chains. As the electronic properties of the donor atoms remain unaffected with chain length, the variation in the catalytic activities of **1–4** with the nature of the alkyl chain has to be ascribed to some other factor.

Table 1 Suzuki coupling reactions catalyzed by **1–4**[a]

Aryl Bromide + $PhB(OH)_2$ → Ar–Ph

Entry No.	Aryl Bromide	Yield (%)			
		1[b]	**2**[b]	**3**[b]	**4**[c]
1.	1-Bromo-4-nitrobenzene	25	85	86	90
2.	4-Bromobenzonitrile	28	82	82	88
3.	4-Bromobenzaldehyde	26	83	84	95[d]
4.	4-Bromobenzoic acid	23	81	83	87
5.	Bromobenzene	29	80	85	86[d]
6.	4-Bromotoluene	23	77	80	84[d]
7.	4-Bromoanisol	20	79	79	87
8.	2-Bromopyridine	17	85	84	93
9.	5-Bromopyrimidine	19	84	81	90

[a] *Reaction conditions*: 1.0 equiv. of aryl bromide, 1.3 equiv. of phenylboronic acid, and 2 equiv of base (K_2CO_3), 0.5 mol% of catalyst, aqueous DMF as solvent and temperature of bath 100 °C. Reaction time 12 h. [b] NMR % Yield. [c] Isolated yield after column chromatography. [d] Reaction time 6 h.

In the course of Suzuki reactions black particles appear. Therefore, it is possible that **1–4** are pre-catalysts and give nanosized Pd(0) species during the reaction. The observed variation in catalytic efficiency may be due to some difference in these species generated *in situ* during the course of catalysis by **1–4**. Thus the species obtained from **1** and **4** in the course of catalysis of the coupling reaction of 1-bromo-4-nitrobenzene with $PhB(OH)_2$ under optimum reaction conditions, were analyzed so that a possible correlation between the length of alkyl chains present on the ligand's framework, catalytic activity and nature of these species (possibly true catalysts) can be understood. The black particles were isolated and characterized by HRTEM (Fig. 3), TEM-EDX (Fig. S1.1 and S1.4 in ESI†) and SEM-EDX (Fig. S1.3 and S1.6 in ESI†). These studies revealed that spherical shaped nano-particles of average size ~3 nm were formed in case of both the complexes. The nanoparticles, formed in the case of **4** (Fig. 3) are much more uniformly dispersed than those formed from **1** (Fig. 3).

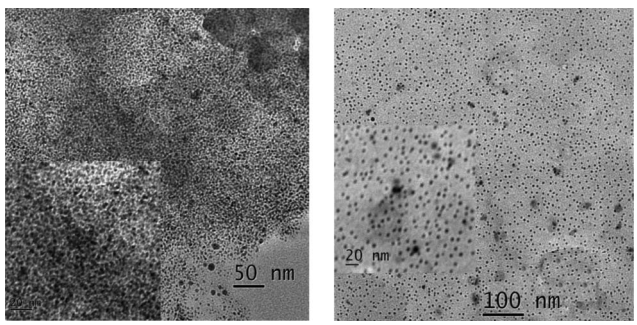


Fig. 3 HRTEM images of nanoparticles obtained in catalytic reactions with **1** and **4** respectively.

The -CH_3 group is present on the ligand framework of **1** and the linear -$C_{18}H_{37}$ group on that of **4**. The large size of alkyl chain in the case of **4** appears to have made the nanoparticles more uniformly dispersed resulting in its higher catalytic activity.

Such an influence in systems like dendrimers is reported[10] because palladium is fully encapsulated by the dendritic ligand structure, whereas in non-dendritic molecular Pd(II) complexes it is observed for the first time.

Table 2 Suzuki coupling reactions catalyzed by nanoparticles[a]

Entry No.	Aryl Halide	Yield (%)[b]	
		Pd NPs obtained from **1**	Pd NPs obtained from **4**
1.	4-Bromobenzaldehyde	30	94
2.	Bromobenzene	26	90
3.	4-Bromoanisol	25	91

[a] *Reaction conditions*: 1.0 equiv. of aryl bromide, 1.3 equiv. of phenylboronic acid and 2.0 equiv. of base (K_2CO_3), catalyst: nanoparticles (Pd ~ 2 mol%), aqueous DMF as solvent and temperature of bath 100 °C. Reaction time 8 h. [b] Isolated yield after column chromatography.

The EDX (SEM as well as TEM) has revealed that Pd:Se ratios in nanoparticles generated from **1** and **4** are ~51 : 49 and 40 : 60 respectively. The nanoparticles obtained from **4** are richer in Se. Thus the effect of alkyl chain lengths on the catalytic activity appears to occur due to their influence on the nature of the real catalyst, the nanoparticles.

This is shown independently by the catalytic activity of nanoparticles for Suzuki coupling (Table 2). However, to attain an efficiency similar to the one shown by *in situ* generated particles, the quantity of isolated nanoparticle (*i.e.* mol% of Pd) needed is higher, which is very much expected. The % yields in Table 1 also indicate that chain length has a greater influence than their number on the benzene ring.

To establish the nature of the real catalysts, hot filtration experiments[14] were carried out. The catalytic reaction is expected to be quenched or drastically reduced in the filtrate. The latter happened in our case as the maximum conversion dropped (Table 1) from 95% (6 h) to 72% (15 h). The catalytic reaction continued because some of the palladium was leached from *in situ* generated NPs. The palladium leaching estimated by AAS, was found to be 5.9% of initial catalyst loading. A mercury poisoning test[14] performed on a representative coupling reaction of 4-bromobenzaldehyde was found negative. The catalysis by NPs, obtained as a by-product during the course of catalysis, is also not quenched by Hg. The triphenyphosphine poisoning test[14] was performed. The biaryl product was obtained in 100% yield when the reaction was carried out for 24 h in the presence of PPh_3. These results suggest that Pd(0) nanoparticles are protected by organoselenium species as the presence of Se is indicated by EDX results. The weight loss (%) in TGA (Fig. S5.1 to S5.3 in ESI†) up to 500 °C was 22.56, 47.97 and 67.20 in the case of NPs obtained during Suzuki-coupling by **1**, **2** and **4** respectively, which is most likely due to organselenium skeletons present. However the nature of the organic entity could not be established unequivocally by spectroscopic methods.

4. Conclusions

The complexes [Pd(**L**–H)Cl] (**1–4**; **L** = Schiff base ligands of (Se, N, O^-) type) have been synthesized. The crystal structure solved for **1** indicates that selenated Schiff bases (**L1–L4**) ligate in a tridentate mode. Suzuki–Miyaura coupling reactions have been catalyzed by **1–4**. The catalytic efficiency depends on the length of the pendent alkyl chain present on the ligand, and is highest for **4**. It appears that Pd-complexes are pre-catalysts, generating *in situ* real catalytic species, ~3 nm size nanoparticles of Pd(0) protected by organoselenium species. Most probably the difference in catalytic efficiency occurs due to variation in the dispersion and composition of these nanoparticles with alkyl chain lengths.

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References

1 (*a*) Recent selected books: J. Tsuji, *Palladium Reagents and Catalysts*, John Wiley & Sons, Chichester, 1995; (*b*) F. Diederich and P. J. Stang, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, Weinheim, 1998; (*c*) M. T. Reetz, *Transition Metal Catalysed Reactions* (ed.: S. G. Davies, S.-I. Murahashi), Blackwell Science, Oxford, 1999; (*d*) N. Miyaura, *Cross-Coupling Reactions*, Springer, Berlin, 2002.
2 (*a*) A. Suzuki, *Pure Appl. Chem.*, 1991, **63**, 419; (*b*) S. Kotha, K. Lahiri and D. Kashinath, *Tetrahedron*, 2002, **58**, 9633; (*c*) A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147; (*d*) S. P. Stanforth, *Tetrahedron*, 1998, **54**, 263; (*e*) N. Miyaura and A. Suzuki, In *Advances in Metal–Organic Chemistry*, L. S. Liebeskind, Ed.; JAI: London, 1998, 6, 187; (*f*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
3 (*a*) T. Kinzel, Y. Zhang and S. L. Buchwald, *J. Am. Chem. Soc.*, 2010, **132**, 14073; (*b*) P. Štěpnička, J. Schulz, T. Klemann, U. Siemeling and I. Císařová, *Organometallics*, 2010, **29**, 3187; (*c*) R. Ghosh, N. N. Adarsh and A. Sarkar, *J. Org. Chem.*, 2010, **75**, 5320; (*d*) J. I. van der Vlugt, M. A. Siegler, M. Janssen, D. Vogt and A. L. Spek, *Organometallics*, 2009, **28**, 7025; (*e*) J. Ma, X. Cui, L. Gao and Y. Wu, *Inorg. Chem. Commun.*, 2007, **10**, 762; (*f*) C. A. Fleckenstein and H. Plenio, *Organometallics*, 2007, **26**, 2758; (*g*) S. Teo, Z. Weng and T. S. A. Hor, *Organometallics*, 2006, **25**, 1199; (*h*) A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 4176.
4 (*a*) C. Fliedel and P. Braunstein, *Organometallics*, 2010, **29**, 5614; (*b*) H. V. Huynh, C. H. Yeo and Y. X. Chew, *Organometallics*, 2010, **29**, 1479; (*c*) B. Karimi and P. F. Akhavan, *Chem. Commun.*, 2009, 3750; (*d*) H. Türkmen, R. Can and B. Çetinkaya, *Dalton Trans.*, 2009, 7039; (*e*) O. Diebolt, P. Braunstein, S. P. Nolan and C. S. J. Cazin, *Chem. Commun.*, 2008, 3190; (*f*) C. Fleckenstein, S. Roy, S. Leuthäußer and H. Plenio, *Chem. Commun.*, 2007, 2870; (*g*) S. K. Yen, L. L. Koh, H. V. Huynh and T. S. A. Hor, *Dalton Trans.*, 2007, 3952; (*h*) R. Singh, M. S. Viciu, N. Kramareva, O. Navarro and S. P. Nolan, *Org. Lett.*, 2005, **7**, 1829; (*i*) O. Navarro, H. Kaur, P. Mahjoor and S. P. Nolan, *J. Org. Chem.*, 2004, **69**, 3173; (*j*) G. Altenhoff, R. Goddard, C. W. Lehmann and F. Glorius, *J. Am. Chem. Soc.*, 2004, **126**, 15195; (*k*) V. C. Vargas, R. J. Rubio, T. K. Hollis and M. E. Salcido, *Org. Lett.*, 2003, **5**, 4847; (*l*) C. W. K. Gstottmayr, V. P. W. Böhm, E. Herdtweck, M. Grosche and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1363.
5 (*a*) D. A. Alonso, C. Nájera and M. C. Pacheco, *J. Org. Chem.*, 2002, **67**, 5588; (*b*) D. A. Alonso, C. Nájera and M. C. Pacheco, *Org. Lett.*, 2000, **2**, 1823.
6 (*a*) J. Zhou, X. Li and H. Sun, *J. Organomet. Chem.*, 2010, **695**, 297; (*b*) A. D. Zotto, F. I. Prat, W. Baratta, E. Zangrando and P. Rigo, *Inorg. Chim. Acta*, 2009, **362**, 97; (*c*) B. Mu, T. Li, W. Xu, G. Zeng, P. Liu and Y. Wu, *Tetrahedron*, 2007, **63**, 11475; (*d*) C. Xu, J.-F. Gong, S.-F. Yue, Y. Zhu and Y.-J. Wu, *Dalton Trans.*, 2006, 4730; (*e*) D. Domin, D. Benito-Garagorri, K. Mereiter, J. Fröhlich and K. Kirchner, *Organometallics*, 2005, **24**, 3957; (*f*) C.-L. Chen, Y.-H. Liu, S.-M. Peng and S.-T. Liu, *Organometallics*, 2005, **24**, 1075; (*g*) J. Cui, M. Zhang and Y. Zhang, *Inorg. Chem. Commun.*, 2010, **13**, 81; (*h*) C. Rocaboy and J. A. Gladysz, *Org. Lett.*, 2002, **4**, 1993.
7 (*a*) A. Kumar, M. Agarwal and A. K. Singh, *Inorg. Chim. Acta*, 2009, **362**, 3208; (*b*) A. Kumar, M. Agarwal and A. K. Singh, *J. Organomet. Chem.*, 2008, **693**, 3533; (*c*) P. R. Kumar, S. Upreti and A. K. Singh, *Polyhedron*, 2008, **27**, 1610; (*d*) I. D. Kostas, B. R. Steele, A. Terzis, S. V. Amosova, A. V. Martynov and N. A. Makhaeva, *Eur. J. Inorg. Chem.*, 2006, 2642; (*e*) I. D. Kostas, G. A. Heropoulos, D. K. -Demertzi, P. N. Yadav, J. P. Jasinski, M. A. Demertzis, F. J. Andreadaki, G. Vo-Thanh, A. Petit and A. Loupy, *Tetrahedron Lett.*,

2006, **47**, 4403; (*f*) I. D. Kostas, F. J. Andreadaki, D. K. -Demertzi, C. Prentjas and M. A. Demertzis, *Tetrahedron Lett.*, 2005, **46**, 1967; (*g*) M.-T. Chen, C.-A. Huang and C.-T. Chen, *Eur. J. Inorg. Chem.*, 2006, 4642.

8 (*a*) C. Najera, J. Gil-Molto, S. Karlstrom and L. R. Falvello, *Org. Lett.*, 2003, **5**, 1451; (*b*) A. Schnyder, A. F. Indolese, M. Studer and H.-U. Blaser, *Angew. Chem., Int. Ed.*, 2002, **41**, 3668; (*c*) Z. Xiong, N. Wang, M. Dai, A. Li, J. Chen and Z. Yang, *Org. Lett.*, 2004, **6**, 3337; (*d*) C. A. Kruithof, A. Berger, H. P. Dijkstra, F. Soulimani, T. Visser, M. Lutz, A. L. Spek, R. J. M. K. Gebbink and G. V. Koten, *Dalton Trans.*, 2009, 3306; (*e*) M. Dai, B. Liang, C. Wang, J. Chen and Z. Yang, *Org. Lett.*, 2004, **6**, 221.

9 (*a*) T. Fujihara, S. Yoshida, H. Ohta and Y. Tsuji, *Angew. Chem., Int. Ed.*, 2008, **47**, 8310; (*b*) P. Servin, R. Laurent, A. Romerosa, M. Peruzzini, J.-P. Majoral and A.-M. Caminade, *Organometallics*, 2008, **27**, 2066; (*c*) A. K. Diallo, C. Ornelas, L. Salmon, J. R. Aranzaes and D. Astruc, *Angew. Chem., Int. Ed.*, 2007, **46**, 8644.

10 (*a*) A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.-M. Basset and V. Polshettiwar, *Chem. Soc. Rev.*, 2011, **40**, 5181; (*b*) L. Wu, Z.-W. Li, F. Zhang, Y.-M. He and Q.-H. Fan, *Adv. Synth. Catal.*, 2008, **350**, 846; (*c*) L. Wu, B. L. Li, Y. Y. Huang, H. F. Zhou, Y. M. He and Q.-H. Fan, *Org. Lett.*, 2006, **8**, 3605; (*d*) N. T. S. Phan, M. Van Der Sluys and C. W. Jones, *Adv. Synth. Catal.*, 2006, **348**, 609; (*e*) D. Astruc, F. Lu and J. R. Aranzaes, *Angew. Chem., Int. Ed.*, 2005, **44**, 7852.

11 (*a*) D. V. Aleksanyan, V. A. Kozlov, Y. V. Nelyubina, K. A. Lyssenko, L. N. Puntus, E. I. Gutsul, N. E. Shepel, A. A. Vasil'ev, P. V. Petrovskii and I. L. Odinets, *Dalton Trans.*, 2011, **40**, 1535; (*b*) D. Yuan and H. V. Huynh, *Organometallics*, 2010, **29**, 6020; (*c*) V. A. Kozlov, D. V. Aleksanyan, Y. V. Nelyubina, K. A. Lyssenko, A. A. Vasil'ev, P. V. Petrovskii and I. L. Odinets, *Organometallics*, 2010, **29**, 2054; (*d*) G. K. Rao, A. Kumar, J. Ahmed and A. K. Singh, *Chem. Commun.*, 2010, **46**, 5954; (*e*) D. Das, P. Singh, M. Singh and A. K. Singh, *Dalton Trans.*, 2010, **39**, 10876; (*f*) D. Das, P. Singh and A. K. Singh, *J. Organomet. Chem.*, 2010, **695**, 955; (*g*) D. Das, G. K. Rao and A. K. Singh, *Organometallics*, 2009, **28**, 6054; (*h*) D. Das, M. Singh and A. K. Singh, *Inorg. Chem. Commun.*, 2009, **12**, 1120; (*i*) P. Singh, M. Singh and A. K. Singh, *J. Organomet. Chem.*, 2009, **694**, 3872; (*j*) V. A. Kozlov, D. V. Aleksanyan, Y. V. Nelyubina, K. A. Lyssenko, E. I. Gutsul, A. A. Vasil'ev, P. V. Petrovskii and I. L. Odinets, *Dalton Trans.*, 2009, 8657; (*k*) S.-Q. Bai and T. S. A. Hor, *Chem. Commun.*, 2008, 3172; (*l*) V. A. Kozlov, D. V. Aleksanyan, Yu. V. Nelyubina, K. A. Lyssenko, E. I. Gutsul, L. N. Puntus, A. A. Vasil'ev, P. V. Petrovskii and I. L. Odinets, *Organometallics*, 2008, **27**, 4062; (*m*) D. Zim, S. M. Nobre and A. L. Monteiro, *J. Mol. Catal. A: Chem.*, 2008, **287**, 16; (*n*) O. Piechaczyk, M. Doux, L. Ricard and P. le Floch, *Organometallics*, 2005, **24**, 1204; (*o*) W. Zhang and M. Shi, *Tetrahedron Lett.*, 2004, **45**, 8921; (*p*) Q. Yao, E. P. Kinney and C. Zheng, *Org. Lett.*, 2004, **6**, 2997; (*q*) A. S. Gruber, D. Zim, G. Ebeling, A. L. Monteiro and J. Dupont, *Org. Lett.*, 2000, **2**, 1287; (*r*) D. Zim, A. S. Gruber, G. Ebeling, J. Dupont and A. L. Monteiro, *Org. Lett.*, 2000, **2**, 2881; (*s*) D. Zim, A. L. Monteiro and J. Dupont, *Tetrahedron Lett.*, 2000, **41**, 8199; (*t*) D. E. Bergbreiter, P. L. Osburn, A. Wilson and E. M. Sink, *J. Am. Chem. Soc.*, 2000, **122**, 9058.

12 A. Khanna, A. Bala and B. L. Khandelwal, *J. Organomet. Chem.*, 1995, **494**, 199.

13 (*a*) K. Kimura, S. Kohama and Y. Yamashita, *Macromolecules*, 2002, **35**, 7545; (*b*) M.-A. Guillevic, M. J. Danks, S. K. Harries, S. R. Collinson, A. D. Pidwell and D. W. Bruce, *Polyhedron*, 2000, **19**, 249; (*c*) J. Barbera, R. Gimenez, M. Marcos, J. L. Serrano, P. J. Alonso and J. I. Martinez, *Chem. Mater.*, 2003, **15**, 958.

14 J. A. Widegren and R. G. Finke, *J. Mol. Catal. A: Chem.*, 2003, **198**, 317.