Supplementary Information:

Palladium(II) complexes of first Pincer (Se, N, Se) ligand - 2,6-bis(phenyl-selenomethyl)pyridine(L): solvent dependent formation of [PdCl(**L**)]Cl and Na[PdCl(**L**)][$PdCl_4$]. Applications as catalyst for Heck reaction

Dipanwita Das, G.K. Rao and Ajai K Singh*
Department of Chemistry, Indian Institute of Technology. Delhi, New Delhi 110016, India

Table 1. Crystal data and structural refinements for ligand **L** and complexes **1**, **2**

Compound	**L**	**1**	**2**
Empirical formula	$C_{19}H_{17}NSe_2$	$C_{19}H_{17}ClNPdSe_2ClO$	$C_{19}H_{17}C_{15}NNaPd_2Se_2$
Formula wt.	417.26	610.60	830.30
Crystal size [mm]	0.26× 0.30× 0.32	0.26× 0.30× 0.34	0.167 × 0.215 × 0.463
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	*P-1*	*Pbca*	*P-1*
Unit Cell dimension	a = 9.408(4)Å b = 9.707(3)Å c= 10.528(5)Å β = 114.299(6)°	a = 11.447(2)Å b = 10.947(2)Å c= 35.508(7)Å β = 90.00°	a =8.792(3)Å b =12.411(4)Å c=12.624(4)Å β = 84.604(6)°
Volume [$Å^3$]	829.1(6)	4449.5(15)	1321.6(8)
Z	2	8	2
Density (Calc.) [$Mg \cdot m^{-3}$]	1.671	1.823	2.085
Absorption coeff. [mm^{-1}]	4.455	4.354	4.645
F(000)	412	2352	788
θ range [°]	2.22–29.57	2.29–29.57	2.34–28.23
Index ranges	$-11 \leq h \leq 11$ $-11 \leq k \leq 11$ $-12 \leq l \leq 12$	$-15 \leq h \leq 15$ $-15 \leq k \leq 15$ $-49 \leq l \leq 49$	$-10 \leq h \leq 10$ $-14 \leq k \leq 14$ $-15 \leq l \leq 15$
Reflections collected	4252	49162	12503
Independent reflections($R_{int.}$)	2871 (0.0305)	6230 (0.0484)	4586 (0.0267)
Max./min. Transmission	0.317/ 0.258	0.324/ 0.249	0.459/0.315
Data/restraints/ parameters	2871 /0 / 200	5511 /0 / 235	4586 /0 / 271
Goodness-of-fit on F^2	1.020	1.128	1.080
Completeness to maximum	0.986	1.000	0.984
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0538 wR_2 = 0.1402	R_1 = 0.0452 wR_2 = 0.1157	R_1 = 0.0590 wR_2 =0.1815
R indices (all data)	R_1 = 0.0636 wR_2 = 0.1499	R_1 = 0.0665 wR_2 = 0.1241	R_1 = 0.0636 wR_2 =0.1857
Largest diff. peak/hole [e.$Å^{-3}$]	1.540/ -1.915	0.842/ -0.449	3.448/ -0.922

Table 2. Bond Lengths and Bond Angles of **L**, **1** and **2**

	Bond Length [Å]		Bond Angle [°]	
L	Se(2)—C(14)	1.920(5)	C(14)–Se(2)–C(13)	101.3(2)
	Se(2)—C(13)	1.953(5)	C(6)–Se(1)–C(7)	98.1(2)
	Se(1)—C(6)	1.927(5)	C(12)–N(1)–C(8)	117.3(4)
	Se(1)—C(7)	1.967(5)	C(15)–C(14)–Se(2)	123.9(4)
	N(1)—C(12)	1.340(6)	C(19)–C(14)–Se(2)	116.1(4)
	N(1) —C(8)	1.351(6)	C(12)–C(13)–Se(2)	115.5(3)
	C(13)—C(12)	1.502(7)	N(1)–C(8)–C(7)	115.9(4)
	C(8)—C(7)	1.500(7)	C(8)–C(7)–Se(1)	113.4(3)
			N(1)–C(12)–C(13)	115.3(4)
			C(5)–C(6)–Se(1)	119.6(4)
			C(1)–C(6)–Se(1)	120.8(4)
1	Pd(1)—N(1)	1.985(3)	N(1)–Pd(1)–Cl(1)	177.99(11)
	Pd(1)—Cl(1)	2.2309(12)	N(1)–Pd(1)–Se(1)	90.87(11)
	Pd(1)—Se(1)	2.3891(7)	Cl(1)–Pd(1)–Se(1)	88.86(5)
	Pd(1)—Se(2)	2.4313(7)	N(1)–Pd(1)–Se(2)	85.15(11)
	Se(1)—C(7)	1.906(5)	Cl(1)–Pd(1)–Se(2)	94.91(5)
	Se(1)—C(6)	1.937(5)	Se(1)–Pd(1)–Se(2)	172.65(2)
	Se(2)—C(13)	1.907(5)	C(7)–Se(1)–C(6)	100.2(3)
	Se(2)—C(14)	1.966(6)	C(7)–Se(1)–Pd(1)	91.50(17)
	N(1)—C(8)	1.311(6)	C(6)–Se(1)–Pd(1)	99.48(19)
	N(1)—C(12)	1.395(6)	C(13)–Se(2)–C(14)	102.4(2)
			C(13)–Se(2)–Pd(1)	93.34(16)
			C(14)–Se(2)–Pd(1)	100.42(15)
			C(12)–N(1)–Pd(1)	121.1(3)
2	Cl(1)—Pd(1)	2.295(2)	C(8)–N(1)–C(12)	119.2(8)
	Cl(2)—Pd(2)	2.299(3)	C(8)–N(1)–Pd(1)	120.5(6)
	Cl(3)—Pd(2)	2.243(2)	C(12)–N(1)–Pd(1)	119.6(6)
	Cl(4)—Pd(2)	2.296(3)	N(1)–Pd(1)–Cl(1)	178.5(2)
	Cl(5)—Pd(2)	2.310(3)	N(1)–Pd(1)–Se(2)	87.3(2)
	N(1)—Pd(1)	2.032(7)	Cl(1)–Pd(1)–Se(2)	91.25(7)
	Pd(1)—Se(2)	2.3910(13)	N(1)–Pd(1)–Se(1)	87.6(2)
	Pd(1)—Se(1)	2.4229(12)	Cl(1)–Pd(1)–Se(1)	93.93(7)
	C(13)—Se(2)	1.965(9)	Se(2)–Pd(1)–Se(1)	165.94(4)
	C(14)—Se(2)	1.947(9)	Cl(3)–Pd(2)–Cl(4)	86.99(10)
	C(6)—Se(1)	1.934(10)	Cl(3)–Pd(2)–Cl(2)	92.62(9)
	C(7)—Se(1)	1.955(9)	Cl(4)–Pd(2)–Cl(2)	178.47(10)
	C(8)—N(1)	1.363(12)	Cl(3)–Pd(2)–Cl(5)	176.74(11)
	C(12)—N(1)	1.368(12)	Cl(4)–Pd(2)–Cl(5)	89.91(11)

		Cl(2)–Pd(2)–Cl(5)	90.46(11)
		C(6)–Se(1)–C(7)	101.1(4)
		C(6)–Se(1)–Pd(1)	95.9(3)
		C(7)–Se(1)–Pd(1)	92.4(3)
		C(14)–Se(2)–C(13)	98.2(4)
		C(14)–Se(2)–Pd(1)	100.5(3)
		C(13)–Se(2)–Pd(1)	91.1(3)

IR Data

L (KBr, cm^{-1}): 3059(m; $\nu_{C—H(aromatic)}$), 2923(s; $\nu_{C—H(aliphatic)}$), 1574–1443(m; $\nu_{C=C(aromatic)}$ and $\nu_{C=N(aromatic)}$), 733(s; C—H(aromatic bend)

1 (KBr, cm^{-1}): 3052(m; $\nu_{C—H(aromatic)}$), 2893(s; $\nu_{C—H(aliphatic)}$), 1594–1466(m; $\nu_{C=C(aromatic)}$ and $\nu_{C=N(aromatic)}$), 738(s; C—H(aromatic bend)

2 (KBr, cm^{-1}): 3053(m; $\nu_{C—H(aromatic)}$), 2893(s; $\nu_{C—H(aliphatic)}$), 1594– 1459(m; $\nu_{C=C(aromatic)}$ and $\nu_{C=N(aromatic)}$), 736(s; C—H(aromatic bend)

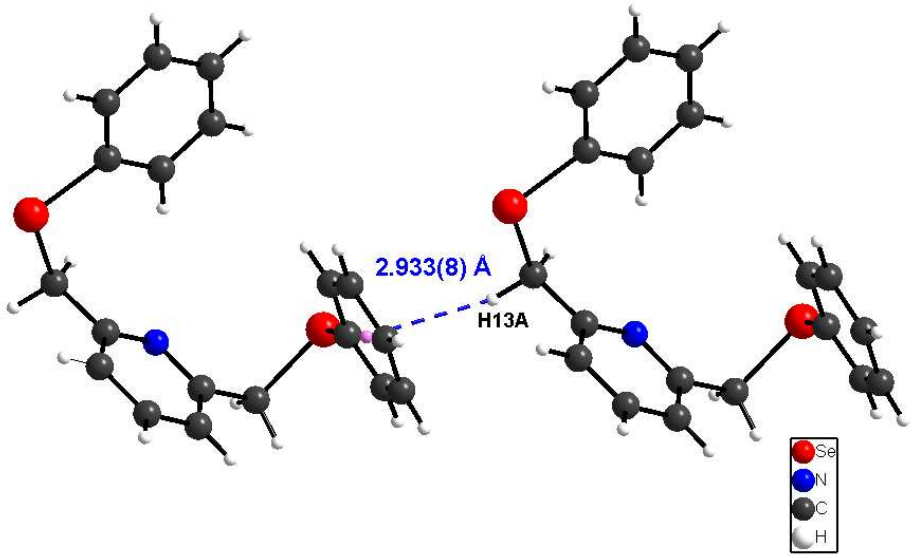

Fig S.1. C–H---π interactions in **L** Distance between π e cloud of Ph and H(13A): 2.933(8)Å

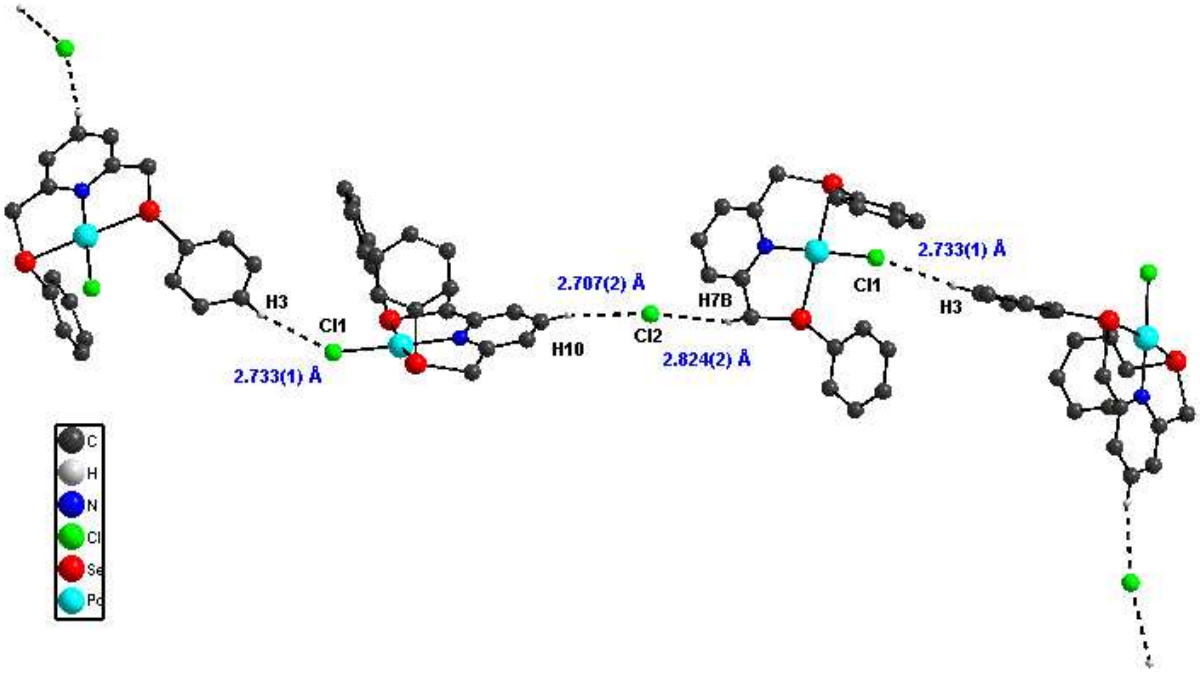

Fig S.2 Chloride acting as a bridging unit in linear chain in **(1)**

(Oxygen has been omitted for clarity) hydrogen bond lengths (Å): Cl(1)–H(3), 2.733(1); Cl(2)–H(7B), 2.824(2); Cl(2)–H(10), 2.707(2)

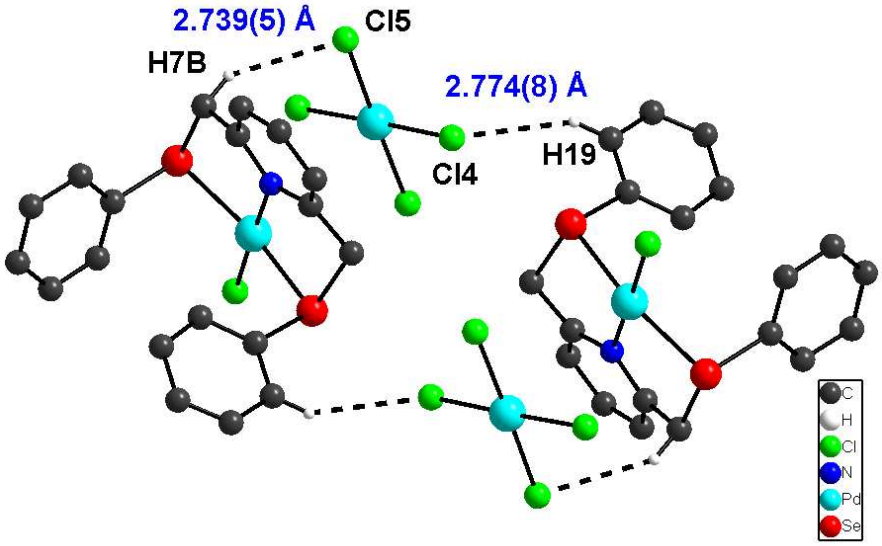

Fig. S.3 Dimer formation in **2** with $[PdCl_4]^{2-}$ as a bridging unit (Sodium has been omitted for clarity); Selected bond lengths (Å): Cl(4)–H(19), 2.774(8); Cl(5)–H(7B), 2.739(5)

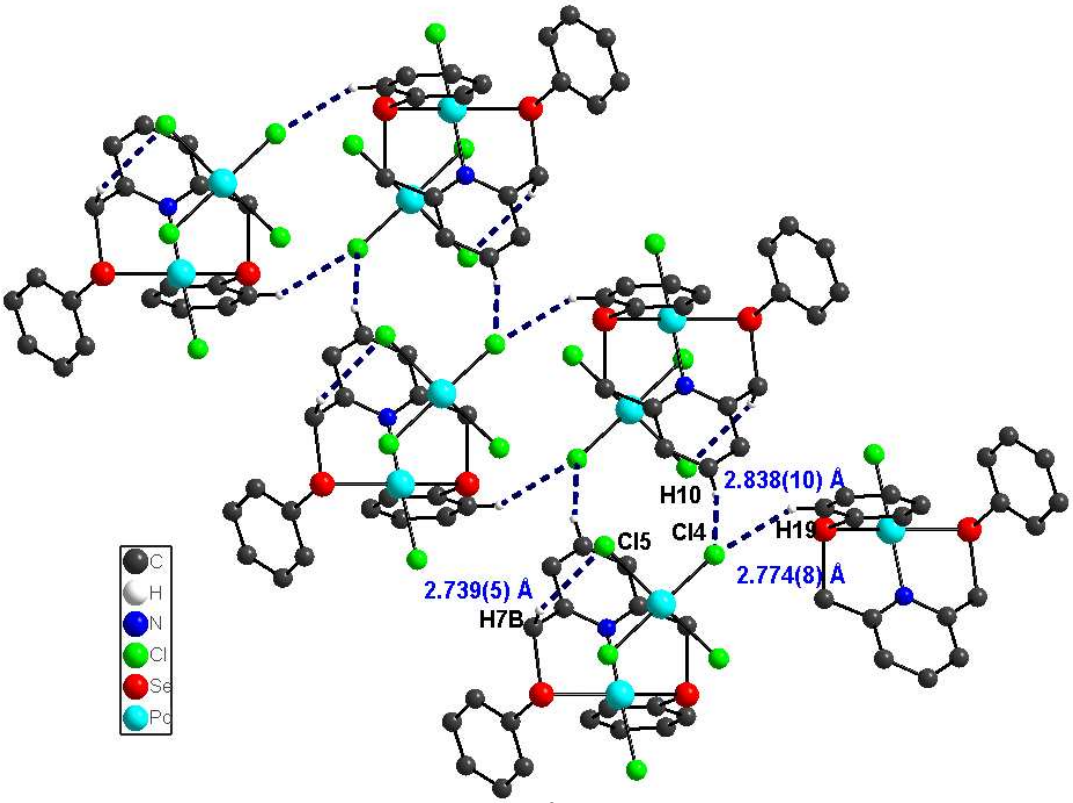

Fig.S.4 3-D structure of **(2)** showing $[PdCl_4]^{2-}$ as a bridging unit (Sodium has been omitted for clarity) Selected bond lengths (Å): Cl(4)–H(19), 2.774(8); Cl(4)–H(10), 2.838(10); Cl(5)–H(7B), 2.739(5)

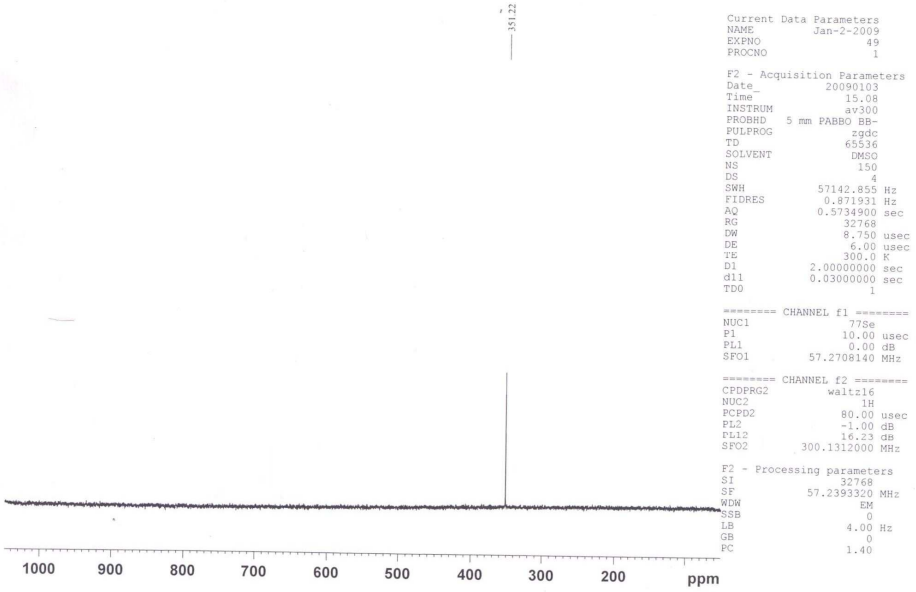

Fig1. $^{77}Se\{^{1}H\}$ NMR of **L**

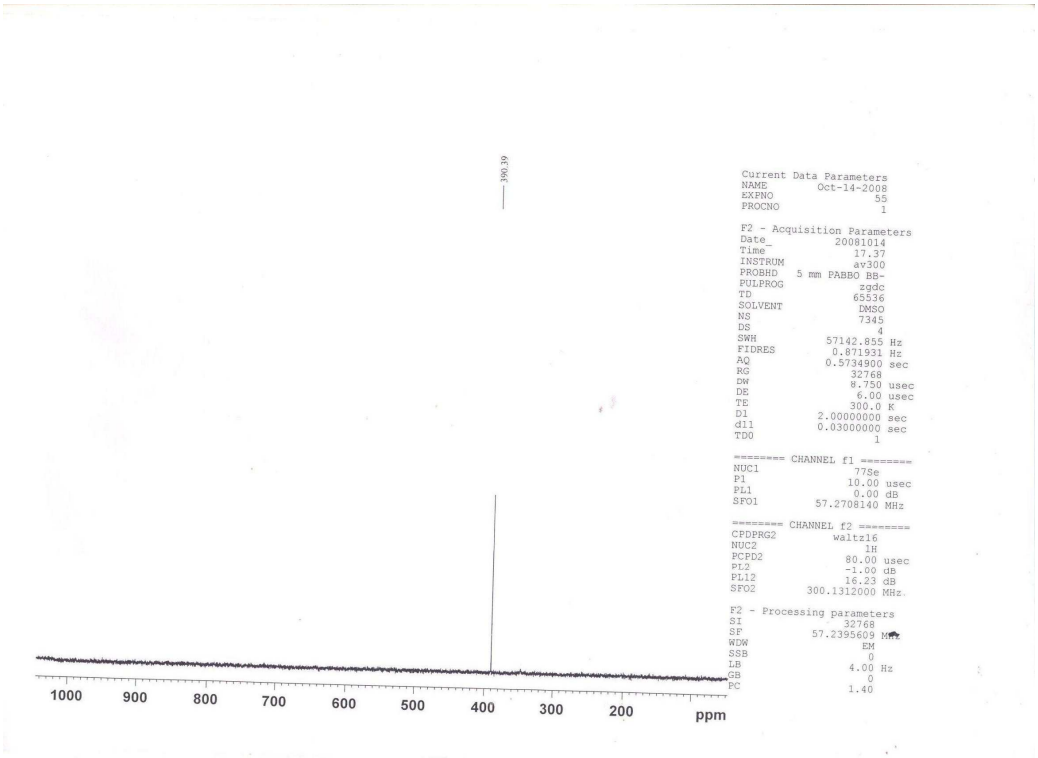

Fig 2. $^{77}Se\{^{1}H\}$ NMR of **1**

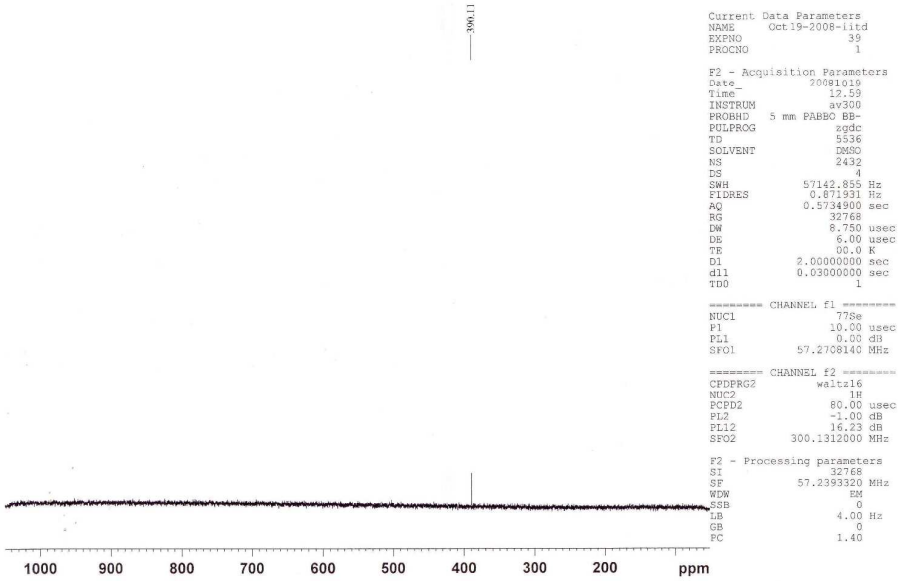

Fig 3. $^{77}Se\{^{1}H\}$ NMR of **2**