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ARTICLE TYPE

Sterically hindered selenoether ligands: palladium(II) complexes as catalytic activators for Suzuki-Miyaura coupling

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2-Hydroxy/(benzyloxy)-3,5-ditertbutyl benzaldehyde reacts with $PhSeCH_2CH_2NH_2$ resulting in sterically hindered selenoether ligand (Schiff base) [2−HO−3,5−$(C(CH_3)_3)_2$−C_6H_2−C=N−$(CH_2)_2$SePh] (**L1**)/ [2−$PhCH_2O$−3,5−$(C(CH_3)_3)_2$−C_6H_2−CH_2−NH−$(CH_2)_2$SePh] (**L2**). The reactions of **L1** and **L2** with Na_2PdCl_4 in methanol and acetone-water mixture at room temperature have resulted in complexes, [PdCl (**L1**-H)] (**1**) and [$PdCl_2$(**L2**)] (**2**)], respectively. Both the complexes and their ligands have been characterized with ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectroscopy. The molecular structures of complexes **1** and **2** have been determined with single crystal X-ray diffraction. The Pd−Se bond lengths in **1** and **2** are 2.370(1) and 2.366(1) Å, respectively. The geometry around palladium in both the complexes is nearly square planar. Complexes **1** and **2** (0.1 mol % Pd) have been found efficient as catalyst for Suzuki-Miyaura C−C coupling reactions in the presence of K_2CO_3 in ethanol. The catalysis in water with complex **1** in the presence of K_2CO_3 was found feasible but with low conversion (up to 40%). The efficiency of **1** in carrying out the coupling is marginally better than that of **2**.

Introduction

The strong electron-donor ability of selenium has led to the synthesis of many transition metal complexes of organoselenium ligands, which have been found promising as catalysts for various organic transformations.[1] This has made organoselenium ligands currently important for designing catalysts for a variety of organic reactions. A wide range of such ligands is known e.g. selenocarbonyl,[2] pincer type,[3] and Schiff bases[4] promising for catalyst designing. One notable feature of transition metal complexes of organoselenium ligands is that they are much less insensitive to air and moisture in comparison to those which have traditional phosphorous donors. At present palladium complexes of organoselenium ligands in terms of catalytic activity are considered not only rivals of their respective phosphorus and sulphur analogues but have been found in many cases to outperform them.[3a]

The steric properties of ligands significantly influence the rate and selectivity of the reactions catalyzed by their transition metal complexes. The steric bulk of a ligand can increase the stability of the catalyst in its coordinatively unsaturated intermediate form or accelerate some steps, such as reductive elimination in cross-coupling reactions which are sterically sensitive.[5] Thus steric bulk of a ligand may play a role in tailoring efficiency of its complex as a catalyst for Suzuki–Miyaura cross-coupling reactions.[6] Palladium complexes derived from electron-rich and sterically demanding ligands, of the type monophosphanes,[7] N-heterocyclic carbenes,[8] and C_2-symmetric bis-hydrazone,[9] have been found effective catalyst for Suzuki–Miyaura cross-coupling reactions. However no report on sterically hindered organoselenium ligands is in our knowledge inspite of several reports on activation of Suzuki-Miyaura coupling with palladium complexes and palladacycles[10] of several organochalcogen donors including Se ones,[4a,c-e,11] and chalcogenated carbenes,[12] which have high efficiency and can be modified with ease.

We report herein the synthesis and structural characterization of sterically hindered selenoether ligands, [2−HO−3,5−$(C(CH_3)_3)_2$−C_6H_2−C=N−$(CH_2)_2$SePh] (**L1**) and [2−$PhCH_2O$−3,5−$(C(CH_3)_3)_2$−C_6H_2−CH_2−NH−$(CH_2)_2$SePh] (**L2**) and their palladium(II) complexes of the type , [PdCl (**L1**-H)] (**1**) and [$PdCl_2$(**L2**)] (**2**)], respectively. Two complexes **1** and **2** have been found suitable activators for Suzuki and Miyaura $C(sp^2)$−$C(sp^2)$ coupling reactions, which are powerful synthetic tools in organic synthesis,[13,14] along with other transition metal-catalyzed carbon-carbon bond forming reactions such as Heck, Sonogashira, Hiyama, Stille and Kumada coupling reactions. Suzuki and Miyaura coupling has made a significantly higher impact than others in the laboratory and the chemical industries due to three key reasons: (i) The reaction is feasible with a wide range of substrates and many functional groups are tolerated due to mild reaction conditions. This is very helpful in the total synthesis of complex molecules including drugs. (ii) Phenylboronic acid, starting material is readily available, stable and sustainable.[15] (iii) The product biaryl is a very important core component of various biologically and pharmaceutically important compounds (viz. anti-hypertensive, anti-cancer, anti-biotic, anti-inflammatory, and antifungal) and in nonlinear optical materials.[16]

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Experimental Section

Materials and methods: Diphenyl diselenide, 2-hydroxy-3,5-ditert-butyl benzaldehyde, 2-chloroethyl amine, sodium tetrachloropalladate, phenylboronic acid, potassium carbonate, and aryl bromides were procured from Sigma-Aldrich (USA). Reagents (commercially available from local sources) were used as received without further purification. $PhSe(CH_2)_2NH_2$ and 2-(benzyloxy)-3,5-di-tert-butylbenzaldehyde were prepared by a following the methods reported in the literature.[17,18] The progress of every coupling reaction was monitored with NMR spectroscopy. The products of Suzuki reactions were authenticated by matching their spectroscopic data with the reported literature values. ^{1}H, ^{13}C{^{1}H} and ^{77}Se{^{1}H} NMR spectra were recorded on a Bruker Spectrospin DPX 300 NMR spectrometer at 300.13, 75.47 and 57.24 MHz respectively. The chemical shifts are reported in ppm relative to internal standard (tetramethylsilane in case of ^{1}H, and ^{13}C{^{1}H} NMR and Me_2Se for ^{77}Se{^{1}H} NMR). Elemental analyses were carried out with a Perkin–Elmer 2400 Series II C, H, N analyzer.

X-ray diffraction data of crystals of **1** were collected on a Bruker AXS SMART-APEX diffractometer with a CCD area detector.[19] Similar data of **2** were collected on an Oxford Xcalibur S diffractometer with Sapphire-3 CCD detector.[20] Mo Kα radiations were used in both the cases. Both Crys Alis Pro software suite[21] and SADABS[22] software were used as per requirement. The structures were refined using the SHELX-97 program package and SHELXL97 (within the Win GX program package).[23-26] Non-hydrogen atoms were refined anisotropically. The molecular structures were created with the Diamond program.[27] Crystallographic data are given in Table 1.

Synthesis of L1: The selenated amine $C_6H_5Se{-}(CH_2)_2{-}NH_2$ (0.412 g, 2.06 mmol) and 2-hydroxy-3,5-ditert-butyl benzaldehyde (0.469 g, 2.00 mmol) were reacted in absolute ethanol (20 mL) at room temperature for 12 h. The volatiles from resulting reaction mixture were removed using rotary evaporator which resulted ligand **L1** as yellow viscous liquid in 93% yield (0.776 g, 1.86 mmol). ^{1}H NMR ($CDCl_3$): δ (ppm) = 1.36 (s, 9 H, C(CH_3)$_3$), 1.51 (s, 9 H, C(CH_3)$_3$), 3.24 (t, 2 H, SeCH_2), 3.91 (t, 2 H, NCH_2), 7.12–7.58 (7 H, Ar–*H*), 8.35(S, 1 H, C*H*=*N*), 13.55 (broads, 1 H, O*H*). ^{13}C{^{1}H} ($CDCl_3$): δ(ppm) = 28.3 (Se*C*H$_2$), 29.5 and 31.5 (C(*C*H$_3$)$_3$), 34.1 and 35.0 (*C*(CH$_3$)$_3$), 59.6 (N*C*H$_2$), 117.7, 126.0, 127.1, 129.2, 129.6, 132.9, 136.7, 140.1, 158.0 (Ar–*C*) 166.9 (N=*C*H). (^{77}Se {^{1}H} NMR, $CDCl_3$): δ(ppm) = δ 281.1.

Synthesis of L2: The selenated amine $C_6H_5Se{-}(CH_2)_2{-}NH_2$ (0.412 g, 2.06 mmol) and 2-(benzyloxy)-3,5-di-tert-butylbenzaldehyde (0.650 g, 2.00 mmol) were reacted in absolute ethanol (30 mL) at room temperature for 12 h. The volatiles were removed using rotary evaporator which resulted in yellow liquid. The yellow liquid formed was reacted with $NaBH_4$ (0.080 g, 2.11 mmol) in ethanol to obtain ligand **L2** as colourless viscous liquid in 91% yield (0.925 g, 1.82 mmol). ^{1}H NMR ($CDCl_3$): δ (ppm) = 1.32 (s, 9 H, C(CH_3)$_3$), 1.43 (s, 9 H, C(CH_3)$_3$), 1.74 (broad s, 1 H, N*H*), 2.86 (t, J_{HH} = 7.05 Hz, 2 H, SeCH_2), 2.97 (t, J_{HH} = 6.45 Hz, 2 H, NCH_2CH$_2$), 3.82 (s, 2 H, CH_2N), 5.00 (s, 2 H, OCH_2), 7.16–7.49 (broad m, 12 H, Ar–*H*). ^{13}C{^{1}H} ($CDCl_3$): δ(ppm) = 28.3 (*C*H$_2$Se), 31.2 and 31.5 (C(*C*H$_3$)$_3$), 34.4 and 35.3 (*C*(CH$_3$)$_3$), 48.7 (NH*C*H$_2$), 48.8(*C*H$_2$NH), 75.3 (O*C*H$_2$), 123.2, 125.2, 126.4, 126.6, 127.3, 128.3, 128.8, 129.8, 132.5, 132.8, 138.0, 141.8, 145.8 and 154.1 (Ar–*C*). (^{77}Se{^{1}H} NMR, $CDCl_3$): δ(ppm) = 267.8.

Synthesis of complex 1: The Na_2PdCl_4 (0.147 g, 0.5 mmol) was dissolved in 20 mL of methanol. The homogeneous methanolic solution of ligand **L1** (0.208 g, 0.5 mmol dissolved in 10 mL of methanol) was added with stirring. The mixture was further stirred for 6 h. The orange red coloured precipitate was obtained which was filtered and dried under vacuo. The single crystals of **1** were grown from $CH_3OH{-}CH_3CN$ mixture (1:1) by slow evaporation of its solution for one week. Yield: 88% (0.245 g, 0.44 mmol). Anal. Calcd for $C_{23}H_{30}ClNOPdSe$ (Mw: 557.29): C, 49.57; H, 5.43; N, 2.51%. Found: C, 49.60; H, 5.24; N, 2.64.^{1}H NMR (DMSO-d_6): δ (ppm) = 1.23 (s, 9 H, C(CH_3)$_3$),1.37 (s, 9 H, C(CH_3)$_3$), 3.10–3.20 (m, 2 H, CH_2), 3.72 (m, 1 H, CH_2), 4.46–4.50 (m, 1 H, CH_2), 7.17–8.18 (broad m, 5 H, C_6H_5), 8.09 (s, 1 H, N=C*H*), 7.35 (s, 1 H, C_5H_2), 8.19 (s, 1 H,C_5H_2). ^{13}C{^{1}H} ($CDCl_3$): δ(ppm) = 29.9 and 31.7 (C(*C*H$_3$)$_3$), 32.9 (*C*H$_2$Se), 34.0 and 35.8 (*C*(CH$_3$)$_3$), 65.7 (N=*C*H$_2$), 119.3, 125.6, 128.7,129.9,130.4, 130.5, 133.5, 136.1, 138.8, 161.3 (Ar–*C*), 162.4 (N=*C*H). (^{77}Se{^{1}H} NMR, $CDCl_3$): δ(ppm) = 432.1.

Synthesis of 2: The Na_2PdCl_4 (0.147 g, 0.5 mmol) was dissolved in 5.0 mL of water. A solution of ligand **L2** (0.254 g, 0.5 mmol) made in 10 mL of acetone was added to homogenized aqueous solution of Na_2PdCl_4 drop wise with vigorous stirring. The mixture was further stirred for 2 h resulting orange-red precipitate. It was poured into cold water (40 mL) and extracted with chloroform (4 x 30 mL). The combined extract was dried over anhydrous sodium sulphate. Its solvent was reduced to 5 mL and complex was precipitated using *n*-hexane. The precipitate was filtered and dried under vacuo. The single crystals of **2**, as **2**·CH_3CN were grown from $CH_3OH{-}CH_3CN$ mixture (1:1) by slow evaporation of its solution for one week. Yield: 84% (0.306 g, 0.42mmol). Anal. Calcd for $C_{30}H_{38}Cl_2NOPdSe{\cdot}CH_3CN$ (Mw: 725.93): C, 52.94; H, 5.69; N, 3.86%. Found: C, 52.82; H, 5.67; N, 3.78.^{1}H NMR ($CDCl_3$): δ (ppm) = 1.35 (s, 9 H, C(CH_3)$_3$),1.39 (s, 9 H, C(CH_3)$_3$), 2.63–2.65 (m, 2 H, CH_2), 3.55–3.58 (broad m, 2 H, CH_2), 4.19–4.27 (m, 1 H, CH_2), 4.69–4.73 (m, 1 H, CH_2), 4.80–4.90 (m, 2 H, OCH_2), 7.20–7.87 (broad m, 12 H, Ar–*H*). ^{13}C{^{1}H} ($CDCl_3$): δ (ppm) = 29.3 and 29.7 (C(*C*H$_3$)$_3$), 29.6 and 33.4 (*C*(CH$_3$)$_3$), 33.0 (*C*H$_2$Se), 33.5 (NH*C*H$_2$), 49.0 (NH(*C*H$_2$)Ar), 51.0 (OCH_2Ph), 123.4, 124.5, 125.4,125.6,125.9, 126.6, 126.8, 128.1, 128.2, 131.2, 135.1, 140.0, 145.9, 152.9 (Ar–*C*). (^{77}Se{^{1}H} NMR, $CDCl_3$): δ(ppm) = 489.3.

Procedure for Suzuki reaction of aryl bromides with phenylboronic acid: An oven dried flask was charged with aryl bromide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol) and ethanol (4.0 mL). The flask was placed on an oil bath at 80 ºC under aerobic condition and the reaction mixture stirred until maximum conversion of aryl bromide to coupled product occurred, as revealed with NMR spectroscopy. The mixture was extracted with diethyl ether (100 mL). The extract was washed with water (100 mL) and dried over anhydrous Na_2SO_4.

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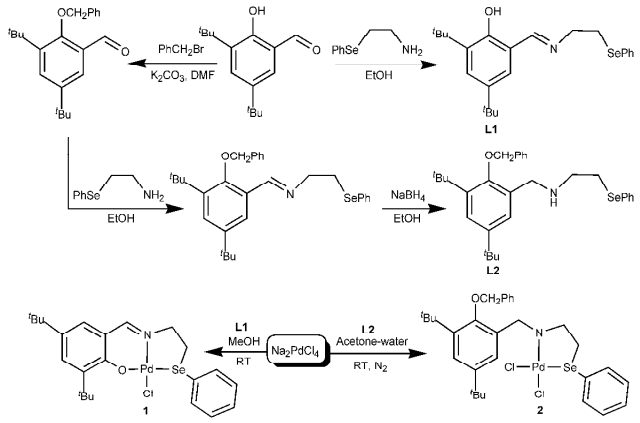
Results and discussion

Synthesis: The synthetic details of ligands **L1** and **L2**, and their corresponding palladium metal complexes **1** and **2** are summarized in Scheme 1. The **L1**, **L2**, **1** and **2**·CH_3CN are stable under ambient conditions. The complexes can be stored for six month without noticeable decomposition. The ligands and their complexes **1** and **2** have been characterized by their ^1H and $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$NMR spectra (See ESI for the spectra). These data are consistent with the structures depicted for them in Scheme 1.

Crystal structures: Molecular structures of **1** and **2** were determined with single crystal X-ray diffraction. The crystal and structure refinement data are given in Table 1. The Fig. 1 depicts molecular structure of **1** (Ellipsoid at 30% probability level; hydrogen atoms have been omitted for clarity). The palladium in **1** is surrounded by O1, N1, Se1 and Cl1 resulting in almost square planner geometry as shown in Fig. 1. The ligand in complex **1**, coordinates with Pd in a mono anionic tridentate (Se, N, O^-) mode forming a six and five membered chelate ring. The six membered ring is formed *via* O^- and N whereas five membered *via* Se and N. The Pd–N bond length 1.996(4) Å in **1** is comparable to the reported values of 1.985(4) Å for [PdCl{2−O−3−$CH(CH_2CH_3)_2$−C_6H_3−C=N−$(CH_2)_2$SeMe}] (**I**) and 2.003(7)Å for [PdCl{2−O−$C_6H_4C(CH_3)$=N$(CH_2)_2$SePh}] (**II**).[4a,4b] However, it is slightly shorter than those reported for [PdCl{2−O−$C_6H_4C(C_6H_5)$=N$(CH_2)_2$SePh}] (**III**) 2.010(4) Å and [PdCl{2−O−$C_{10}H_6C(CH_3)$=N$(CH_2)_2$SePh}] (**IV**) 2.010(3) Å.[4c,4d] The Pd–O distance 2.001(3) Å in **1** is comparable with values reported for (**I**) 2.017(4) and (**III**) 1.993(3) Å and longer than those of (**II**) 1.977(6) and (**IV**) 1.973(2)Å. Similarly Pd–Se bond distance 2.370(1) Å in **1** is comparable with values for (**I**) 2.365(1) and (**II**) 2.367(1) Å and longer than those of (**III**) 2.358(1) and (**IV**) 2.360(1) Å. The Pd–Cl distance 2.302(1) Å in **1** is comparable with the value reported for (**II**) 2.305(2) Å and little shorter than those of (**I**) 2.323(2), (**III**) 2.315(2) and (**IV**) 2.316(1) Å. The molecular structure of **2** is shown in Fig. 2 (Ellipsoid at 30% probability level; hydrogen atoms have been omitted for clarity). The palladium in **2** has nearly square planner geometry constituted by N1, Se1, Cl1 and Cl2. The bond distances: Pd–Se 2.366(1) and Pd–Cl1 2.306(1) Å in **2** are comparable with the values mentioned above, 2.370(1) Å and 2.302(1) Å in case of **1**, respectively**.** However, the Pd–N distance 1.996(4) Å in **1** is shorter than 2.066(3) Å found in case of **2**·CH_3CN. Significant non-covalent interactions observed in **1** and **2** are listed in Table 2. In the crystal of complex **1** intermolecular C–H···Cl non-covalent interactions exist as shown in Fig. 3. The Cl1 atom acts as a bifurcated hydrogen bond acceptor with H2 (SePh) and H8A (methylene group of adjacent molecule; C8). In crystal of **2**·CH_3CN C–H···N hydrogen bonding interactions are present in addition to intermolecular C–H···Cl non-covalent interactions as shown in Fig. 4. In this crystal**,** the Cl2 atom acts as a bifurcated hydrogen bond acceptor with H8B (methylene group; C8) and H20 (CH_2Ph) of another adjacent molecule. The Cl1 atom is hydrogen bonded with H31B (CH_3CN) of adjacent molecule. In addition, the N2 atom of CH_3CN acts as hydrogen bond acceptor with H16A (C16 of CH_2Ph group) of adjacent molecule.



Scheme 1 Synthesis of ligands **L1** and **L2** and their Pd(II) complexes.

Table 1 Crystallographic data and structure refinement summary for **1** and **2**.

	1	**2**·CH_3CN
Formula	$C_{23}H_{30}NOPdClSe$	$C_{32}H_{41}N_2OPdCl_2Se$
Formula weight	557.29	725.93
T/*K*	298(2)	298(2)
λ/Å	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a/Å	10.9228(4)	12.3315(5)
b/Å	10.0631(4)	10.4554(4)
c/Å	43.0466(17)	26.1643(10)
α/deg	90.00	90.00
β/deg	90.00	97.856(4)
γ/deg	90.00	90.00
Vol/Å^3	4731.5 (3)	3341.7 (2)
Z	8	4
D_{calcd}/ g.cm^{-3}	1.565	1.443
F(000)	2240	1476
*θ*range/deg	2.91−25.00	3.06−25.00
Reflections measured	4159	5885
Reflections used	3702	5337
Parameters	259	359
μ(Mo Kα) (cm^{-1})	2.449	1.830
R_1, $wR_2[I > 2\sigma(I)]^a$	0.0488, 0.0558	0.0357, 0.0407
R_1, wR_2 (all data)^b	0.1014, 0.1040	0.0818, 0.0840
GooF^c	1.302	1.216

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^bwR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $^cS = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)^2]\}^{1/2}$

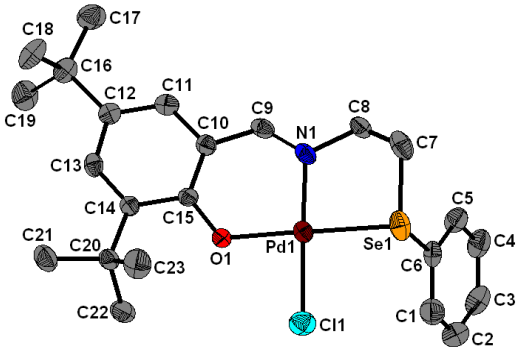


Fig. 1 ORTEP representation of **1**. Selected bond lengths (Å) and angles (°): Pd1–N1 1.996(4), Pd1–O1 2.001(3), Pd1–Se1 2.370(1), Pd1–Cl1 2.302(1); N1–Pd1–O1 92.5(2), N1–Pd1–Cl1 178.3(1), O1–Pd1–Cl1 88.3(1), N1–Pd1–Se1 89.1(1), O1– Pd1–Se1 177.2(1), Cl1–Pd1–Se1 90.1(1).

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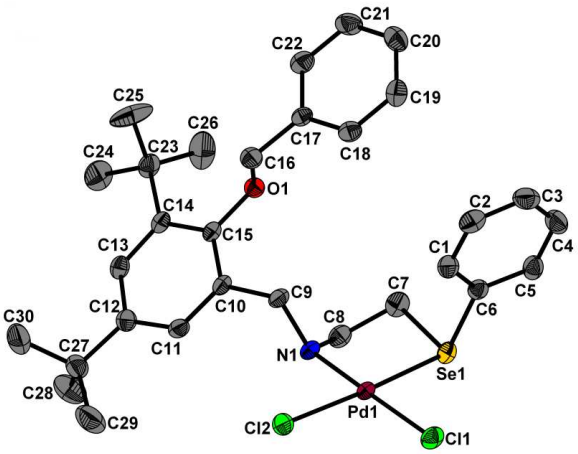

Fig. 2 ORTEP representation of **2**. Selected bond lengths (Å) and angles (°): Pd1–N1 2.066(3), Pd1–Se1 2.366(1), Pd1–Cl1 2.306(1), Pd1–Cl2 2.331(1); N1–Pd1–Cl1 176.0(1), N1–Pd1–Cl2 88.0(1), Cl1–Pd1–Cl2 95.1(1), N1–Pd1–Se1 88.9(2), Cl1– Pd1–Se1 87.9(4), Cl2–Pd1–Se1 176.8(1).

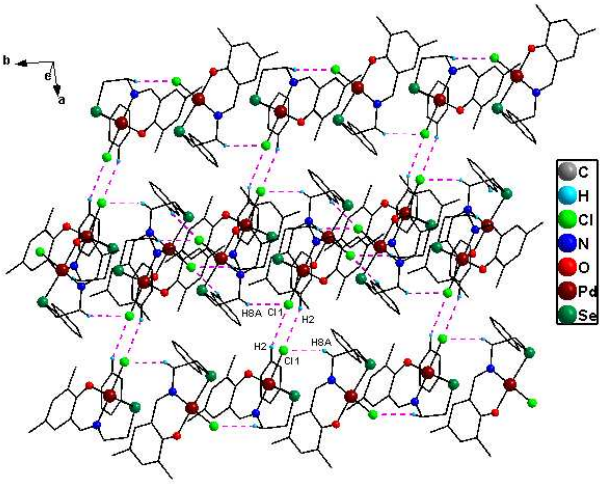

Fig. 3 Packing diagram of **1** illustrating intermolecular C–H···Cl hydrogen bonding in the crystal lattice.

Table 2 Selected non-covalent interactions of **1** and **2** (Inter atomic distances in Å and bond angles in deg).

D–H····A	D–H	H····A	D····A	D–H····A
		1		
C8–H8A····Cl1[a]	0.97	2.68	3.45	140
C2–H2····Cl1[b]	0.93	2.85	3.69	151
		2		
C16–H16A····N2[c]	0.97	2.69	3.55	148
C31–H31B····Cl1[d]	0.96	2.79	3.71	162
C20–H20····Cl2[e]	0.93	2.90	3.61	135
C8–H8B····Cl2[f]	0.97	2.90	3.68	139

a = ½-x,-1/2+y,z; b=1-x,1-y,-z; c= 1-x,1-y,1-z; d= x,y,1+z; e= -1+x, y, z; f = 1-x,-y,2-z.

Spectroscopic studies: The ^{1}H and ^{13}C{^{1}H} NMR spectra of ligand **L1** and **L2** have been found consistent with their structures depicted in Scheme 1. The signal of OH proton in ^{1}H NMR spectrum of **L1** has been observed at δ 13.55 ppm. The ^{77}Se{^{1}H}NMR spectrum of **L1** has a signal at δ 281.1 ppm

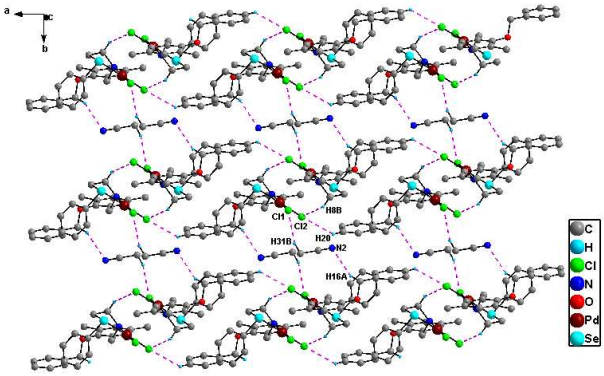

Fig. 4 Packing diagram of **2**·CH_3CN illustrating intermolecular C–H···Cl and C–H···N hydrogen bonding in the crystal lattice.

consistent with the value reported in literature (δ 281.5 ppm for selenoether[4d]). In ^{1}H NMR spectrum of ligand **L2**, the signal of NH proton appears as a broad singlet at δ 1.74 ppm. The signals for CH_2N and OCH_2 protons in proton NMR spectrum of ligand **L2** appear at δ 3.82 and 5.00 ppm, respectively. All expected signals were observed in ^{13}C{^{1}H} NMR spectra of ligands **L1** and **L2**. ^{77}Se{^{1}H}NMR spectrum **L2** shows a signal at δ 268.9 ppm. In complex **1**, the ligand **L1** coordinates to Pd in a mono anionic tridentate (Se, N, O^-) mode which is corroborated by its single crystal structure. The signal of phenolic proton present at δ = 13.55 ppm in the NMR spectrum of ligand **L1** has been found disappeared on complexation. This indicates the deprotonation of phenolic OH on formation of complex **1**. In ^{1}H NMR spectrum of complex **1**, each proton of both CH_2 groups becomes diastereotopic and this results in three multiplets at δ, 3.10–3.20, 3.72 and 4.46–4.50 ppm (2H, 1H and 1H, respectively; see Fig. S7 in ESI), supporting Pd–N and Pd–Se bond formation. The ^{77}Se{^{1}H}NMR spectrum of complex **1** has a signal at δ 432.1 ppm which is highly deshieded (151 ppm) compared to that of free ligand. This may be ascribed due to coordination of selenium to palladium. The large deshielding may be due to formation of five membered chelate ring[4d] with Pd. In complex **2** the ligand **L2** coordinates to Pd in a neutral bidentate (Se, N) mode as corroborated by its single crystal structure. In ^{1}H NMR spectrum of complex **2** also, protons of each CH_2 group become diastereotopic and result in five multiplets at δ2.63–2.65, 3.55–3.58, 4.19–4.27, 4.69–4.73 and 4.80–4.90 ppm (2H, 2H, 1H, 1H, and 2H, respectively see Fig. S10 in ESI), consistent with Pd–N and Pd–Se bond formation, which makes the NCH_2 and CH_2Se protons rigid. The ^{77}Se{^{1}H}NMR spectrum of complex **2** has a signal at δ 489.3 ppm, highly deshieded (221.5 ppm) compared to that of free ligand, indicating the coordination of selenium with palladium.

Suzuki-Miyaura C−C coupling catalyzed with 1 and 2: Suzuki-Miyaura C−C coupling reactions were carried out in the presence of complexes **1** and **2** as catalyst and results obtained are summarized in Table 3 and 4. The optimization of reaction conditions with present catalyst **1** was carried out by coupling 4-bromotoulene and phenylboronic acid under aerobic conditions at 80 ºC for 5 h using different bases and solvents. The best results were obtained with K_2CO_3 and ethanol (Table 3, Entry 6). The conversion was also observed in water (up to 40%) with K_2CO_3 (Table 3, Entry 13). The coupling reaction of 4-bromo-

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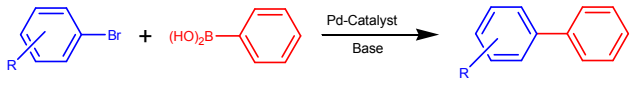
Table 3 Optimization of reaction conditions for Suzuki-Miyaura C−C coupling reactions of 4-bromotoluene with phenylbronic acid[a]

Entry No	Solvent	Base	Yield[b] (%)
1	1,4-dioxane (4 mL)	CH_3ONa	42
2	1,4-dioxane (4 mL)	K_2CO_3	50
3	DMF (4 mL)	CH_3ONa	41
4	DMF (4 mL)	K_2CO_3	47
5	EtOH (4 mL)	CH_3ONa	82
6	EtOH (4 mL)	K_2CO_3	88
7	1,4-dioxane: water (3:1 mL)	CH_3ONa	41
8	1,4-dioxane: water (3:1 mL)	K_2CO_3	42
9	DMF: water (3:1 mL)	CH_3ONa	33
10	DMF: water (3:1 mL)	K_2CO_3	39
11	EtOH: water (3:1 mL)	CH_3ONa	52
12	EtOH: water (3:1 mL)	K_2CO_3	68
13	Water (4 mL)	K_2CO_3	40

[a]Reaction conditions: 1.0 equiv of aryl halide, 1.2 equiv of phenylboronic acid, and 2 equiv of base and temperature of bath 80 °C. Catalyst **1**: 0.1 mol% Pd. Time: 5 h; [b]NMR(%) yield.

Table 4 Suzuki−Miyaura Coupling Reaction Catalyzed by Catalysts **1** and **2**.[a]



Entry No	Aryl halide	Catalyst	Yield[b] (%) (TON)	TOF(h^{-1})
1	4-Bromonitrobenzene	**1**	100(1000)	200
2	4-Bromonitrobenzene	**2**	100(1000)	200
3	4-Bromobenzonitrile	**1**	100(1000)	200
4	4-Bromobenzonitrile	**2**	100(1000)	200
5	4-Bromoacetophenone	**1**	100(1000)	200
6	4-Bromoacetophenone	**2**	100(1000)	200
7	4-Bromotoluene	**1**	88(880)	176
8	4-Bromotoluene	**2**	82(820)	164
9	4-Bromobenzaldehyde	**1**	75(750)	150
10	4-Bromobenzaldehyde	**2**	71(710)	142
11	4-Bromoanisol	**1**	35(350)	70
12	4-Bromoanisol	**2**	32(320)	64
13	4-Bromobenzoic acid	**1**	70(700)	140
14	4-Bromobenzoic acid	**2**	61(610)	122

[a]Reaction conditions: 1.0 equiv of aryl halide, 1.2 equiv of phenylboronic acid, and 2 equiv of base (K_2CO_3), solvent: EtOH (4 mL) and temperature of bath 80 °C. Catalyst: 0.1 mol% Pd; Time: 5 h. [b]NMR(%) yield.

nitrobenzene/4-bromobenzo-nitrile/4-bromoacetophenone with phenylboronic acid in the presence of 0.1 mol% of **1** or **2** in 5 h at 80 °C, resulted in corresponding biaryl in 100% yield (Table 4, Entry 1-6). The coupling between 4-bromotoluene and phenylboronic acid in the presence of 0.1 mol% of **1** for 5 h at 80 °C, resulted in corresponding biaryl in 88% yield (Table 4, Entry 7). However, when catalyst **2** was used for the same coupling under similar reaction conditions yield of corresponding coupling product, biaryl reduced to 82% (Table 4, Entry 8). Similar trends were observed in the case of 4-bromobenzaldehyde, 4-bromoanisole and 4-bromobenzoic acid under similar reaction condition which gave 75, 35 and 70% conversion to corresponding biaryl with catalyst **1** and 71, 32 and 61% with catalyst **2**. These trends are due to the fact that the catalytic activity is dependent on the nature of the electron withdrawing group on the aryl ring, the reactivity increases in the order of NO_2 > H > OMe. The catalytic efficiency of **1** appears to be slightly higher than that of **2**. In comparison to palladium complexes[4a,c-e,9,11] other than the palladacycles and pincer ligand based ones the performance of **1** and **2** is comparable or better in comparison to those containing N/S donors. Similarly the present complexes are comparable (in some cases favourably) with palladium nanoparticle based catalytic systems.[28] Air and moisture insensitivity of **1** and **2** are their additional advantages. However they cannot be recycled for catalytic applications

Conclusions

Two sterically hindered selenated Schiff bases and their palladium(II) complexes have been synthesized and structurally characterized with ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra. In $^{77}Se\{^1H\}$ NMR spectra deshielding of signal on complexation was up to 221.5 ppm compared to that of corresponding free ligand. The ligand **L1** coordinates as tridentate (N, Se, O^-) mode in complex **1** whereas **L2** coordinates as a bidentate (N, Se) ligand in **2** as revealed by single crystal structure. Complexes **1** and **2** are efficient catalysts for Suzuki-Miyaura C−C coupling reactions for aryl bromide with phenylboronic acid in presence of K_2CO_3 in ethanol at 80 ºC in 5 h. The reactivity increases on the nature of the substituent on the aryl ring and follows the order NO_2 > H > OMe. The catalytic conversion was also observed up to 40% with K_2CO_3 in water with catalyst **1**. The efficiency of **1** in carrying out the coupling is slightly higher than that of **2**.

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† Electronic Supplementary Information (ESI) available: ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra of **L1**, **L2**, **1** and **2**; Crystallographic data in CIF format for complexes **1** and **2** (CCDC1009785 and 1009786). For ESI and crystallographic data in CIF or other electronic format. See DOI: 10.1039/b000000x/

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Graphical Abstract

Sterically hindered selenoether ligands: palladium(II) complexes catalytic activators for Suzuki-Miyaura coupling

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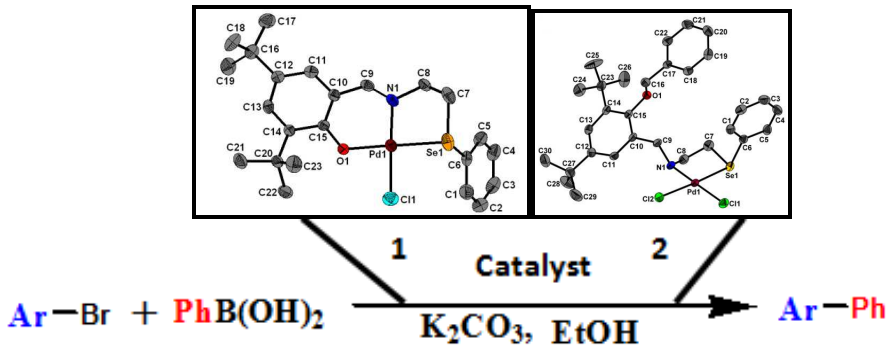

[PdCl(**L**-H)](**1**)/[$PdCl_2$**L**](**2**)](**L:** Schiff base) and catalyze (at 0.1 mol% loading of Pd) Suzuki coupling in ethanol at 80 °C. TON/TOF: 100/200