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## Palladium(II) complexes of pyrazolated thio/selenoethers: syntheses, structures, single source precursors of Pd<sub>4</sub>Se and PdSe nano-particles and potential for catalyzing Suzuki-Miyaura coupling

Kamal Nayan Sharma, Hemant Joshi, Ved Vati Singh, Pradhumn Singh and Ajai Kumar Singh\*



The Pd(II)-complexes (1-4) of four pyrazolated thio/selenoether have been synthesized and found efficient catalysts for Suzuki-Miyaura coupling reactions. The *in situ* generated Pd-chalcogen NPs (size ~ 3-19 nm) appear to be real catalysts. Single source one pot synthesis of Pd<sub>4</sub>Se and PdSe NPs (size ranges 8-26 nm), capped with TOP, have been done by thermolysis of **2** and **4** at 200-250 °C in TOP. The PdP<sub>2</sub> NPs were formed in the attempts made to prepare NPs of palladium-sulfide by thermolysis of **1** and **3** in TOP.

### **ARTICLE TYPE**

### Palladium(II) complexes of pyrazolated thio/selenoethers: syntheses, structures, single source precursors of Pd<sub>4</sub>Se and PdSe nano-particles and potential for catalyzing Suzuki-Miyaura coupling

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The reactions of 4–bromo–1–(2–chloroethyl)–1*H*–pyrazole prepared from 4– bromopyrazole with the *in situ* generated PhSNa, PhSeNa, Na<sub>2</sub>S, and Na<sub>2</sub>Se have resulted in thio/selenoether ligands L1-L4 respectively. The complexes [PdL1/L2Cl<sub>2</sub>](1-2) and [PdL3/L4Cl]BF<sub>4</sub> (**3-4**) of these ligands have been synthesized by reacting them with [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] in CH<sub>3</sub>CN at 70°C. The L1-L4 and their complexes <sup>10</sup> (1-4) have been characterized with spectroscopic techniques viz. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>77</sup>Se{<sup>1</sup>H} NMR, IR and HR-MS. Single crystal structures of **1-4** determined by X-ray diffraction reveal nearly square planar geometry around Pd in each case. Thermally stable, moisture/air insensitive complexes **1-4** have been found efficient catalysts for Suzuki-Miyaura coupling reactions (Yield up to 96% in 2 h). Nano-particles (NPs) (size ~3-19 nm) were formed in the beginning of these reactions. They are composed of Pd and S or Se with more % of Pd. These NPs also catalyze Suzuki coupling and appear to be playing important role in catalysis. Single source one pot <sup>15</sup> synthesis of Pd<sub>4</sub>Se and PdSe NPs (size ranges ~8-26 nm), capped with trioctylphosphine (TOP), have been developed by thermolysis of **2** and **4** at 200-250 °C in TOP. HR-TEM, SEM, SEM-EDX and powder XRD have been used to authenticate these nano-particles. The NPs of PdP<sub>2</sub> are formed when attempts were made to prepare nano-sized phases of palladium-sulfide by thermolysis of **1** and **3** in TOP.

#### Introduction

Pyrazolyl groups are among the important building units used in <sup>20</sup> ligand design<sup>1</sup> and supramolecular chemistry.<sup>2</sup> The pyrazolates, are known as robust bridging ligands.<sup>3</sup> Their metal complexes have been used as precursors for chemical vapor phase deposition and found to show luminescent properties.<sup>4</sup> The pyrazole and pyrazolate moieties can be integrated as part of many polydentate <sup>25</sup> donors.<sup>5</sup> The polypyrazolylborates are among the most useful and

- widely employed ligands.<sup>6</sup> In addition to their ligand chemistry, there are reports on their biological importance.<sup>7</sup> The antitumor activities of metal-complexes of pyrazolyl ligands have been widely investigated and many of them have cytotoxicity <sup>30</sup> comparable or superior than those of standard drugs. For
- instance, compounds of the type  $[{AuCl_2(L)}_2]$  (L = pyrazole, 3methylpyrazole) have been reported more cytotoxic than *cis*platin toward the MOLT-4 and C2C12 tumor cell lines.<sup>8</sup> Rocha et al.<sup>9</sup> have reported that the cytotoxic activity of complex
- $_{35}$  [PdI<sub>2</sub>(tdmPz)] (tdmPz = 1-thiocarbamoyl-3,5-dimethylpyrazole) towards mammary adenocarcinoma murine tumor cell line (LM3) is comparable to that of *cis*-platin. However, chemistry of pyrazole based organosulfur and selenium based ligands is unexplored. Their Pd(II) complexes may be very interesting
- <sup>40</sup> because this metal has outstanding application potential for C–C bond formation,<sup>10</sup> for example Suzuki-Miyaura coupling reaction.<sup>11</sup> Pd-complexes of bulky and electron-rich phosphines<sup>12</sup> and carbenes<sup>13</sup> are considered to be of immense importance for such coupling but most of them are air/moisture sensitive. <sup>45</sup> Chalcogen ligands have emerged as alternatives to phosphines

due to strong donor properties of chalcogen atoms, which make them suitable for designing catalyst for C-C coupling reactions.14 The potential of pyrazole based ligands in designing metal 50 complexes having good catalytic activity has been already recognized. The catalytic processes viz. oxidation,<sup>15</sup> ethylene polymerization,16 hydroamination,17-18 redox isomerisation of allylic alcohols,<sup>19</sup> ethylene oligomerization<sup>20</sup> and polymerization of rac-lactide<sup>21</sup> based on metal complexes of pyrazole based 55 ligands have been found promising. Thus Pd-complexes of pyrazole based chalcogen ligands would be worth exploring for Suzuki-Miyaura coupling. Platinum group metal chalcogenides have found applications in catalysis.<sup>22</sup> Their properties such as semiconducting nature,<sup>23</sup> photoelectrochemical behavior<sup>24</sup> etc are 50 attractive. They have also shown promise for lithiographic films,<sup>25</sup> optical disc recording films<sup>26</sup> and as light image receiving material.<sup>27</sup> The various important selenides of palladium identified are PdSe, Pd<sub>17</sub>Se<sub>15</sub>, Pd<sub>7</sub>Se<sub>4</sub>, Pd<sub>2.5</sub>Se, Pd<sub>3</sub>Se, Pd<sub>7</sub>Se, Pd<sub>4</sub>Se, Pd<sub>4.5</sub>Se, Pd<sub>8</sub>Se and PdSe<sub>2</sub>. Nano-sized forms of some of 65 them may become more interesting due to the favorable tuning of their semiconducting properties.<sup>23</sup> The Pd-complexes of pyrazole based chalcogenated ligands may be used as a single source precursor for currently important nano-particles of some of these palladium selenides and may abandon presently used volatile 70 and/or toxic species like H<sub>2</sub>Se. Nano-particles of PdSe<sub>2</sub> and Pd<sub>17</sub>Se<sub>15</sub> have been recently grown using palladium complex viz.  $bis(N,N-diethyl-N\phi-naphthoylselenoureato)palladium(II)$  as a single source precursor.<sup>28</sup> Thus Pd(II)-complexes of pyrazole based organochalcogen may be worth exploring on this count 75 also as they may be used for low temperature preparation of

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palladium selenides. The known routes for the preparation of such phases typically involve heating of the two constituent elements in an evacuated sealed tube followed by annealing at high temperatures for several days.

<sup>5</sup> In present paper we report the synthesis of pyrazole based sulphur/selenated ligands and their palladium(II) complexes. These palladium(II) complexes were explored for their potential as catalyst for Suzuki-Miyaura cross coupling reaction and as single source precursors of Pd<sub>4</sub>Se and PdSe nano-particles.

#### 10 Experimental

#### Physical measurement

The C, H and N analyses were carried out with a Perkin-Elmer 2400 Series II C, H, N analyzer. The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>77</sup>Se{<sup>1</sup>H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 15 NMR spectrometer at 300.13, 75.47 and 57.24 MHz respectively. IR spectra in the range 4000-400 cm<sup>-1</sup> were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. The diffraction data on single crystals of 1-4 were collected on a Bruker AXS SMART Apex CCD diffractometer using Mo-Ka (0.71073 Å) 20 radiations at 298(2) K. The software SADABS<sup>29</sup> was used for absorption correction (if needed) and SHELXTL for space group, structure determination and refinements.<sup>30</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters 25 set at 1.2 times that of the carbon atom to which they are attached. The least-square refinement cycles on  $F^2$  were performed until the model converged. Powder X-ray diffraction (XRD) patterns of the dried powders were recorded on a Bruker D8 Advance diffractometer using Ni-filtered Cu-Ka radiation, at <sup>30</sup> a scanning step of 0.0334°, using Cu-Ka radiation ( $\lambda = 1.5406$  Å) in the range of  $\theta$ =20-80°. Samples for high resolution

prepared by drying a drop of dispersion of nano-crystals in cyclohexane or ethanol on carbon-coated copper grids. High-<sup>35</sup> resolution TEM characterization revealing particle sizes and shapes was performed with a Philips Tecnai F20 operated at 200 kV. The morphologies of nano-sized phases were studied with a Carl ZEISS EVO50 scanning electron microscope (SEM). Sample was mounted on a circular metallic sample holder with a

transmission electron microscopy (HR-TEM) analysis were

<sup>40</sup> sticky carbon tape. Elemental composition of these phases has been obtained by associated EDX system Model QuanTax 200, which is based on the SDD technology and provides an energy resolution of 127 eV at Mn-K $\alpha$ . The melting points determined in an open capillary are reported as such. Yields refer to isolated <sup>45</sup> yields of compounds which have purity  $\geq$  95%.

#### Chemicals and reagents

4–Bromopyrazole, thiophenol, diphenyl diselenide, sulphur/selenium powder, sodium borohydride, palladium chloride, silver tetrafluoroborate and trioctylphosphine (Technical <sup>50</sup> grade), procured from Sigma-Aldrich (USA) and Fluka were used as received All the solvents were dried and distilled before use

as received. All the solvents were dried and distilled before use by standard procedures.<sup>31</sup> The common reagents and chemicals available commercially within the country were used.

#### Synthesis of 4-bromo-1-(2-chloroethyl)-1H-pyrazole (A)

ss 4–Bromopyrazole (2.205 g, 15.0 mmol) was mixed with potassium carbonate (4.146 g, 30.0 mmol) and tetrabutylammonium bromide (0.484 g, 1.5 mmol). The mixture



Scheme 1 Synthesis of L1-L4 and 1-4.

<sup>60</sup> was added to 40 mL (taken in excess) of 1, 2–dichloroethane and the resulting reaction mixture was refluxed for 12 h. A light yellow suspension was formed. Its organic phase was decanted off. The solid residue was extracted with dichloromethane (2 × 25 mL). All the extracts were combined with the organic phase. The <sup>65</sup> volume of resulting combined organic phase was reduced on a rotary evaporator to 50%. The concentrated organic phase was washed with water and dried over sodium sulphate. Its solvent was removed under reduced pressure on a rotary evaporator resulting in **A** as light yellow oil.

<sup>70</sup> Yield: 2.828 g, 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, vs Me<sub>4</sub>Si) :  $\delta$  (ppm): 3.86 (t, <sup>3</sup>*J*<sub>H-H</sub> = 6.0 Hz, 2H, ClCH<sub>2</sub>), 4.40 (t, <sup>3</sup>*J*<sub>H-H</sub> = 6.0 Hz, 2H, NCH<sub>2</sub>), 7.51 (s, 2H, H<sub>a</sub> and H<sub>b</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C, vs Me<sub>4</sub>Si) :  $\delta$  (ppm): 42.5 (ClCH<sub>2</sub>), 53.9 (NCH<sub>2</sub>), 92.9 (BrC), 130.3 (C<sub>a</sub>), 140.5 (C<sub>b</sub>). IR (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3128 (m; v<sub>C</sub>-7<sup>5</sup> H<sub>(aromatic</sub>)), 2959 (s; v<sub>C-H(aliphatic</sub>)), 1518 (s; v<sub>C-N(aromatic</sub>)), 1439 (s; v<sub>C-C(aromatic</sub>)), 1141 (m; v<sub>C-N(aliphatic</sub>)), 847 (m; v<sub>C-H(aromatic</sub>)), 654 (m; v<sub>C</sub>-

#### Syntheis of L1

Cl(aliphatic)).

Thiophenol (0.441 g, 4.0 mmol) was added to sodium hydroxide <sup>80</sup> (0.160 g, 4.0 mmol) dissolved in 30 mL of EtOH and refluxed for 1h. 4–Bromo–1–(2–chloroethyl)–1*H*–pyrazole (0.837 g, 4.0 mmol) dissolved in 20 mL of EtOH was added to it. The resulting reaction mixture was further refluxed for 5 h. Thereafter, the reaction mixture was stirred for overnight at room temperature. It <sup>85</sup> was poured into cold water (30 mL). The L1 was extracted with chloroform (4 × 25 mL). The extract was washed with water (3 ×

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40 mL) and dried over anhydrous sodium sulphate. The solvent was evaporated off under reduced pressure on a rotary evaporator resulting L1 as light yellow oil.

- Yield: 1.019 g, 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, vs Me<sub>4</sub>Si):  $\delta$ <sup>5</sup> (ppm): 3.27 (t,  ${}^{3}J_{H-H} = 6.9$  Hz, 2H, H<sub>5</sub>), 4.19 (t,  ${}^{3}J_{H-H} = 6.9$  Hz, 2H, H<sub>6</sub>), 7.16-7.33 (m, 6H, H<sub>1</sub>,H<sub>2</sub>,H<sub>3</sub> and H<sub>7</sub>), 7.42 (s, 1H, H<sub>9</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C, vs Me<sub>4</sub>Si): δ (ppm): 33.6 (C<sub>5</sub>), 51.5 (C<sub>6</sub>), 92.6 (C<sub>8</sub>), 126.6 (C<sub>1</sub>), 128.9 (C<sub>2</sub>), 129.6 (C<sub>7</sub>), 129.7 (C<sub>3</sub>), 134.0 (C<sub>4</sub>), 139.9 (C<sub>9</sub>). IR (KBr,  $v_{max}/cm^{-1}$ ): 2928 (m;  $v_{C-1}$
- <sup>10</sup> H(aromatic)), 2855 (s; v<sub>C-H(aliphatic)</sub>), 1648 (s; v<sub>C-N(aromatic)</sub>), 1438 (s; v<sub>C-</sub> <sub>C(aromatic)</sub>), 1309 (m; v<sub>C-N(aliphatic)</sub>), 743 (m; v<sub>C-H(aromatic)</sub>). HR-MS  $[M+Na]^+$  (m/z) 304.9719; calc. Value for  $C_{11}H_{11}BrN_2NaS$ ; 304.9724 (δ: -3.3 ppm).

#### Synthesis of L2

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- 15 Diphenyldiselenide (0.312 g, 1.0 mmol) dissolved in 30 mL of EtOH was stirred under reflux in N2 atmosphere. Sodium borohydride (0.080 g, 2.0 mmol) was added to it as solid so that it became colorless due to the formation of PhSeNa. 4-Bromo-1-(2-chloroethyl)-1H-pyrazole (0.419 g, 2.0 mmol) dissolved in 10
- 20 mL of ethanol was added to the colourless solution with constant stirring and the mixture was further refluxed for 5 h. It was extracted with chloroform (4  $\times$  25 mL). The extract was washed with water  $(3 \times 40 \text{ mL})$  and dried over anhydrous sodium sulphate. The solvent from extract was evaporated off under 25 reduced pressure on a rotary evaporator to get L2 as yellow oil.
- Yield: 0.594 g, 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, vs Me<sub>4</sub>Si):  $\delta$ (ppm): 3.23 (t,  ${}^{3}J_{H-H} = 6.9$  Hz, 2H, H<sub>5</sub>), 4.28 (t,  ${}^{3}J_{H-H} = 6.9$  Hz, 2H, H<sub>6</sub>), 7.22-7.27 (m, 6H, H<sub>1</sub>, H<sub>2</sub>), 7.33 (s, 1H, H<sub>7</sub>), 7.41 (s, 1H, H<sub>9</sub>), 7.44–7.48 (m, 2H, H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C, vs <sup>30</sup> Me<sub>4</sub>Si): δ (ppm): 26.9 (C<sub>5</sub>), 52.7 (C<sub>6</sub>), 92.8 (C<sub>8</sub>), 127.5 (C<sub>1</sub>), 128.3 (C<sub>4</sub>), 129.2 (C<sub>2</sub>), 129.5 (C<sub>7</sub>), 133.1 (C<sub>3</sub>), 140.1 (C<sub>9</sub>). <sup>77</sup>Se{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C, vs Me<sub>2</sub>Se):  $\delta$  (ppm): 282.56. IR (KBr,  $v_{max}/cm^{-1}$ ): 2927 (m;  $v_{C-H(aromatic)}$ ), 2853 (s;  $v_{C-H(aliphatic)}$ ),

1645 (s; v<sub>C-N(aromatic)</sub>), 1474 (s; v<sub>C-C(aromatic)</sub>), 1254 (m; v<sub>C-N(aliphatic)</sub>),  $_{35}$  794 (m; v<sub>C-H(aromatic)</sub>). HR-MS [M+Na]<sup>+</sup> (m/z) 352.9160; calc.

Value for C<sub>11</sub>H<sub>11</sub>BrN<sub>2</sub>NaSe; 352.9180 (δ: -5.6 ppm).

#### Synthesis of L3 and L4

Sulphur powder (0.032 g, 1 mmol)/selenium powder (0.078 g, 1 mmol) added in 30 mL of ethanol were stirred under reflux in N2

- 40 atmosphere. Solid sodium borohydride (0.151 g, 4.0 mmol) was added to it so that it became colorless. 4-Bromo-1-(2chloroethyl)-1H-pyrazole (0.418 g, 2 mmol) dissolved in 10 mL of ethanol was added with constant stirring and the mixture stirred with refluxing for further 5 h. It was extracted with
- $_{45}$  chloroform (4 × 25 mL). The extract was washed with water (3 × 40 mL) and dried over anhydrous sodium sulphate. The solvent was evaporated off under reduced pressure on a rotary evaporator to get L3/L4 as yellow oil.

**L3:** Yield: 0.323 g, 85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, vs Me<sub>4</sub>Si):  $\delta$ 

- <sup>50</sup> (ppm): 2.80 (t,  ${}^{3}J_{H-H} = 6.3$  Hz, 4H, H<sub>5</sub>), 4.19 (t,  ${}^{3}J_{H-H} = 6.6$  Hz, 4H, H<sub>4</sub>), 7.42 (s, 2H, H<sub>3</sub>), 7.50 (s, 2H, H<sub>1</sub>).  $^{13}C\{^{1}H\}$  NMR  $(CDCl_3, 25 \ ^{\circ}C, vs Me_4Si): \delta (ppm): 31.8 (C_5), 52.2 (C_4), 92.7$ (C<sub>2</sub>), 129.8 (C<sub>3</sub>), 140. (C<sub>1</sub>). IR (KBr,  $v_{max}/cm^{-1}$ ): 2924 (m;  $v_{C-1}$ ) H(aromatic)), 2854 (s; v<sub>C-H(aromatic)</sub>), 1643 (s; v<sub>C-N(aromatic)</sub>), 1460 (s; v<sub>C-</sub>
- 55 C(aromatic)), 1261 (m; v<sub>C-N(aliphatic)</sub>), 898 (m; v<sub>C-H(aromatic)</sub>). HR-MS

 $[M+H]^+$  (m/z) 378.9232; calc. Value for C<sub>10</sub>H<sub>13</sub>Br<sub>2</sub>N<sub>4</sub>S; 378.9222  $(\delta: -2.5 \text{ ppm}), [M+Na]^+ (m/z) 400.9042;$  calc. Value for C<sub>10</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>4</sub>NaS; 400.9027 (δ: 3.7 ppm).

60 L4: Yield: 0.384 g, 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, vs Me<sub>4</sub>Si): δ (ppm): 2.83 (t,  ${}^{3}J_{H-H} = 6.9$  Hz, 4H, H<sub>5</sub>), 4.26 (t,  ${}^{3}J_{H-H} = 6.9$  Hz, 4H, H<sub>4</sub>), 7.43 (s, 2H, H<sub>3</sub>), 7.48 (s, 2H, H<sub>1</sub>).  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>, 25 °C, vs Me<sub>4</sub>Si):  $\delta$  (ppm): 23.4 (C<sub>5</sub>), 53.2 (C<sub>4</sub>), 92.9 (C<sub>2</sub>), 129.7 (C<sub>3</sub>), 140.2 (C<sub>1</sub>). <sup>77</sup>Se{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C, vs 65 Me<sub>2</sub>Se):  $\delta$  (ppm): 144.12. IR (KBr,  $v_{max}/cm^{-1}$ ): 2925 (m;  $v_{C}$ -H(aromatic)), 2855 (s; v<sub>C-H(aromatic)</sub>), 1645 (s; v<sub>C-N(aromatic)</sub>), 1460 (s; v<sub>C-N(a</sub> <sub>C(aromatic)</sub>), 1260 (m; v<sub>C-N(aliphatic)</sub>), 792 (m; v<sub>C-H(aromatic)</sub>). HR-MS  $[M+H]^+$  (m/z) 426.8660; calc. Value for  $C_{10}H_{13}Br_2N_4Se$ ; 426.8665 (δ: 1.4 ppm).

#### 70 Synthesis of complex 1 and 2

Solid [Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>] (0.052 g, 0.2 mmol) taken in CH<sub>3</sub>CN (20 mL) was stirred under reflux until a clear light yellow colored solution was obtained. The L1/L2 (0.057/0.066 g, 0.2 mmol) dissolved in CH<sub>3</sub>CN (5 mL) was added. The reaction mixture was 75 further refluxed for 5 h. It was cooled thereafter to room temperature, concentrated upto 7 mL on a rotary evaporator and mixed with diethyl ether (10 mL). The 1 or 2 resulting as orange colored solid was filtered, washed with diethyl ether (10 mL) and dried in *vacuo*. Single crystals of 1/2 were grown by slow 80 evaporation of its solution in DMSO.

- 1: Yield: 0.083 g, 90%. m.p. 230.0 °C. Anal. Calc. for C<sub>11</sub>H<sub>11</sub>BrCl<sub>2</sub>N<sub>2</sub>PdS: C, 28.69; H, 2.41; N, 6.08%. Found: C, 28.51; H, 2.36; N, 6.81%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 25 °C, vs Me<sub>4</sub>Si):  $\delta$  (ppm): 3.16 (broad singlet, 1H, H<sub>5</sub>), 3.53 (broad singlet,
- 85 1H, H<sub>5</sub>), 4.36 (broad singlet, 1H, H<sub>6</sub>), 4.78 (broad singlet, 1H, H<sub>6</sub>), 7.41–7.61 (m, 3H, H<sub>1</sub>, H<sub>2</sub>), 8.10–8.12 (m, 2H, H<sub>3</sub>), 8.28 (s, 1H, H<sub>7</sub>), 8.45 (s, 1H, H<sub>9</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>, 25 °C, vs Me<sub>4</sub>Si): δ (ppm): 36.1 (C<sub>5</sub>), 49.7 (C<sub>6</sub>), 92.6 (C<sub>8</sub>), 129.3 (C<sub>4</sub>), 129.7 (C<sub>2</sub>), 130.8 (C<sub>1</sub>), 133.0 (C<sub>3</sub>), 135.9 (C<sub>7</sub>), 143.3 (C<sub>9</sub>). IR 90 (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3131 (m; v<sub>C-H(aromatic)</sub>), 2978 (s; v<sub>C-H(aliphatic)</sub>),
- 1633 (s; v<sub>C-N(aromatic)</sub>), 1437 (s; v<sub>C-C(aromatic)</sub>), 1300 (m; v<sub>C-N(aliphatic)</sub>), 813 (m;  $v_{C-H(aromatic)}$ ). HR-MS  $[M+K]^+$  (m/z) 496.7828; calc. Value for C<sub>11</sub>H<sub>11</sub>BrCl<sub>2</sub>KN<sub>2</sub>PdS; 496.7865 (δ: 7.4 ppm).
- 95 2: Yield: 0.091 g, 90%. m.p. 235.0 °C. Anal. Calc. for C<sub>11</sub>H<sub>11</sub>BrCl<sub>2</sub>N<sub>2</sub>PdSe: C, 26.04; H, 2.19; N, 5.52%. Found: C, 26.10; H, 2.12; N, 5.69%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 25 °C, vs Me<sub>4</sub>Si):  $\delta$  (ppm): 2.93 (m, 1H, H<sub>5</sub>), 3.45 (m, 1H, H<sub>5</sub>), 4.77 (m, 1H, H<sub>6</sub>), 4.90 (m, 1H, H<sub>6</sub>), 7.32-7.511 (m, 3H, H<sub>1</sub>+ H<sub>2</sub>), 7.98-8.00 (m, 2H,  $100 H_3$ ), 8.14 (s, 1H, H<sub>9</sub>), 8.37 (s, 1H, H<sub>7</sub>).  $^{13}C{^1H}$  NMR (DMSO-d<sub>6</sub>, 25 °C, vs Me<sub>4</sub>Si):  $\delta$  (ppm): 31.48 (C<sub>5</sub>), 51.16 (C<sub>6</sub>), 92.6 (C<sub>8</sub>), 129.1 (C<sub>4</sub>), 129.9 (C<sub>2</sub>), 130.2 (C<sub>1</sub>), 133.1 (C<sub>3</sub>), 135.7 (C<sub>7</sub>), 143.5 (C<sub>9</sub>). <sup>77</sup>Se{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>, 25 °C, vs Me<sub>2</sub>Se):  $\delta$ (ppm): 366.93. IR (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3129 (m; v<sub>C-H(aromatic)</sub>), 2968 105 (s; v<sub>C-H(aliphatic)</sub>), 1633 (s; v<sub>C-N(aromatic)</sub>), 1437 (s; v<sub>C-C(aromatic)</sub>), 1246 (m;  $v_{C-N(aliphatic)}$ ), 815 (m;  $v_{C-H(aromatic)}$ ). HR-MS  $[M+K]^+$  (m/z) 544.7311; calc. Value for C<sub>11</sub>H<sub>11</sub>BrCl<sub>2</sub>KN<sub>2</sub>PdSe; 544.7285 (δ: 4.8 ppm).

#### Synthesis of complex 3 and 4

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Solid  $[Pd(CH_3CN)_2Cl_2]$  (0.052 g, 0.2 mmol) taken in CH<sub>3</sub>CN (20 mL) was stirred under reflux until a clear light yellow colored solution was obtained. The solution of ligand L3 (0.076 g, 0.2 mmol)/L4 (0.085 g, 0.2 mmol) dissolved in CH<sub>3</sub>CN (5 mL) was

- <sup>5</sup> added. The reaction mixture was further refluxed for 5 h. Thereafter solid AgBF<sub>4</sub> (0.038 g, 0.2 mmol) was added and the mixture refluxed further for 2 h. It was cooled to room temperature and precipitated AgCl was filtered off through celite. The filtrate was concentrated to 5 mL on a rotary evaporated and <sup>10</sup> mixed with diethyl ether (10 mL) to obtain **3/4** as yellow solid,
- which was filtered and dried in *vacuo*. The single crystals of 3/4 were grown by slow evaporation of its solution in CH<sub>3</sub>CN.
- **3:** Yield: 0.103 g 85%; m.p. 170.0 °C (d).  $\Lambda_{\rm M}$  = 158.2 S cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calc. for C<sub>10</sub>H<sub>12</sub>Br<sub>2</sub>ClN<sub>4</sub>PdS.BF<sub>4</sub>.: C, 19.73; H, 1.99;
- <sup>15</sup> N, 9.20%. Found: C, 19.71; H, 1.99; N, 9.22%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 25 °C, vs Me<sub>4</sub>Si):  $\delta$  (ppm) 3.31–3.60 (m, 4H, H<sub>5</sub>, merged with DMSO), 5.01–5.06 (m, 2H, H<sub>4</sub>), 5.27–5.35 (m, 2H, H<sub>4</sub>), 8.13 (s, 2H, H<sub>1</sub>), 8.43 (s, 2H, H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>, 25 °C, vs Me<sub>4</sub>Si):  $\delta$  (ppm): 36.0 (C<sub>5</sub>), 53.3 (C<sub>4</sub>), 93.4 (C<sub>2</sub>), 136.6
- <sup>20</sup> (C<sub>1</sub>), 143.8 (C<sub>3</sub>). IR (KBr,  $v_{max}/cm^{-1}$ ): 3169 (m;  $v_{C-H(aromatic)}$ ), 2962 (s;  $v_{C-H(aliphatic)}$ ), 1627 (s;  $v_{C-N(aromatic)}$ ), 1443 (s;  $v_{C-C(aromatic)}$ ), 1259 (m;  $v_{C-N(aliphatic)}$ ), 810 (m;  $v_{C-H(aromatic)}$ ). HR-MS [{M-BF<sub>4</sub>}+H]<sup>+</sup> (m/z) 519.7945; calc. Value for C<sub>10</sub>H<sub>13</sub>Br<sub>2</sub>ClN<sub>4</sub>PdS; 519.7944 ( $\delta$ : 0.3 ppm).
- <sup>25</sup> **4:** Yield: 0.112 g 85%; m.p. 160.0 °C (d).  $\Lambda_{\rm M} = 149.9$  S cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calc. for C<sub>10</sub>H<sub>12</sub>Br<sub>2</sub>ClN<sub>4</sub>PdSe.BF<sub>4</sub>: C, 18.32; H, 1.84; N, 8.54%. Found: C, 18.13; H, 1.92; N, 9.01%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 25 °C, vs Me<sub>4</sub>Si): δ (ppm): 3.24–3.31 (m, 2H, H<sub>5</sub>), 3.58–3.61 (m, 2H, H<sub>5</sub>), 5.17–5.22 (m, 2H, H<sub>4</sub>), 5.33–5.38 (m, 2H, H<sub>3</sub>), 8.42 (s, 2H, H<sub>1</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>, 25 °C, vs Me<sub>4</sub>Si): δ (ppm): 32.3 (C<sub>4</sub>), 54.3 (C<sub>5</sub>), 93.5 (C<sub>2</sub>), 136.4 (C<sub>3</sub>), 143.6 (C<sub>1</sub>). <sup>77</sup>Se{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>, 25 °C, vs Me<sub>2</sub>Se): δ (ppm): 342.42. IR (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3133 (m; v<sub>C</sub>-H(aromatic)), 3017 (s; v<sub>C-H(aliphatic)</sub>), 1631 (s; v<sub>C-H(aromatic)</sub>), 1447 (s; v<sub>C-H(aromatic)</sub>), 1256 (m; v<sub>C-N(aliphatic)</sub>), 844 (m; v<sub>C-H(aromatic)</sub>). HRMS [M–BF<sub>4</sub>]<sup>+</sup> (m/z) 566.7311; calc. Value for C<sub>10</sub>H<sub>12</sub>Br<sub>2</sub>ClN<sub>4</sub>PdSe; 566.7308 (δ: –0.5 ppm).

#### Procedure for the Suzuki-Miyaura coupling reaction

An oven-dried flask was charged with aryl bromide (1.0 mmol), <sup>40</sup> phenylboronic acid (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), DMF (3.0 ml), H<sub>2</sub>O (2.0 ml) and complex **1-4**. The flask was placed on an oil bath at 90°C with air condensor and the reaction mixture was stirred. The reaction monitored by TLC was carried out until maximum conversion of aryl halide to product occurred. The

<sup>45</sup> mixture was extracted with diethyl ether (2 × 20 mL), washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent of the extract was completely removed with a rotary evaporator to obtain the product, which was further purified by a column chromatography on silica gel. All coupling products were <sup>50</sup> authenticated by <sup>1</sup>H and <sup>13</sup>C {<sup>1</sup>H} NMR spectra.



Scheme 2 Suzuki-Miyaura Coupling Reaction

#### Hg poisoning test

For the mercury poisoning test an excess of Hg (Hg:Pd: 400 : 1) <sup>55</sup> 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 catalyst (1.0 mol%) as catalyst was carried out in the flask under optimum conditions. The conversion was not observed even after 2 h of <sup>60</sup> reaction. This may be ascribed to Hg poisoning.

#### PPh<sub>3</sub> poisoning test

To the coupling reaction of 4-bromobenzaldehyde with phenylboronic acid, PPh<sub>3</sub> (0.5 mol%) was added under optimal conditions before addition of catalyst (1.0 mol%). Even after 2 h <sup>65</sup> of reaction no cross-coupled products were obtained.

#### Isolation of nano-particles generated from 1-4 during Suzuki-Miyaura coupling

A mixture of Pd(II) complex 1/2/3/4 (0.5 mmol), phenylboronic acid (1.5 mmol), 4-bromobenzaldehyde (1.0 mmol) and K<sub>2</sub>CO<sub>3</sub>

70 (2.0 mmol) in DMF (4.0 mL) and water (4.0 mL) was heated at 100°C for 2 h and then cooled to room temperature. The solvent was decanted and the black residue (NPs) was washed with water-acetone mixture (1:3) and dried in *vacuo*. The NPs were characterized by SEM-EDX, and TEM.

#### 75 Procedure for Suzuki-Miyaura coupling catalyzed by NPs obtained from 1-4

The coupling reactions of 4-bromobenzaldehyde and 4bromoanisole under optimum conditions similar to those used with complexes **1-4** (except that 0.01 g of NPs obtained from **1-4** <sup>80</sup> replaced them) were carried out. All coupling products were authenticated by <sup>1</sup>H and <sup>13</sup>C {<sup>1</sup>H} NMR spectra.

#### Synthesis of Pd<sub>4</sub>Se and PdSe nano-particles

A mixture of 5.0 mL (11.0 mmol) of tri–*n*–octylphosphine (TOP) and 2/4 (0.507 / 0.655 g, 1.0 mmol) was heated to 200-250 °C <sup>85</sup> under N<sub>2</sub> atmosphere in a three neck flask for 2 h with continuous stirring. The colour of the mixture changed from yellowish to red-brown within 30 min and brown-black precipitate started appearing thereafter. The mixture was cooled to room temperature and 20 mL of acetone was added into the flask to <sup>90</sup> obtain a brown-black precipitate which was separated by centrifugation. The precipitate was washed three times with methanol (20 mL) and dried in vacuo.



Scheme 3 Synthesis of Pd<sub>4</sub>Se and PdSe Nano-Particles

95

55

#### **Results and discussion**

The syntheses of 4–bromo–1–(2–chloroethyl)–1*H*–pyrazole (**A**) is shown in equation (1), The synthesis of **L1-L4** and their Pd(II)complexes **1-4** are summarized in (Scheme 1). The molar <sup>5</sup> conductance values in acetonitrile indicate a 1:1 electrolyte nature of **3-4**. All the ligands were found soluble in common organic solvents. The solubility of complexes **1** and **2** was good in DMF and DMSO, moderate in CH<sub>3</sub>CN and almost negligible in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>OH, diethyl ether, THF and hexane. On <sup>10</sup> other hand complexes **3-4** showed good solubility in DMF, DMSO and CH<sub>3</sub>CN and were found sparingly soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CH<sub>3</sub>OH. In diethyl ether and hexane they were found insoluble.

#### NMR and IR spectra

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- <sup>15</sup> The  $^{77}$ Se{<sup>1</sup>H} NMR spectra of ligands (L2 and L4) and their corresponding complexes (2 and 4) are given in Figures S3-S6 of ESI<sup>†</sup>. The signals in the  $^{77}$ Se{<sup>1</sup>H} NMR spectra of 2 and 4 appear shifted to higher frequencies by 84.2 and 198.3 ppm respectively with respect to those of free L2 and L4, implying  $_{20}$  coordination of Se with palladium center. The  $^{1}H$  and  $^{13}C{^{1}H}$ NMR spectra (see ESI<sup>+</sup>, Figures S7-S22) of L1-L4 and their complexes 1-4 have been found consistent with their molecular structures (Scheme 1). The signals in the <sup>1</sup>H and  ${}^{13}C{}^{1}H$  NMR spectra of L1 and L2 have been found shifted to lower 25 frequencies upto 0.59 and 8.86 ppm and 0.63 and 15.56 ppm respectively with respect to 4-bromo-1-(2-chloroethyl)-1Hpyrazole (A), as Se is less electronegative than Cl. In  $^{1}$ H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of complexes **1-4** signals of various protons and carbon atoms generally appear at higher frequency 30 relative to those of free ligands which coordinate with palladium
- in a bidentate (1 and 2) or tridentate (3 and 4) mode. In <sup>13</sup>C{<sup>1</sup>H} NMR spectra of 1 and 2 signals of C5 and C9 are more deshielded relative to those of other carbon atoms present in the molecules. Same is true for C1 and C5 in case of 3 and 4. The <sup>35</sup> protons attached to all these carbon atoms also appear somewhat more deshielded than other protons of the four complex
- molecules. The high magnitude of shift for these four carbon atoms is probably due to the fact that they are very close to donor sites.
- <sup>40</sup> IR spectra of **L1-L4** have bands at 1254–1269 and 1643–1648 cm<sup>-1</sup> may be ascribed to C—N (aliphatic) and C—N (aromatic) stretching. On complex formation both these bands show red shift upto 8 and 16 cm<sup>-1</sup> respectively.

#### **Crystal structure**

- <sup>45</sup> The single crystal structures of complexes 1-4 have been solved. The details of crystal data and refinements are given in Tables S1 of ESI<sup>†</sup>. The ORTEP diagrams of 1-4 are given in Figures 1-4 with selected bond lengths and angles (more values are given in Table S2 of ESI<sup>†</sup>). The 1 and 2 are iso-structural. The geometry
- <sup>50</sup> around Pd in complexes 1-4 is nearly square planar and the ligands are coordinated with Pd in a bidentate (S/Se, N) or tridentate (N, S/Se, N) mode forming one (in case of 1 and 2) and two (in case of 3 and 4) six membered chelate rings respectively.



Figure 1. ORTEP diagram of 1 with ellipsoids at the 30% probability level; H atoms are omitted for clarity. Bond length(Å): Pd(1)—S(1) 2.273(11), Pd(1)—N(2) 2.028(2), 60 Pd(1)—Cl(1) 2.277(11), Pd(1)—Cl(2) 2.292(11); bond angle(°): Cl(1)—Pd(1)—S(1) 86.6(5), Cl(2)—Pd(1)—S(1) 175.7(3), N(2)—Pd(1)—S(1) 94.2(8), N(2)—Pd(1)—Cl(1) 179.1(7), N(1)—Pd(1)—Cl(2) 89.3(8), Cl(2)—Pd(1)—Cl(1) 89.9(5).



<sup>65</sup> Figure 2. ORTEP diagram of 2 with ellipsoids at the 30% probability level; H atoms are omitted for clarity. Bond length(Å): Pd(1)—Se(1) 2.381(7), Pd(1)—N(2) 2.035(3), Pd(1)—Cl(1) 2.287(11), Pd(1)—Cl(2) 2.315(11); bond angle(°): Cl(1)—Pd(1)—Se(1) 85.4(4), Cl(2)—Pd(1)—Se(1) 175.0(3), 70 N(2)—Pd(1)—Se(1) 94.4(9), N(2)—Pd(1)—Cl(1) 179.8(9), N(2)—Pd(1)—Cl(2) 89.8(9), Cl(2)—Pd(1)—Cl(1) 90.9(4).



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**Figure 4.** ORTEP diagram of **4** with ellipsoids at the 30% probability level; H atoms and BF<sub>4</sub> are omitted for clarity. Bond length(Å): Pd(1)—Se(1) 2.385(5), Pd(1)—N(2) 1.993(5), <sup>5</sup> Pd(1)—N(4), 2.005(5) Pd(1)—Cl(1) 2.284(16); bond angle(°): Cl(1)—Pd(1)—Se(1) 177.2(5), N(2)—Pd(1)—Se(1) 90.3(14), N(4)—Pd(1)—Se(1) 91.5(15), N(2)—Pd(1)—Cl(1) 89.2(14), N(4)—Pd(1)—Cl(1) 89.1(15), N(2)—Pd(1)—N(4) 177.5(2).

10 The Pd-S bond lengths of complexes 1/3 are 2.2731(11)/2.288(4)values14p,32 Å. consistent with earlier reported 2.270(16)-2.286(12) Å for [PdCl(O, N, S)ligand] and [PdCl(S, N, Se)ligand]<sup>+</sup>. These values are shorter than the reported values [2.299(3)-2.2976(10) Å ] for [PdCl<sub>2</sub>(S, N)ligand].<sup>34</sup> This 15 difference may be due to combined effect of difference in chelate ring size, substituent on S, donor strength of nitrogen and ligand architecture. The Pd-Se bond lengths of complex 2, 2.3806(7) Å and 4, 2.3854(5) Å are similar, probably because coordinating skeletons are identical in their ligand systems, but somewhat 20 shorter than the sum of covalent radii 2.44 Å. They are consistent with earlier reported value14i 2.3891(7) Å for [PdCl(Se, N, Se)ligand]<sup>+</sup> and somewhat longer than 2.353(2)-2.3669(11) Å reported for [PdCl(O<sup>-</sup>, N, Se)ligand] and [PdCl<sub>2</sub>(N, Se)ligand].<sup>14k-l,14p-q</sup> The Pd-N bond lengths of complexes 1-4 are 25 from 1.993(5) to 2.035(3) Å consistent with the sum of covalent radii 2.03 Å. Further the present Pd-N bond distances are within the range 1.985(3)-2.045(1) Å reported for [PdCl(Se, N, Se)ligand]<sup>+16i</sup> and [PdCl<sub>2</sub>(S, N)ligand].<sup>23-24</sup> The Pd-Cl bond lengths in 1-4 are also normal (in the range 30 2.2770(11)-2.3152(11) Å).<sup>14i, 14k-l,14p-q, 32-34</sup>



**Figure 5.** Inter and intra-molecular Cl····H, Br····H, C–H··· $\pi$  and  $\pi$ ··· $\pi$  interactions in **2**.

The bond angles at the coordinating S/Se and N atoms are as <sup>35</sup> expected for nearly trigonal-pyramidal and tetrahedral geometries, respectively.



**Figure 6.** Inter and intra-molecular Cl····H, Br····H, B-F····H  $_{40}$  interactions in **4**.

In the crystals of 1-4, due to secondary interactions (See Table S3 of ESI† for inter-atomic distances) several supramolecular structural patterns (see ESI†, Figures S23-S26 and Figures 5-6) have been observed. The inter-molecular/intra-<sup>45</sup> molecular Cl…H [2.722(1)–2.954(1) Å], Br…H [2.873(4)– 2.838(5) Å] C–H… $\pi$  [3.077(1)–3.150(1) Å] and  $\pi$ … $\pi$  [3.948(4)– 3.951(7) Å] interactions result in chain structures for complexes 1 and 2. In Figure 5 such structure for 2 is shown. In complexes 3 and 4 out of above four secondary interactions  $\pi$ … $\pi$  one is absent <sup>50</sup> and an additional B–F…H interaction exists (See Figure 6 for complex 4). Each BF<sub>4</sub> group is caged between complex cations. In 1 and 2, one-dimensional (1D) chain structures are formed along *b*-axis. The C–H… $\pi$  interactions in 3 [3.304(49)–3.405(62) Å] (see ESI†, Figure S24) are shorter than those of 4 [3.443(6)– <sup>55</sup> 3.815(3) Å].

#### Application in Suzuki-Miyaura coupling reaction

Suzuki-Miyaura reaction (Scheme 2) an important palladium catalyzed cross coupling is of wide interest.<sup>11</sup> In view of air and moisture sensitivity of complexes of phosphorus ligands, there is <sup>60</sup> a current interest in palladium complexes of phosphine-free ligands for the Suzuki-Miyaura reaction.<sup>35-37</sup> Complexes **1-4** have been explored for Suzuki-Miyaura reaction of aryl bromide with phenylboronic acid, as they offer the advantage of stability under ambient conditions. In Table 1 substrates, reaction time, mol% of <sup>65</sup> Pd used and percentage yield are given.

For carrying out Suzuki-Miyaura reactions of aryl bromide with phenylboronic acid the reaction conditions used were similar to those used for analogous phosphine-free systems.<sup>14e,14k</sup> The complexes **1-4** were found to show promising <sup>70</sup> catalytic activity<sup>14e</sup> for several aryl bromides (Table 1) including electron rich ones, as their low catalyst loading (~0.01 mol%) was found sufficient for good conversion in several cases. The highest yield (96%) was obtained in case of 4–bromobenzonitrile and 1–bromo–4–nitrobenzene both, when **4** was used as catalyst. <sup>75</sup> When Suzuki coupling was started a black precipitate appeared causing curiosity about the role of this precipitate in catalytic reaction. It is possible that **1-4** are only pre-catalysts and give nano-sized Pd(0) containing species during the reaction which in turn are responsible for catalysis. The black precipitates appeared

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during the course of catalysis of coupling of 4-bromobenzaldehyde with phenylboronic acid under optimum reaction conditions by 1-4, were isolated, washed, dried and subjected to SEM-EDX (see ESI<sup>†</sup>; Figure S47 and S50) and TEM <sup>5</sup> (Figure 7). They are of nano-size and spherical in shape. The sizes of NPs are ~19, ~2, ~5 and ~3 nm obtained from 1-4

- sizes of NPs are ~19, ~2, ~5 and ~3 nm obtained from 1-4 respectively. The SEM-EDX has revealed that they can be approximately formulated as  $Pd_4S$ ,  $Pd_2Se$ ,  $Pd_5S_2$  and PdSe respectively for complexes 1-4. These NPs were found 10 catalytically active as shown by results of representative coupling reactions given in Table 2. As expected isolated NPs appear to be somewhat deactivated in comparison to those generated *in situ* as their amount needed for comparable conversions is more than those of 1-4. Thus real catalysts appear to be NPs formed from 1-
- <sup>15</sup> 4, which are their dispensers only. This explains the little effect of change in ligand on catalytic efficiency also. To identify whether the reaction is heterogeneous or homogeneous Hgpoisoning<sup>14a</sup> and triphenylphosphine<sup>14a</sup> tests were carried out. Both the tests were positive further suggesting heterogeneous
  <sup>20</sup> nature of catalysis, which proceeds most probably via NPs composed of Pd-S/Se.<sup>14a,e</sup> The present results of catalytic coupling were found comparable with the earlier reports viz. Suzuki C–C coupling catalyzed with [PdCl<sub>2</sub>(N, S/Se) ligands]]<sup>14k</sup> and [PdCl(O<sup>-</sup>, N, Se)ligand],<sup>14p</sup> The short reaction time, 2 h in <sup>25</sup> present case is much lower than 24 h reported earlier for other catalysts<sup>14</sup> used for Suzuki coupling. The catalyst loading (0.01 mol %) in the present case is also lower compared to some previously reported complex catalysts [PdCl<sub>2</sub>(N, S/Se) ligands]]<sup>14k</sup> and [PdCl(O<sup>-</sup>, N, Se)ligand].

Further in comparison to several complex catalysts<sup>14</sup> which are giving good conversions at lower loading than the present one, the required reaction time in our case is very short. The additional advantage of using these catalysts is that they are air stable and also not moisture sensitive.



(a)

(b)



**Figure 7.** TEM images palladium-chalcogenide (Pd-S/Se) NPs <sup>40</sup> (a, b, c and d) obtained from **1-4** respectively.

		-								
Entry	Aryl Bromides	Mol %	1		2		3		4	
No.		Pd	Time	Yield	Time	Yield	Time	Yield	Time	Yield
			(h)	(%)	(h)	(%)	(h)	(%)	(h)	(%)
1										
-	Br NO <sub>2</sub>	0.01	2	90	2	92	2	94	2	96
2										
	Вг — СНО	0.01	2	88	2	90	2	93	2	95
3										
	Br CN	0.01	2	90	2	94	2	94	2	96
4										
	Br	0.01	2	86	2	90	2	92	2	94
5										
	Br — CH <sub>3</sub>		12	65	12	65	12	67	12	72
		1.0				-				o <b>-</b>
			24	75	24	78	24	82	24	85
6			10	(0	12	$(\mathbf{c})$	12	(5	12	(9
		1.0	12	60	12	62	12	65	12	68
			24	70	24	74	24	85	24	80

 Table 1 Suzuki-Miyaura coupling reactions catalyzed by 1-4.

isolated from 1-4.

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Aryl Bromides NP1 NP2 NP3 NP4 Entry Time No. (h) СНС 2 92 92 95 96 1 OCH 2 2 64 64 68 70 OCH. 97 3 12 85 87 95

Table 2 Suzuki-Miyaura coupling catalyzed by NPs (10 mg)

One pot single source synthesis of Pd<sub>4</sub>Se and PdSe nano-5 particles

The synthesis of nano-structured palladium selenides important due their potential applications (see Introduction) requires harsh condition or sophisticated experimental set up. We have observed that high quality TOP capped nano-particles of two such 10 selenides Pd<sub>4</sub>Se and PdSe may be synthesized by thermolysis of complexes 2 and 4 respectively (Scheme 3) at lower temperature (200-250 °C) as compared to other synthetic procedure reported in literature.<sup>28a</sup> Further our synthesis is one pot, based on single source precursor (for both Pd and Se). TOP acts potentially

- 15 surface ligand that stabilizes and mediates the growth of these NPs. It appears that palladium selenide phases formed are somewhat dependent on structure of precursor complexes. There are not many such examples reported earlier.<sup>38</sup> The NPs of Pd<sub>4</sub>Se and PdSe were authenticated by powder XRD patterns which 20 have been found matching with those reported for such phases
- (See ESI<sup>+</sup>, Figure S35-S38 and text below them). Both types of nano-particles are tetragonal. The sharp nature of the powder XRD patterns (see ESI<sup>+</sup>, Figures S35-S38) is consistent with their high crystallinity and nano-size. SEM-EDX and HR-TEM have
- 25 supported their compositions. The morphology of these nanoparticles as revealed by SEM is shown in Figure S31-S34 of ESI<sup>†</sup>. The results of SEM-EDX show that they are capped with TOP (see ESI<sup>+</sup>, Figures S35-S38). HR-TEM images have revealed size of TOP capped nano-particles spherical in shape, <sup>30</sup> obtained from **2** and **4** is in the range 8-26 nm (Figures 8 and 9).
- Attempts to synthesize palladium sulfide phases in nano-size by thermolysis of 1 and 3 in TOP (following a procedure analogous to one given in Scheme 3) has resulted in  $PdP_2$  instead of palladium sulphide. The phosphorus present in
- <sup>35</sup> PdP<sub>2</sub> nano-particles probably has come from capping ligand TOP. The phosphorous donors are considered stronger than sulphur ones and presence of three alkyl groups makes TOP further

stronger. Consequently TOP substitutes sulphur ligand and decomposition of Pd-TOP complex results in PdP<sub>2</sub>. Since TOP is 40 absent during coupling reaction, formation of palladium sulphide phases is not hindered. On the other hand Se is a strong donor and TOP fails to substitute Se lgands. Thus thermolysis of 2 and 4 has resulted palladium selenide nano-particles (Pd<sub>4</sub>Se and PdSe respectively). Probably formation of PdP<sub>2</sub> is not due to 45 decomposition of TOP otherwise it would have been observed as a serious impurity with Pd-selenide phases. The PdP<sub>2</sub> nanoparticles are of size 21 nm and authenticated by powder XRD, SEM-EDX and HR-TEM (see ESI<sup>†</sup>, Figures S35, S37, S39, S41, S43, S45, S51 and S52).





Figure 8. TEM image and distribution of Pd<sub>4</sub>Se NPs.





Figure 9. TEM image and distribution of PdSe NPs.

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#### Conclusions

- The four pyrazolated thio/selenoethers (L1-L4) have been synthesized by reaction of 4–bromo–1–(2–chloroethyl)–1*H* pyrazole with the *in situ* generated PhSNa, PhSeNa, Na<sub>2</sub>S, and <sup>5</sup> Na<sub>2</sub>Se and characterized by using <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>77</sup>Se {<sup>1</sup>H} NMR, IR and HRMS. Their Pd(II) complexes (1-4) have been synthesized by reacting them with [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] in CH<sub>3</sub>CN at 70 °C and also authenticated with <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>77</sup>Se {<sup>1</sup>H} NMR, IR, HRMS and single crystal X-ray diffraction. The
- <sup>10</sup> complexes 1–4 were found efficient pre-catalysts for the Suzuki-Miyaura coupling reaction, as the yield was found upto 96% in just 2 h. TOP capped nano-particles of Pd<sub>4</sub>Se and PdSe (size ranges 8-26 nm) have been obtained under mild conditions by thermolysis 1-4 at 200-250 °C. HRTEM, SEM, SEM-EDX and <sup>15</sup> powder XRD have authenticated these nano-particles. Attempt to prepare nano-particles composed of palladium and sulphur by a procedure similar to the one used for palladium-selenide phases resulted in PdP<sub>2</sub> nano-particles.

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<sup>25</sup> crystal X-ray (FIST) and HR-TEM (NSIT) facilities at IIT Delhi. HJ thanks University Grants Commission (India) for JRF.

#### Notes and references

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*E-mail: aksingh@chemistry.iitd.ac.in, ajai57@hotmail.com (A. K. Singh)* † Electronic Supplementary Information (ESI) available: NMR spectra (Figures S1–S22), Crystal data and refinement parameters (Table S1),

- <sup>35</sup> bond lengths and angles (Table S2), distances of non-covalent interactions (Table S3), non-covalent interactions with bond lengths (Figures S23–S26), Mass spectra (Figures S27–S34), PXRD (Figures S35–S38), SEM images (Figures S39–S42), SEM–EDX images (Figures S43–S50) and TEM images (Figures S51–S52). CIFs for 1–4. CCDC
- 40 numbers: 885700 (For 1), 885701 (For 2), 885702 (For 3) and 885703 (For 4). For ESI<sup>†</sup> and crystallographic data in CIF or other electronic formate see DOI: 10.1039/b000000x/
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## Palladium(II) complexes of pyrazolated thio/selenoethers: syntheses, structures, single source precursors of Pd<sub>4</sub>Se and PdSe nano-particles and potential for catalyzing Suzuki-Miyaura coupling

Kamal Nayan Sharma, Hemant Joshi, Ved Vati Singh, Pradhumn Singh and Ajai Kumar Singh\*



Pd(II)-complexes (characterized by X-ray crystallography) give Pd<sub>4</sub>Se/PdSe nano-particles and efficiently catalyze Suzuki-Miyaura coupling via *in situ* generated Pd-S/Se NPs.