Tetradentate selenium ligand as a building block for homodinuclear complexes of Pd(II) and Ru(II) having seven membered rings or bis-pincer coordination mode: high catalytic activity of Pd-complexes for Heck reaction†

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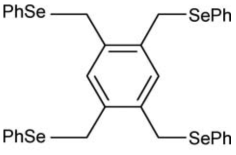
1,2,4,5-Tetrakis(phenyselenomethyl)benzene (**L**) has been synthesized by reaction of *in situ* generated PhSe$^-$ with 1,2,4,5-tetrakis(bromomethyl)benzene in N_2 atmosphere. Its first bimetallic complexes and a bis-pincer complex having compositions $[(\eta^3\text{-}C_3H_5)_2Pd_2(\mathbf{L})][ClO_4]_2$ (**1**) $[Pd_2(C_5H_5N)_2(\mathbf{L})][BF_4]_2$ (**2**) and $[(\eta^6\text{-}C_6H_6)_2Ru_2(\mathbf{L})Cl_2][PF_6]_2$ (**3**) have been synthesized by reacting **L** with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, $[Pd(CH_3CN)_4][BF_4]_2$ and $[(\eta^6\text{-}C_6H_6)_2RuCl_2]_2$ respectively. The structures of ligand **L** and its all three complexes have been determined by X-ray crystallography. In **1** and **3**, ligand **L** forms with two organometallic species seven membered chelate rings whereas in **2** it ligates in a bis-pincer coordination mode. The geometry around Pd in **1** or **2** is close to square planar whereas in **3**, Ru has pseudo-octahedral half sandwich "Piano–Stool" geometry. The Pd–Se bond distances are in the ranges 2.4004(9)–2.4627(14) Å and follow the order **1** > **2**, whereas Ru–Se bond lengths are between 2.4945(16) and 2.5157(17) Å. The **1** and **2** have been found efficient catalysts for Heck reaction of aryl halides with styrene and methyl acrylate. The **2** is superior to **1**. The TON and TOF values (per Pd) are up to ~ 47500 and ~2639 h^{-1} respectively.

Introduction

Metal complexes of a variety of pincer ligands having N, P, S and Se donors in side arms and one of B, C, N and P as central donor atom have received attention in the recent past[1–12] mainly due to their applications in catalyst designing. The interest in selenium containing pincer ligands appears to be as strong as in others. Selenylation of propargyl-, allyl-, benzyl-, and benzoyl halides under mild reaction conditions using trimethylstannylphenylselenide as selenylating agent has been catalyzed[13] with a complex of palladium(II) with pincer ligand of Se–C–Se type. The Pd(II) complex of a similar type of pincer ligand[14] is involved in an efficient route to functionalized allylboronic acids and potassium trifluoro(allyl)borates. One-pot efficient synthesis of stereo-defined α-amino acids and homoallyl alcohols was designed by integration of the Pd(II)-pincer ligand S–C–S / Se–C–Se complex catalyzed borylation of allyl alcohols in the Petasis borono-Mannich reaction and in allylation of aldehydes and ketones[2] respectively. A palladium-pincer Se–C–Se ligand complex catalyzes direct boronation of allyl alcohols with diboronic acid under mild conditions.[15] Highly regio- and stereoselective coupling of allyl alcohols with aldehydes has been achieved using 5 mol % of Se–C–Se pincer-Pd complex catalyst and *p*-toluenesulfonic acid in the presence of diboronic acid.[16] Coupling of allylboronic acids with iodobenzenes, which results in selective formation of the branched allylic products in the absence of directing groups, has been catalyzed by a Se–C–Se pincer-Pd complex,[17] which has also been used in the catalytic system for single pot synthesis of homoallyl alcohols.[5] There is one report in which Heck reaction[18a] has been catalyzed by Se–C–Se pincer-Pd complex. The outstanding activity of Se–C–Se pincer in selective synthesis[18b] of organometallic compounds has also been reported. The pincer ligand of Se–N–Se type was recently reported by our group[12] and its Pd-complex was found to show high catalytic activity for Heck coupling. There are few reports on S–C–S type bis-pincer ligands. They have been used as building blocks for supramolecular arrays[19] and polymers.[20,21] Only two reports[22,23] on the bis-pincer ligands of Se–C–Se type are in our knowledge. In one[22] analogues of present ligand **L** having different organic groups in the place of Ph are reported, which have been found to show propensity for trapping Hg(II). The other one describes structurally characterized 1 : 1 complex of $Mo(CO)_4$ unit with methyl analogue of **L**.[23]



(**L**)

No bimetallic complex (metal: ligand ratio 2 : 1) of a Se–C–Se type bis-pincer ligand has been structurally characterized so far. It was therefore thought worthwhile to synthesize **L** and such complexes and structurally characterize them. The reactions of **L** with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, $[Pd(CH_3CN)_4][BF_4]_2$ and $[(\eta^6\text{-}C_6H_6)_2RuCl_2]_2$ result in two type of species. With $(CH_3CN)_4Pd(II)$, it behaves as a Se–C–Se type bis-pincer ligand, whereas with $(\eta^3\text{-}C_3H_5)Pd(II)$ and $(\eta^6\text{-}C_6H_6)Ru(II)$ it forms a pair of seven membered

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† Electronic supplementary information (ESI) available: Tables of additional crystal data and refinement parameters (Table S1), bond lengths and angles (Table S2), IR data, Figures of non-covalent interactions with bond lengths (Figs S1–S5), ^{77}Se NMR spectra (Table S6–S9). CCDC reference numbers 763938 (**L**), 765901 (**1**), 763939 (**2**) and 770943 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00561d

chelate rings. The two Pd(II) complexes show high catalytic activities for Heck reaction. The results of these investigations are presented in this paper.

Experimental

Materials and instruments

Diphenyldiselenide, 1,2,4,5-tetrakis(bromomethyl)benzene and tetrakis(acetonitrile) palladium(II) tetrafluoroborate procured from Sigma–Aldrich (USA) were used as received. μ-Dichlorobis(η^3-allyl)palladium(II) and di-μ-chlorobis(η^6-benzene) dichlororuthenium(II) were prepared according to literature methods.[24,25] All the solvents were dried and distilled before use, by well known standard procedures. The common reagents and chemicals available commercially in the country were used. The C, H and N analyses were carried out with a Perkin–Elmer 2400 Series II C, H, N analyzer. The ^{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. IR spectra in the range 4000-400 cm^{-1} were recorded on a Nicolet Protége 460 FT–IR spectrometer as KBr pellets. For single crystal structure data were collected with a Bruker AXS SMART Apex CCD diffractometer using Mo-Kα (0.71073 Å) radiation at 273(2) K. The software SADABS[26] was used for absorption correction (if needed) and SHELXTL for space group, structure determination and refinements.[27] Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached in all cases. The melting points determined in open capillary are reported as such.

Synthesis of ligand L

Diphenyldiselenide (0.64 g, 2 mmol) dissolved in 30 mL of EtOH was stirred under nitrogen atmosphere and sodium borohydride (0.152 g, 4 mmol) dissolved in 5 mL of aqueous NaOH (5%) was added to it dropwise till it became colorless due to the formation of PhSeNa. 1,2,4,5-Tetrakis(bromomethyl)benzene (0.449 g, 1 mmol) dissolved in 15 mL mixture (1 : 1) of ethanol and THF was mixed with the colorless solution with constant stirring and the mixture stirred further for 3 h. It was poured into cold water (30 mL). The ligand **L** was extracted with chloroform (4 × 25 mL) from aqueous layer. The extract was washed with water (3 × 40 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated off under reduced pressure on a rotary evaporator to get a pale yellow solid, which on recrystallization from chloroform–hexane (1 : 1), resulted in pale yellow single crystals of **L**. Yield (0.53 g, 70%). mp 83 °C. (Found C, 53.95; H, 3.92; calc. for $C_{34}H_{30}Se_4$: C, 53.98; H, 3.88%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 4.02 (8 H, s, C5-H), 6.69 (2 H, s, C7-H), 7.22-7.28 (12 H, m, C1-H + C2-H), 7.38 (8 H, d, J_{H-H} 7.5 Hz, C3-H); δ_C(75.47 MHz; $CDCl_3$; Me_4Si) 29.1 (C5), 127.5 (C1), 129.0 (C2), 130.2 (C4), 132.7 (C7), 133.8 (C3), 135.3 (C6); δ_{Se}(57.24 MHz; $CDCl_3$; Me_2Se) 361.2.

Synthesis of [(η^3-C_3H_5)$_2$$Pd_2$(L)][$ClO_4$]$_2$ (1)

The solution of [Pd(η^3-C_3H_5)Cl]$_2$ (0.0366 g, 0.1 mmol) made in 25 ml of CH_2Cl_2, **L** (0.075 g, 0.1 mmol) and $NaClO_4\cdot H_2O$ (0.2 mmol), both dissolved in ~10 mL of methanol, were mixed and stirred for ~2 h at room temperature. The resulting light orange coloured solution was filtered and the solvent was evaporated off under reduced pressure on a rotary evaporator to get a pale orange solid **1**. Its single crystals were grown from a 1 : 1 : 1 mixture of dichloromethane, acetonitrile and methanol. Yield (0.098 g, 79%). mp 135 °C. (Found: C, 38.13; H, 2.97%. calc. for $C_{40}H_{40}Pd_2Se_4\cdot 2ClO_4$: C, 38.15; H, 3.93%); δ_H(300.13 MHz; DMSO-d$_6$; Me_4Si) 4.33 (8 H, br s, C5-H + 4 H, br s, C allyl-H$_{syn}$), 5.81-5.84 (2 H, m, C allyl-H$_{central}$), 7.48-7.62 (14 H, m, C1-H + C2-H + C3-H + C7-H), the signal of C allyl-H$_{anti}$ merged with DMSO-d$_6$. signal; δ_C(75.47 MHz; DMSO-d$_6$; Me_4Si) 34.0 (C5), 73.4 (C terminal allyl), 119.6 (C central allyl), 128.8 (C1), 130.2 (C2), 130.4 (C3), 133.1 (C7), 133.8 (C4), 135.5 (C6), one C terminal allyl peak merged with that of DMSO-d$_6$; δ_{Se}(57.24 MHz; $CDCl_3$; Me_2Se) 394.5.

Synthesis of [Pd_2(C_5H_5N)$_2$(L)][BF_4]$_2$ (2)

[Pd(CH_3CN)$_4$][BF_4]$_2$ (0.088 g, 0.2 mmol) and **L** (0.075 g, 0.1 mmol), each dissolved in 10 mL of acetonitrile, were mixed and the mixture refluxed for ~3 h. Thereafter the mixture was stirred with pyridine (~0.2 mmol) at room temperature for 0.5 h. The resulting orange solution was filtered and solvent from the filtrate was evaporated off under reduced pressure on a rotary evaporator until its volume reduced to ~5 ml. Diethyl- ether (~15 mL) was mixed with the concentrate resulting in pale orange solid **2**. Its single crystals were grown by slow diffusion of diethyl ether into its acetonitrile solution. Yield (0.110 g, 85%). mp 168 °C. (Found: C, 40.43; H, 2.62; N 2.12%. calcd. for $C_{44}H_{38}N_2Pd_2Se_4\cdot 2BF_4$: C, 40.45; H, 2.65; N, 2.16%); δ_H(300.13 MHz; CD_3CN; Me_4Si) 3.4–3.6 (8 H, m, C benzylic-H), 7.46–7.98 (20 H, m, C aryl-H), 8.52–8.81 (10 H, m, C pyridine-H); δ_C(75.47 MHz; CD_3CN; Me_4Si) 21.5 (C5), 127.4, 130.1, 130.2, 132.7, 147.7, 151.1 (C aryl), 126.4, 134.0, 152.0 (C pyridine); δ_{Se}(57.24 MHz; CD_3CN; Me_2Se) 396.4.

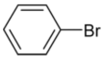
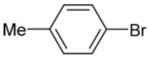
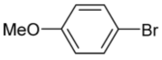
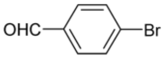
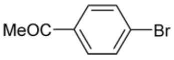
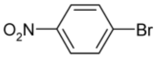
Synthesis of [(η^6-C_6H_6)$_2$$Ru_2(L)Cl_2$][$PF_6$]$_2$ (3)

[η^6-(C_6H_6)$_2$$RuCl_2$]$_2$ (0.05 g, 0.1 mmol) dissolved in 10 mL of dry methanol was treated with the solution of **L** (0.075 g, 0.1 mmol) made in 10 mL of dry methanol with vigorous stirring. The reaction mixture was stirred further for 10 h at room temperature. Its volume was reduced to ~5 mL on a rotary evaporator and ammonium hexafluorophosphate (0.2 mmol) was added to get an orange precipitate of **3**. The precipitate was filtered and washed with cold methanol. The single crystals of **3** were grown from chloroform–acetonitrile mixture (1 : 1). Yield (0.10 g, 70%). mp 153 °C. (Found C, 37.89; H, 2.75%; calc. for $C_{46}H_{42}Cl_2Ru_2Se_4\cdot 2PF_6$: C, 37.87; H, 2.77%); δ_H(300.13 MHz; CD_3CN; Me_4Si) 4.03 (8 H,s, C5-H), 5.61 (12 H, s, C–Ru–Ar–H), 6.70 (2 H, s, C7-H), 7.19–7.32 (12 H, m, C1-H + C2-H), 7.38 (8 H, d, J_{H-H} 7.5 Hz, C3-H); δ_C(75.47 MHz; CD_3CN; Me_4Si) 29.6 (C5), 88.4 (CRu–Ar), 127.5 (C1), 129.0 (C2), 130.2 (C4), 132.7 (C7), 133.8 (C3), 135.3 (C6); δ_{Se}(57.24 MHz; CD_3CN; Me_2Se): (δ, ppm) 392.0.

General procedure for catalytic Heck reaction

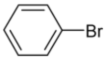
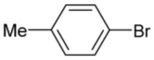
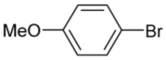
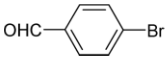
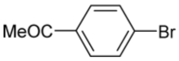
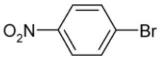
A mixture of styrene–methyl acrylate (2 mmol), aryl bromide (1 mmol), n-butylamine (0.146 g, 2.0 mmol), DMA (~ 4 mL)

Table 1 Catalytic performance[a] of **1** and **2** in Heck reactions of aryl bromide with styrene

	Catalyst **1**			Catalyst **2**		
Ar–X	% Yield	TON	TOF/h^{-1}	% Yield	TON	TOF/h^{-1}
	30	15000	833	43	21500	1194
	25	12500	694	31	15500	861
	26	13000	722	36	18000	1000
	75	37500	2083	90	45000	2500
	82	41000	2278	92	46000	2555
	82	41000	2278	90	45000	2500

[a] Yield, TON and TOF are per Pd.

Table 2 Catalytic performance[a] of **1** and **2** for Heck reactions of aryl bromide with methyl acrylate

	Catalyst **1**			Catalyst **2**		
Ar–X	% Yield	TON	TOF/h^{-1}	% Yield	TON	TOF/h^{-1}
	35	17500	972	45	22500	1250
	28	14000	778	36	18000	1000
	28	14000	778	38	19000	1055
	79	39500	2194	92	46000	2555
	85	42500	2361	94	47000	2611
	82	41000	2278	95	47500	2639

[a] Yield, TON and TOF are per Pd.

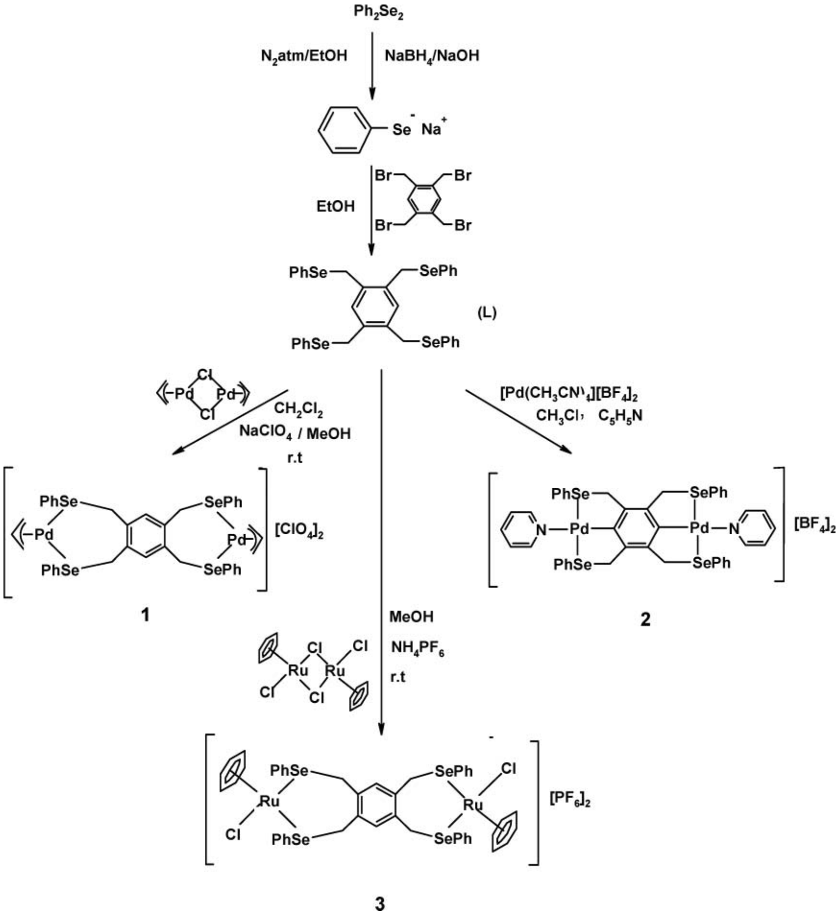
and complex **1** or **2** (10^{-4} M, 100µL (in DMA), ~0.001 mol %) was stirred for 18 h at 100–110 °C on an oil bath. It was cooled to room temperature, treated with chloroform (40 mL) and filtered. The chloroform extract was washed with acidified (HCl) water, dried over anhydrous Na_2SO_4 and its solvent was evaporated on a rotary evaporator to obtain the product which was purified by column chromatography on silica gel using chloroform–hexane mixture (1 : 1). It was characterized by proton and carbon-13 NMR spectra. The % yields, TON and TOF values (per Pd) are given in Tables 1 and 2.

Results and discussion

The synthesis of **L** and its complexes **1–3** are summarized in Scheme 1. The ligand **L** was synthesized by reacting $NaSe^-$ (generated *in situ* by reaction of $NaBH_4$ with diphenyldiselenide in ethanol) with 1,2,4,5-tetrakis(bromomethyl)benzene (Yield 70%). The complexes **1** (Yield 79%) and **3** (Yield 70%) were synthesized by reacting $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and $[\eta^6\text{-}(C_6H_6)_2RuCl_2]_2$ at room temperature in CH_2Cl_2 and methanol with **L** in 1 : 1 molar ratio, respectively. On refluxing **L** with $[Pd(CH_3CN)_4][BF_4]_2$ in 1 : 2 molar ratio in acetonitrile, followed by reaction with pyridine at room temperature resulted in complex **2** in 85% yield. The reaction of **L** with $[Na_2PdCl_4]$ or $[Pd(CH_3CN)_2Cl_2]$ resulted in a highly insoluble non crystalline orange solid, which probably did not have Pd–C bond. Therefore $[Pd(CH_3CN)_4][BF_4]_2$ was chosen as a precursor of Pd(II), as its reaction with **L** gives orange coloured solution instantaneously. This is in agreement with the general observation that if Pd is not bonded to halogen, formation of Pd–C bond is facile.[28] The ligand **L** has good solubility in all common organic solvents *viz.*, $CHCl_3$, CH_2Cl_2, CH_3OH and CH_3CN. The complex **1** is moderately soluble in common organic solvents $CHCl_3$, CH_2Cl_2, CH_3OH and CH_3CN but has good solubility in DMF and DMSO. The complexes **2** and **3** show good solubility in CH_3CN but are moderately soluble in $CHCl_3$, CH_2Cl_2 and CH_3OH. The pale yellow solid **L** is stable and can be stored at room temperature for several months. The solution of complex **1** in DMSO shows signs of decomposition after 24 h, whereas the solutions of complexes **2** and **3** made in CH_3CN are stable for several days.

Crystal structures

Single crystal structure of **L**, **1**, **2** and **3** have been determined by X-ray crystallography The selected crystal data and refinement parameters are given[29] in the section "Notes and Reference" and their more details in ESI (Table S1†). The **L** exhibits two type of bonding modes. In complexes **1** and **3** seven membered chelate rings are formed whereas in **2** it coordinates as a bis-pincer ligand. The ORTEP diagram of **L** with selected bond lengths and angles is shown in Fig. 1. More bond angles and distances are given in ESI (see Table S2†). The Se–C(aryl) is somewhat shorter than Se–C(alkyl). The two Pd–Se bond length of cation of **1** (ORTEP diagram with selected bond lengths and angles is given in Fig. 2), 2.4482(16)–2.4627(14) Å are longer than the values 2.3543(16)–2.3669(11) Å reported for Pd(II)–complexes of tridentate selenated Schiff bases.[30–32] The elongation of Pd–Se bond distance in cation of **1** may be attributed partly due to large size of chelate ring. The ORTEP diagram of cation of **2** is shown in Fig. 3 and in this complex **L** ligates with each Pd in a bis-pincer mode. The geometry around each Pd is slightly distorted square planar. The Pd–Se bond distances in cation of **2**, 2.4004(9) and 2.4083(9) Å are shorter than those of cation of **1**. In complexes in which two Se donor atoms are *trans* to each other this distance is generally around 2.4 Å.[33–36] Some examples followed by their Pd–Se bond lengths (Å) are: Pd–complex of Se–C–Se pincer ligand, 2.430(2);[18] $[PdCl_2\{(C_4H_3S)SeCH_3\}_2]$, 2.439(2);[33] Pd(II) complex of 1,6-$[CH_3SeCH_2CH_2\text{–}NH\text{–}C(=O)]_2C_5H_3N$, 2.425(1), 2.422(1);[34] $(Me_3SiCH_2SeMe)_2PdCl_2$, 2.429;[35] and *trans*-dichlorobis(phenyl-2,4,6-trimethylbenzyl-selenido)palladium(II), 2.4299(6).[36] However, Pd–Se bond distances in cation of **2** are shorter than all



Scheme 1 Synthesis of **L** and complexes **1–3**.

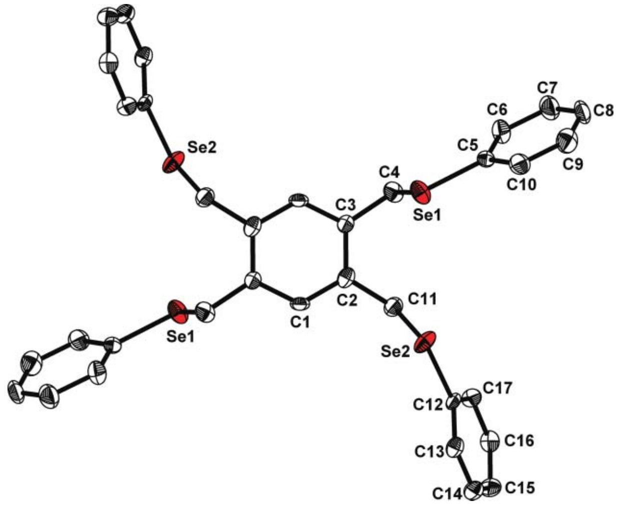


Fig. 1 ORTEP diagram of **L** with ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity. Bond lengths (Å): Se(1)–C(5) 1.907(9), Se(1)–C(4) 1.971(9), Se(2)–C(12) 1.939(8), Se(2)–C(11) 1.973(10); Bond angles (°): C(5)–Se(1)–C(4) 103.5(4), C(12)–Se(2)–C(11) 98.6(4). Symmetry transformation used to generate equivalent atoms: 1−*x*, −*y*, −*z*.

these distances. In Pd complex of (3*H*-1,4,5,7-tetrahydro-2,6-benzodiselenonine) which has Se donor atoms *cis* to each other, Pd–Se bond length is further shorter (2.381(2) Å).[37] The Pd–Se bond distances of complex **1** which has two Se *cis* to each other are longer in comparison to the distances of this *cis* complex. The non-covalent interactions (hydrogen bonds), O···H and H···F in crystals of **1** and **2** have been noticed. The crystal packing factors are among the reasons of their origin (See Figs. S2–S4† in ESI). The Pd–N bond length of cation of complex **2**, 2.147(6) Å, is some what longer than the value ~ 2.0 Å reported for Pd-complexes of tridentate selenated Schiff bases.[30–32]

The ORTEP diagram of cation of **3** is given in Fig. 4 with selected bond lengths and angles. Further details are given in ESI (Table S2†). The **L** ligates with two ruthenium atoms forming two seven membered chelate rings. Each Ru in cation of **3** has pseudo-octahedral half sandwich "Piano–Stool" geometry. The η^6-benzene ring occupies one face of octahedron and Cl and two Se the other one. The half sandwich Ru-complex of selenoether ligands has been scantly investigated. However, Ru(II)(η^6-benzene)- and Ru(II)(η^6-p-cymene)-complexes of selenated pyrrolidine derivative have been reported by our research group recently in which Ru is coordinated through Se and N forming a five membered chelate ring.[38] The **3** is another example of such Ru-selenoether complex. The Ru–C distances (2.162(11)–2.210(10) Å) in the cation of **3** are normal and consistent with the earlier reports.[38–40] In the crystal of **3** also, weak interactions (Figs.S5† in ESI) have been noticed. The Ru–Se bond lengths of the cation of **3** (2.4945(16) and 2.5157(17) Å) fall within the

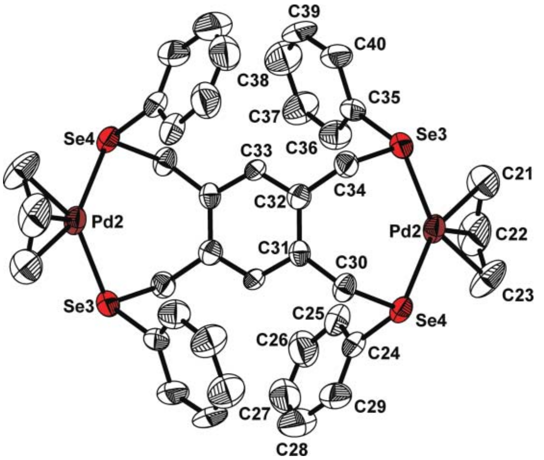


Fig. 2 ORTEP diagram of the cation of **1** with ellipsoids at the 30% probability level. Hydrogen atoms and the ClO_4^- anions have been omitted for clarity. Bond lengths (Å): Pd(2)–C 2.108(14)–2.155(12), Pd(2)–Se(3) 2.4567(15), Pd(2)–Se(4) 2.4627(14); Bond angles (°): C(35)–Se(3)–C(34) 98.5(5), C(24)–Se(4)–C(30) 97.5(4), C–Pd(2)–C 36.1(6)–67.0(6), Se(3)–Pd(2)–Se(4) 109.46(5) C(21)–Pd(2)–Se(3) 91.7(5), C(22)–Pd(2)–Se(3) 127.3(7), C(23)–Pd(2)–Se(3) 157.1(5), C(21)–Pd(2)–Se(4) 157.9(5), C(22)–Pd(2)–Se(4) 122.7(7), C(23)–Pd(2)–Se(4) 91.1(4).. Symmetry transformation used to generate equivalent atoms: (i) 1–*x*, 2–*y*, 2–*z*; (ii) –*x*, 1–*y*, 1–*z*.

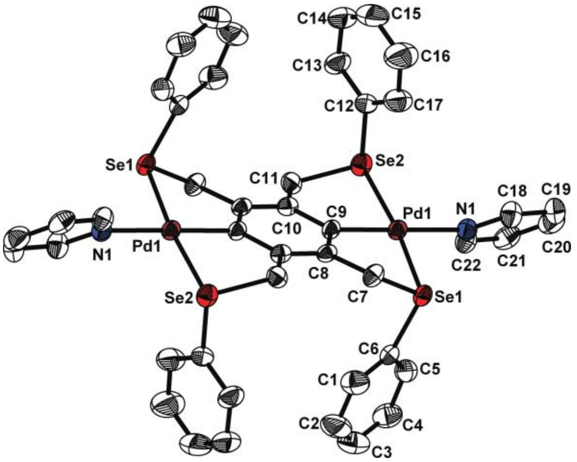


Fig. 3 ORTEP diagram of the cation of **2** with ellipsoids at the 30% probability level. Hydrogen atoms and the BF_4^- anions have been omitted for clarity. Bond lengths (Å): Pd(1)–C(9) 2.008(7), Pd(1)–N(1) 2.147(6), Pd(1)–Se(2) 2.4004(9), Pd(1)–Se(1) 2.4083(9); Bond angles (°): C(9)–Pd(1)–N(1) 178.0(2), C(9)–Pd(1)–Se(2) 86.07(18), N(1)–Pd(1)–Se(2) 92.19(16), C(9)–Pd(1)–Se(1) 85.99(18), N(1)–Pd(1)–Se(1) 95.74(16), Se(2)–Pd(1)–Se(1) 172.06(3). Symmetry transformation used to generate equivalent atoms: 0.5–*x*, 0.5–*y*, –*z*.

range 2.4756(10)–2.5240(9) Å reported for Ru–Se bond lengths in clusters $[Ru_3(\mu_3\text{-}Se)(CO)_7(\mu_3\text{-}CO)(\mu\text{-}dppm)]$ and $[Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)]$.[41] The half sandwich complexes of Ru(II) with selenated pyrrolidine derivative have Ru–Se bond distance[38] in the range 2.4770(5)–2.4918(9) Å consistent with those of cation of **3**. For Ru(IV) complex $[RuCp^*\{\eta^2\text{-}Se_2P(i\text{-}Pr)_2\{\eta^2\text{-}SeP(i\text{-}Pr)_2\}][PF_6]$ the Ru–Se bond lengths[42] are reported in the range 2.538(2)–2.590(2) Å, longer than those of cation of **3** due to steric crowding. The Ru–Se bond distance found in bimetallic species

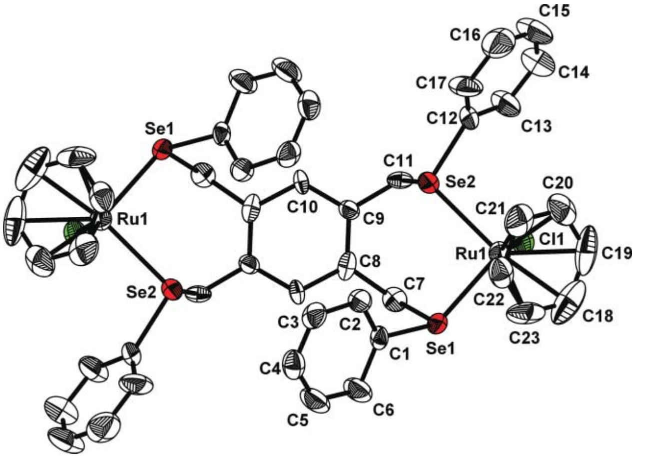


Fig. 4 ORTEP diagram of the cation of **3** with ellipsoids at the 30% probability level. Hydrogen atoms and the PF_6^- anions have been omitted for clarity. Bond lengths (Å): Ru–Se(1) 2.4945(16), Ru–Se(2) 2.5157(17), Ru(1)–Cl(1) 2.394(4), Ru–C 2.162(11)–2.210(10); Bond angles (°): Se(1)–Ru(1)–Se(2) 91.75(5), C(7)–Se(1)–Ru(1) 112.6(3), C(11)–Se(2)–Ru(1) 109.9(3). Symmetry transformation used to generate equivalent atoms: –*x*, *y*, 0.5–*z*.

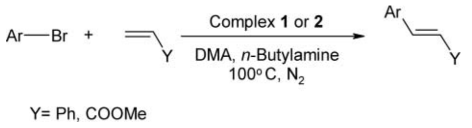
$[RuCp(CO)(C{\equiv}CPh)(\mu\text{-}Se)ZrCp_2]$ 2.494(1) Å,[43] is closer to those of cation of **3**. In $[Ru(\eta^5\text{-}C_5Me_5)(\mu_2\text{-}SeR)_3Ru(\eta^5\text{-}C_5Me_5)]Cl$ (R = Tolyl) Ru–Se bond distances are in the range 2.446(4)–2.466(4) Å[44] and shorter than those of cation of **3**, because RSe^- is expected to be bonded strongly in comparison to a selenoether. In a diselenide bridged complex $[Ru(MeCp)(PPh_3)]_2(\mu\text{-}Se_2)_2(Otf)_2$, Ru–Se bond distances are 2.518(1) and 2.556(1) Å,[45] somewhat longer than those of cation of **3**. The Ru–Cl bond distance of 2.394(4) Å in the cation of **3** is slightly shorter as compared to earlier reports on half sandwich Ru(II) complexes of selenated and tellurated benzotriazoles (2.416(2) and 2.412(3) Å,[46] respectively) but consistent with those reported[38] for similar Ru(II) complexes of thio- and seleno-pyrrolidine derivatives, 2.3815(17) and 2.406(2) Å respectively.

NMR spectra

The signal in $^{77}Se\{^1H\}$NMR spectrum of **L** appearing at 361.2 ppm shifts to higher frequency by ~32–35 ppm on formation of complexes **1–3** and does not split indicating that all four Se donor sites of coordinated **L** are identical in solution. This concurs with the molecular structures (see above) determined by X-ray crystallography on their single crystals. Thus in solution of each of **1** and **3** two seven membered chelate rings are equivalent and in **2** there are two equivalent pincer coordination. In the $^{13}C\{^1H\}$NMR spectrum of complex **1** signal of $CH_2(Se)$ appears at a higher frequency (4.9 ppm) relative to that of free **L** whereas it is shifted to lower frequency (7.6 ppm) on the formation of **2**. However, in $^{13}C\{^1H\}$NMR spectrum of **3** the $CH_2(Se)$ signal shifts to a higher frequency marginally (0.5 ppm) relative to that of free ligand. The signal of Ar–C bonded to Se (C_4) appears at higher frequency (3.6 ppm) relative to that of free **L** in $^{13}C\{^1H\}$NMR spectrum of **1**. However, in the case of complex **3** no shift was noticed in the signal of C_4, which could not be identified unequivocally in the spectrum of **2**. In $^{13}C\{^1H\}$ NMR spectrum of **1** the signals of allyl group appearing at 73.4 and 119.6 ppm ($C_{terminal}$ and $C_{central}$ respectively) are at higher frequencies by 10.5 and 8.4 ppm respectively, relative to those of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$. The signal of another $C_{terminal}$ of allyl was found merged with the signal of DMSO-d^6. In ^1H NMR spectrum of **1** the signal of H_{syn} of allyl group was found merged with $SeCH_2$ signal at 4.33 ppm. The signal of H_{anti} of allyl group also merged with DMSO-d$_6$ signal. The signal of $H_{central}$ of allyl group appearing at 5.82 ppm in the spectrum of **1** is at a higher frequency (0.3 ppm) in comparison to the corresponding signal of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, These observations imply the dispersion of electron density towards Pd in **1**. In comparison to complex of $Pd(\eta^3\text{-}C_3H_5)$ with (Se, N) the dispersion in our case of (Se, Se) ligand is lower,[47] probably due to difference in electronegativity between nitrogen and selenium. In ^1H NMR spectrum of **3** the signal (singlet) of η^6-benzene appears at 5.61 ppm, shifted to lower frequency by 0.3 ppm with respect to that of $[\eta^6\text{-}(C_6H_6)_2RuCl_2]_2$, due substitution of Cl with Se, which has relatively lower electronegativity. Similar observations are reported earlier.[38,39,48,49] The signal of benzene ring in $^{13}C\{^1H\}$ NMR spectrum of **3** at 88.4 ppm is at a lower frequency (2.2 ppm) in comparison to that of $[\eta^6\text{-}(C_6H_6)_2RuCl_2]_2$,[25] implying the presence of somewhat more electron density on the benzene ring in **3** in comparison to that of $[\eta^6\text{-}(C_6H_6)_2RuCl_2]_2$, as corroborated with its ^1H NMR spectrum.

Applications as catalyst in Heck reaction

The Heck reaction is a powerful tool for C–C bond formation in organic synthesis.[50–53] Outstanding catalyst systems developed to date include those that employ sterically bulky and electron-rich phosphine ligands[54–56] or phosphine mimics such as N-heterocyclic nucleophilic carbenes (NHCs).[57,58] Phosphorus-, nitrogen-, and sulfur-containing palladacycles have also emerged recently as powerful catalysts for this reaction.[59–64] The strong donating properties of organoselenides can make their Pd(II) complex good catalyst system.[18] This has motivated us to explore **1** and **2** as catalyst for Heck reaction at concentration 0.001 mol % using *n*-butyl amine as base (eqn (1)).



(1)

All exploratory reactions were carried out for 18 h. The results summarized in Table 1 reveal that complexes **1** and **2** both show very good catalytic activity for Heck reaction. The **2** having **L** coordinated in a bis-pincer mode is somewhat more efficient than **1**. TON and TOF values depend on reaction conditions (solvent, base, temperature, time *etc.*). Thus their comparisons are not straight forward. The presence of two Pd atoms in one molecule of complex **1** and **2** makes the direct comparisons further difficult. However, our TON (per Pd) values (up to 47500) achieved in 18 h reactions are very promising. TOF (per Pd) values when **1** or **2** is used as catalyst are up to 2639 h^{-1}. The Pd–complexes of Se–C–Se mono-pincer ligand,[18a] give values higher than this. In comparison to palladium(II) complexes of tridentate selenated Schiff bases[30–32] the catalytic performance of **1** and **2** is far superior. The Pd(0) based pathway for catalytic activity of **1** and **2** for Heck C–C coupling appears to be most plausible particularly in case of **2**, as it has been reported that release of highly active Pd(0) in tiny amounts is responsible for high catalytic activity of Pd(II) complexes of pincer ligands for Heck reaction.[65] The two soft donor selenium atoms may be further facilitating the formation of Pd(0) resulting in good catalytic activity of **1** and **2** both. In comparison to phosphine or *N*-heterocyclic nucleophilic carbenes (NHCs) based catalysts **1** and **2** have the additional advantage of moisture and air insensitivity.

Conclusions

1,2,4,5-Tetrakis(phenyselenomethyl)benzene (**L**) coordinates as a bis-pincer ligand with Pd(II) in **2** whereas in **1** and **3** it forms two seven membered chelate rings with Pd as well as Ru. Such behaviour is shown for the first time for a tetradentate ligand of type **L**. The Pd–Se bond lengths are in the ranges 2.4004(9)–2.4627(14) Å and follow the order **1** > **2**. The range of Ru–Se bond length is 2.4945(16)–2.5157(17) Å. The geometry around Pd in **1** and **2** both is close to square planar whereas Ru in cation of **3** has pseudo-octahedral half sandwich "Piano–Stool" geometry. Heck reaction between aryl bromides and styrene or methyl acrylate can be efficiently catalyzed homogeneously with **1** and **2** both. The TON (per Pd) and TOF (per Pd) values are up to ~ 47500 and ~2639 h^{-1} respectively. The catalytic efficiency of **2** is somewhat better than that of **1**. In comparison to phosphine or *N*-heterocyclic nucleophilic carbenes (NHCs) based catalysts **1** and **2** have the advantage of moisture and air insensitivity.

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29 Crystal Data: **L**: $C_{34}H_{30}Se_4$, *M*r = 754.42, monoclinic space group *P21/c*, $a = 12.453(5)$, $b = 10.808(4)$, $c = 11.001(5)$ Å, $\alpha = \gamma = 90.00$, $\beta = 94.325(9)$, $V = 1476.4(10)$ Å^3, $Z = 2$, $\rho_c = 1.697$ g cm^{-3}, $F(000) = 740.0$, μ(Mo-Kα) = 4.992 mm^{-1}, A total of 13742 of which 2596 reflections were independent ($R_{int} = 0.0904$). The structure was refined to final $R_1 = 0.0997$ [$I > 2\sigma(I)$], wR_2 = 0.1745 for all data. GOF = 1.373, and residual electron density max./min. = 0.891 and −0.861 e Å^{-3}. **1**: $C_{40}H_{40}Pd_2Se_4{\cdot}2ClO_4$, *M*r = 1248.26, triclinic space group $P\bar{1}$, $a = 11.026(5)$, $b = 14.321(6)$, $c = 15.336(7)$ Å, $\alpha = 91.562(7)$, $\beta = 104.662(5)$, $\gamma = 96.774(7)°$, $V = 2322.3(18)$ Å^3, $Z = 2$, $\rho_c = 1.785$ g cm^{-3}, $F(000) = 1212.0$, μ(Mo-Kα) = 4.070 mm^{-1}, A total of 21172 of which 8180 reflections were independent ($R_{int} = 0.0522$). The structure was refined to final $R_1 = 0.0613$ [$I > 2\sigma(I)$], wR_2 = 0.1600 for all data. GOF = 1.294, and residual electron density max./min. = 1.196 and −0.675 e Å^{-3}. **2**: $C_{44}H_{38}N_2Pd_2Se_4{\cdot}2BF_4$, *M*r = 1297.02, monoclinic space group *C2/c*, $a = 22.765(4)$, $b = 10.926(2)$, $c = 18.967(4)$ Å, $\alpha = \gamma = 90.00$, $\beta = 102.809(3)$, $V = 4600.3(15)$ Å^3, $Z = 4$, $\rho_c = 1.873$ g cm^{-3}, $F(000) = 2504.0$, μ(Mo-Kα) = 4.013 mm^{-1}, A total of 21093 of which 4042 reflections were independent ($R_{int} = 0.0425$). The structure was refined to final $R_1 = 0.0458$ [$I > 2\sigma(I)$], wR_2 = 0.1397 for all data. GOF = 1.250, and residual electron density max./min. = 1.220 and −0.676 e Å^{-3}. **3**: $C_{46}H_{42}Cl_2Ru_2Se_4{\cdot}2PF_6$, *M*r = 1473.62, monoclinic space group *C2/c*, $a = 28.964(8)$, $b = 11.270(3)$, $c = 19.155(6)$ Å, $\alpha = \gamma = 90.00$, $\beta = 115.273(5)$, $V = 5654(3)$ Å^3, $Z = 4$, $\rho_c = 1.731$ g cm^{-3}, $F(000) = 2856.0$, μ(Mo-Kα) = 3.330 mm^{-1}, A total of 12769 of which 4996 reflections were independent ($R_{int} = 0.0850$). The structure was refined to final $R_1 = 0.0836$ [$I > 2\sigma(I)$], wR_2 = 0.1923 for all data. GOF = 1.326, and residual electron density max./min. = 0.848 and −0.682 e Å^{-3}.

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