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Half sandwich complexes of Ru(II) and complexes of Pd(II) and Pt(II) with seleno and thio derivatives of pyrrolidine: Synthesis, structure and applications as catalysts for organic reactions

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ABSTRACT

The reactions of $PhSe^-$, PhS^- and Se^{2-} with *N*-{2-(chloroethyl)}pyrrolidine result in *N*-{2-(phenylseleno)ethyl}pyrrolidine (**L1**), *N*-{2-(phenylthio)ethyl}pyrrolidine (**L2**), and bis{2-pyrrolidene-*N*-yl)ethyl selenide (**L3**), respectively, which have been explored as ligands. The complexes $[PdCl_2(\mathbf{L1}/\mathbf{L2})]$ (**1**/**7**), $[PtCl_2(\mathbf{L1}/\mathbf{L2})]$ (**2**/**8**), $[RuCl(\eta^6\text{-}C_6H_6)(\mathbf{L1}/\mathbf{L2})][PF_6]$ (**3**/**9**), $[RuCl(\eta^6\text{-}p\text{-cymene})(\mathbf{L1}/\mathbf{L2})][PF_6]$ (**4**/**10**), $[RuCl(\eta^6\text{-}p\text{-cymene})(NH_3)_2][PF_6]$ (**5**) and $[Ru(\eta^6\text{-}p\text{-cymene})(\mathbf{L1})(CH_3CN)][PF_6]_2{\cdot}CH_3CN$ (**6**) have been synthesized. The **L1**–**L3** and complexes were found to give characteristic NMR (Proton, Carbon-13 and Se-77). The crystal structures of complexes **1**, **3**–**6**, **9** and **10** have been solved. The Pd–Se and Ru–Se bond lengths have been found to be 2.353(2) and 2.480(11)/2.4918(9)/2.4770(5) Å, respectively. The complexes **1** and **7** have been explored for catalytic Heck and Suzuki–Miyaura coupling reactions. The value of TON has been found up to 85 000 with the advantage of catalyst's stability under ambient conditions. The efficiency of **1** is marginally better than **7**. The Ru-complexes **3** and **9** are good for catalytic oxidation of primary and secondary alcohols in CH_2Cl_2 in the presence of *N*-methylmorpholine-*N*-oxide (NMO). The TON value varies between 8.0×10^4 and 9.7×10^4 for this oxidation. The **3** is somewhat more efficient catalyst than **9**.

1. Introduction

The biological aspects of pyrrolidine derivatives have got attention as they show potential for anti-cancer therapy [1,2], selective inhibition activity against matrix metalloproteinase-2 [3] and characteristics of potent anti-tumor agents [4]. The binding of enantiomers of chiral platinum(II) complex of *N*-methyl-2-aminomethylpyrrolidine to dG, d(GpG) and a 52-mer oligonucleotide has been investigated [5]. Copper(II) complex of pyrrolidine dithiocarbamate has been reported to have potent anti-cancer activity against cisplatin resistant neuroblastoma cells [6]. Recently pyrrolidine based inhibitors of the drug resistant mutant of HIV-1 protease have been reported [7]. We are unaware of any investigation made on any selenated pyrrolidine derivatives (including their ligand chemistry). It was therefore thought worthwhile to synthesize **L1** and **L3** and investigate their ligand chemistry with 'Soft' metallic species (Pd(II), Pt(II) and Ru(II)), with which they are expected to coordinate preferably. The **L3** was found unstable and therefore its ligation could not be investigated. The **L2** also not explored as a ligand, has been included for a comparative study.

Half sandwich complexes having (η^6-*p*-cymene)Ru(II) and (η^6-benzene)Ru(II) units are well known [8,9]. The impetus for the synthesis of new derivatives having these units arises, owing to their catalytic potential in a range of organic transformations [10–25] and very promising cytotoxic properties [26]. The [(η^6-benzene)Ru(en)Cl]$^+$ (en = 1,2-diaminoethane) shows very promising anti-cancer activity [27–29]. The properties of such complexes may be fine tuned by the presence of chelating ligands, particularly when the ligand or its skeleton has biological activity. We are unaware of any half sandwich complex of ruthenium(II) of piano stool geometry that has **L1** or any other (Se, N) ligand. The tellurium analog of **L1** is known [30] but its structurally characterized half sandwich complex is unknown so far. Therefore, such complexes having (η^6-*p*-cymene)Ru(II) or (η^6-benzene)Ru(II) unit and **L1**/**L2** have been studied. The complexes of **L1** and **L2** with (η^6-benzene)Ru(II) have shown promise for catalytic oxidation of primary and secondary alcohols, which has been studied in detail. The present investigations on half sandwich complexes of Ru(II) with **L1**/**L2** are not only expected to be helpful in understanding the effect of these bidentate ligands on relative strength of Ru–benzene ring bonding but also reveal a variety of non-covalent interactions. Recently, palladium complex of a selenium ligand has been reported very promising for Heck C–C coupling reaction [31]. Therefore some palladium complexes of present (Se/S, N) ligands have been

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explored for catalytic C–C coupling of Heck and Suzuki–Miyaura type. The results of all these studies are the part of present paper.

2. Experimental

Perkin–Elmer 2400 Series II C, H, N analyzer was used for elemental analysis. 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. The UV–Vis spectra were recorded on Lambda BIO-20, Perkin–Elmer (USA); model 330. The conductivity measurements were carried out in CH_3CN (concentration ca. 1 mM) using ORION conductivity meter model 162. Single crystal data were collected (at IIT Delhi and IIT Kanpur, India) on a Bruker AXS SMART Apex CCD diffractometer using Mo $K\alpha$ (0.71073 Å) radiations at 298(2) K. The software SADABS was used for absorption correction (if needed) and SHELXTL for space group, structure determination and refinements [32–33]. The catalytic oxidation yields were determined with NUCON Engineers (New Delhi, India) gas chromatograph (with FID detector), model 5765 equipped with an Alltech (Ec^{TM-1}) column of 30 m length, 0.25 mm diameter and having liquid film of 0.25 μm thickness. The cyclic voltammetric studies were performed on BAS CV 50 W instrument at University of Delhi (Department of Chemistry), India. A three-electrode configuration composed of a Pt disk working electrode (3.1 mm^2 area), a Pt wire counter electrode, and an Ag/AgCl reference electrode was used for the measurements. Ferrocene was used as an internal standard ($E_{1/2}$ = 0.500 V versus Ag/AgCl) and all the potentials are expressed with reference to Ag/AgCl. The melting points determined in open capillary are reported as such. The complexes $[\{(\eta^6C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ and $[\{(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)\}_2]$, were prepared according to literature methods [34–35].

2.1. Synthesis of *L1*

Diphenyldiselenide (0.62 g, 2.0 mmol) dissolved in 30 cm^3 of ethanol was treated with a solution (made in 5% NaOH) of $NaBH_4$ (0.14 g, 4.0 mmol) (added drop wise) under N_2 atmosphere until it become colorless due to the formation of PhSeNa. (2-Chloroethyl)pyrrolidine hydrochloride (0.72 g, 4.0 mmol) dissolved in 5 cm^3 of ethanol was mixed to this colorless solution with constant stirring. The mixture was stirred further for 3–4 h and poured into ice-cold 1% (w/v) NaOH (20 cm^3), from which **L1** was extracted into $CHCl_3$ (5 × 40 cm^3). The extract was washed with water (3 × 50 cm^3) and dried over anhydrous sodium sulfate. Its solvent was evaporated off under reduced pressure on a rotary evaporator, resulting in pale yellow oil (**L1**). Yield 0.81 g (~80%). NMR: (^{1}H, $CDCl_3$, 25 °C, versus TMS) δ (ppm): 1.62 (m, 4H, H_8), 2.37 (m, 4H, H_7), 2.65 (t, ^{3}J = 7.5 Hz, 2H, H_5), 2.91 (t, ^{3}J = 7.5 Hz, 2H, H_6), 7.06–7.10 (m, 3H, H_1, H_2), 7.36 (d, ^{3}J = 6.0 Hz, 2H, H_3), ($^{13}C\{^{1}H\}$, $CDCl_3$, 25 °C versus TMS) δ (ppm): 23.4 (C_8), 26.4 (C_5), 53.9 (C_7), 56.5 (C_6), 126.7 (C_1), 129.0 (C_2), 130.4 (C_3), 132.3 (C_4), ($^{77}Se\{^{1}H\}$, $CDCl_3$, 25 °C versus Me_2Se) δ (ppm): 281.3.

2.2. Synthesis of $[PdCl_2(\textbf{L1})]$ (**1**) and $[PtCl_2(\textbf{L1})]$ (**2**)

The solution of **L1** (0.065 g, 0.25 mmol) made in 10 cm^3 of acetone and Na_2PdCl_4 (0.08 g, 0.25 mmol) or K_2PtCl_4 (0.1 g, 0.25 mmol) dissolved in 10 cm^3 of deoxygenated water were stirred together for 30 min at room temperature and poured into 100 cm^3 of distilled water. The complex was extracted into chloroform (2 × 50 cm^3). The extract was dried over anhydrous sodium sulfate, concentrated to ~10 cm^3 with a rotary evaporator and mixed with hexane (20 cm^3). The resulting orange colored **1** or yellow colored **2** was filtered, washed with hexane (10 cm^3) and dried in vacuo. Single crystals of **1** were grown by slow evaporation of its solution in chloroform–hexane mixture (3:2).

1: Yield: 0.076 g (~70%). m.p. 145 °C. Λ_M = 7.9 S cm^2 mol^{-1}. *Anal.* Calc. for $C_{12}H_{17}Cl_2NPdSe$: C, 33.48; H, 3.75; N, 3.25%. Found: C, 34.06; H, 4. 01; N, 3.58%. NMR: (^{1}H, $CDCl_3$, 25 °C versus TMS) δ (ppm): 1.76–2.06 (m, 4H, H_8), 2.55–2.88 (m, 4H, H_7), 3.01–3.34 (m, 2H, H_5), 3.98–4.29 (m, 2H, H_6), 7.50–7.52 (m, 3H, H_1, H_2), 8.22–8.25 (m, 2H, H_3), ($^{13}C\{^{1}H\}$, $CDCl_3$, 25 °C versus TMS) δ (ppm): 21.6 (C_8), 32.4 (C_5), 59.2 (C_7), 63.3 (C_6), 126.6 (C_1), 130.3 (C_2), 130.7 (C_3), 133.5 (C_4), ($^{77}Se\{^{1}H\}$, $CDCl_3$, 25 °C versus Me_2Se) δ (ppm): 472.3.

2: Yield: 0.091 g (~70%). m.p. 150 °C. Λ_M = 9.6 S cm^2 mol^{-1}. *Anal.* Calc. for $C_{12}H_{17}Cl_2NPtSe$.: C, 27.77; H, 3.11; N, 2.70%. Found: C, 28.10; H, 3.39; N, 3.01%. NMR: (^{1}H, DMSO-d_6, 25 °C versus TMS) δ (ppm): 1.78–1.87 (m, 4H, H_8), 2.41–2.81 (m, 4H, H_7), 2.89–3.34 (m, 2H, H_5), 3.84–4.10 (m, 2H, H_6), 7.51–7.61 (m, 3H, H_1, H_2), 8.14–8.19 (m, 2H, H_3), ($^{13}C\{^{1}H\}$, DMSO-d_6, 25 °C versus TMS) δ (ppm): 22.2 (C_8), 33.9 (C_5), 62.2 (C_7), 64.6 (C_6), 125.8 (C_1), 130.1 (C_2), 130.8 (C_3), 133.4 (C_4), ($^{77}Se\{^{1}H\}$, DMSO-d_6, 25 °C versus Me_2Se) δ (ppm): 428.2 (t, ^{1}J (^{195}Pt–Se) 366.53 Hz).

2.3. Synthesis of $[RuCl(\eta^6\text{-}C_6H_6)(\textbf{L1})][PF_6]$ (**3**) and $[RuCl(\eta^6\text{-}p\text{-cymene})(\textbf{L1})][PF_6]$ (**4**)

The solid $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ (0.05 g, 0.1 mmol) or $[\{(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)\}_2]$ (0.12 g, 0.2 mmol) and **L1** (0.051 g, 0.2 mmol) dissolved in CH_3OH (15 cm^3) were stirred together for 10 or 14 h at room temperature. The resulting yellow solution was filtered and the volume of the filtrate was reduced (~7 cm^3) with a rotary evaporator. It was mixed with solid NH_4PF_6 (0.032 g, 0.2 mmol) and the resulting yellow colored microcrystalline solid **3** or **4** was filtered, washed with ice-cold 10 cm^3 CH_3OH and dried in vacuo. Single crystals of **3** or **4** were obtained by diffusion of diethyl ether into its solution (1 cm^3) made in a mixture (1:4) of CH_3OH and CH_3CN.

3: Yield 0.1 g (~85%); m.p. 178 °C. Λ_M = 148.4 S cm^2 mol^{-1}. *Anal.* Calc. for $C_{18}H_{23}ClNRuSe{\cdot}PF_6$: C, 35.23; H, 3.78; N, 2.28%. Found: C, 35.46; H, 3.97; N, 2.35%. NMR: (^{1}H, CD_3CN, 25 °C versus TMS) δ (ppm): 1.95–1.98 (m, 4H, H_8), 2.54–3.16 (m, 4H, H_7), 3.43–3.61 (m, 2H, H_5), 3.69–4.10 (m, 2H, H_6), 5.64 (s, 6H, RuAr–H), 7.39–7.44 (m, 1H, H_1), 7.64–7.66 (m, 2H, H_2), 7.87–7.89 (m, 2H, H_3), ($^{13}C\{^{1}H\}$, CD_3CN, 25 °C versus TMS) δ (ppm): 33.9 (C_8), 55.1 (C_5), 65.2 (C_7), 68.3 (C_6), 87.4 (Ar–C–Ru), 130.1 (C_1), 131.2 (C_2), 132.1 (C_3), 133.1(C_4), ($^{77}Se\{^{1}H\}$,CD_3CN, 25 °C versus Me_2Se) δ (ppm): 384.5.

4: Yield 0.11 g (~80%); m.p. 165 °C Λ_M = 142.7 S cm^2 mol^{-1}. *Anal.* Calc. For $C_{22}H_{31}ClNRuSe{\cdot}PF_6$: C, 39.45; H, 4.66; N, 2.09%. Found: C, 39.41; H, 4.61; N, 2.07%. NMR: (^{1}H, $CDCl_3$, 25 °C, versus TMS) δ (ppm): 1.29 (d, ^{3}J = 6.6 Hz, 3H, CH_3 of *i*-Pr), 1.34 (d, ^{3}J = 6.6 Hz, 3H, CH_3 of *i*-Pr), 1.99–2.11 (m, 4H, H_8), 2.37 (s, 3H, CH_3 *p* to *i*-Pr), 2.51 (sp, ^{3}J = 6.9 Hz, 1H, CH of *i*-Pr), 2.61–2.86 (m, 4H, H_7), 2.97–3.13 (m, 2H, H_5), 3.67–3.89 (m, 2H, H_6), 5.33–5.81 (m, 4H, Ar–H of *p*-cymene), 7.61–7.70 (m, 3H, H_1, H_2), 7.81–7.83 (m, 2H, H_3), ($^{13}C\{^{1}H\}$, $CDCl_3$, 25 °C versus TMS) δ (ppm): 18.1 (CH_3, *p* to *i*-Pr), 21.4, 23.3 (CH_3 of *i*-Pr), 31.0 (CH of *i*-Pr), 32.7 (C_8), 53.2 (C_5), 63.6 (C_7), 66.3 (C_6), 82.9–105.8 (Ar–C of *p*-cymene), 129.9 (C_1), 130.4 (C_2), 131.2 (C_3), 132.0 (C_4), ($^{77}Se\{^{1}H\}$, $CDCl_3$, 25 °C versus Me_2Se) δ (ppm): 385.8.

2.4. Synthesis of $[RuCl(\eta^6\text{-}p\text{-cymene})(NH_3)_2][PF_6]$ (**5**)

The filtrate left after removing **4** (Section 2.3) was stirred for 1 h with solid NH_4PF_6 (0.032 g, 0.2 mmol) and CH_3OH (15 cm^3) and kept aside for one week. The slow evaporation of solvent resulted in single crystals of **5**. m.p. 155 °C. Λ_M = 155.6 S cm^2 mol^{-1}. *Anal.*

Calc. For $C_{10}H_{20}ClN_2Ru{\cdot}PF_6$: C, 26.71; H, 4.48; N, 6.23%. Found: C, 26.68; H, 4.45; N, 6.27%. NMR: (^{1}H, CD_3CN, 25 °C, versus TMS) δ (ppm): 1.19 (d, ^3J = 6.6 Hz, 6H, CH_3 of *i*-Pr), 1.88 (s, 6H, NH_3), 2.01 (s, 3H, CH_3 *p* to *i*-Pr), 2.73 (sp, ^3J = 6.9 Hz, 1H, CH of *i*-Pr), 5.33–5.75 (m, 4H, Ar–H of *p*-cymene), (^{13}C{^{1}H}, CD_3CN, 25 °C versus TMS) δ (ppm): 18.4 (CH_3, *p* to *i*-Pr), 22.3 (CH_3 of *i*-Pr), 31.5 (CH of *i*-Pr), 81.3–104.0 (Ar–C of *p*-cymene).

2.5. Synthesis of [Ru(η^6-p-cymene)(**L1**)(CH_3CN)][PF_6]$_2{\cdot}CH_3CN$ (**6**)

The **4** (0.13 g, 0.2 mmol) dissolved in CH_3CN (10 cm^3) and AgOTf (0.05 g, 0.2 mmol) were mixed and refluxed for 6 h. The precipitated AgCl was filtered off. The yellow filtrate was mixed with solid NH_4PF_6 (0.032 g, 0.2 mmol) and the volume of solution was reduced to 3 cm^3 with a rotary evaporator. The **6** precipitated on the addition of diethyl ether (5 cm^3) was filtered, washed with 10 cm^3 of CH_3CN–diethyl ether mixture (1:5), dried in vacuo and recrystallized with CH_3CN–diethyl ether mixture (1:5). Single crystals of **6** were obtained by diffusion of diethyl ether into its solution (1 cm^3) made in CH_3CN. Yield 0.12 g, (~70%); m.p. 185 °C. Λ_M = 240.9 S cm^2 mol^{-1}. *Anal.* Calc. for $C_{24}H_{34}N_2RuSe{\cdot}[PF_6]_2$: C, 35.14; H, 4.18; N, 3.41%. Found: C, 35.05; H, 4.16; N, 3.38%. NMR (^{1}H, CD_3CN, 25 °C versus TMS) δ (ppm): 1.28 (d, ^3J = 6.6 Hz, 3H, CH_3 of *i*-Pr), 1.32 (d, ^3J = 6.6 Hz, 3H, CH_3 of *i*-Pr), 2.19 (s, 3H, CH_3CN), 1.94–2.00 (m, 4H, H_8), 2.36 (s, 3H, CH_3 *p* to *i*-Pr), 2.41–2.52 (m, 4H, H_7), 2.86 (sp, ^3J = 6.9 Hz, 1H, CH of *i*-Pr), 3.09–3.15 (m, 2H, H_5), 3.31–3.36 (m, 2H, H_6), 5.51–5.72 (m, 4H, Ar–H of *p*-cymene), 7.35–7.45 (m, 3H, H_1, H_2), 7.52–7.60 (m, 2H, H_3), (^{13}C{^{1}H}, CD_3CN, 25 °C versus TMS) δ (ppm): 18.8 (CH_3, *p* to *i*-Pr), 23.7 (CH_3 of CH_3CN), 22.1, 22.3 (CH_3 of *i*-Pr), 30.3 (CH of *i*-Pr), 31.8 (C_8), 55.4 (C_5), 65.3 (C_7), 68.4 (C_6), 82.6–105.9 (Ar–C of *p*-cymene), 128.6 (C_1), 129.0 (C_2), 131.0 (C_3), 131.5 (C_4), 134.1 (CN of CH_3CN). (^{77}Se{^{1}H}, CD_3CN, 25 °C versus Me_2Se) (δ, ppm). 360.8.

2.6. Synthesis of **L2**

Sodium hydroxide (0.440 g, 11 mmol) dissolved in 5 cm^3 of water was added dropwise to thiophenol (0.5 ml, ~5 mmol) refluxed for 0.5 h in 50 cm^3 of dry ethanol under N_2 atmosphere. (2-Chloroethyl)pyrrolidine hydrochloride (0.85 g, 5 mmol) dissolved in 20 cm^3 of ethanol was added dropwise to the reaction mixture and its refluxing continued further for 3 h. The reaction mixture after cooling to room temperature was poured into 100 cm^3 of distilled water, neutralized with dilute sodium hydroxide and extracted with 100 cm^3 of chloroform. The **L2** (pale yellow liquid) was recovered from the extract by a procedure similar to that of **L1**. Yield: 0.65 g (~78%). NMR: (^{1}H, $CDCl_3$, 25 °C versus TMS) δ (ppm): 1.77–1.81 (m, 4H, H_8), 2.52–2.57 (m, 4H, H_7), 2.73 (t, ^3J = 7.5 Hz, 2H, H_5), 3.08 (t, ^3J = 7.5 Hz, 2H, H_6), 7.14–7.19 (m, 1H, H_1), 7.25–7.30 (m, 2H, H_2) 7.32–7.36 (m, 2H, H_3), (^{13}C{^{1}H}, $CDCl_3$, 25 °C versus TMS) δ (ppm): 23.4 (C_8), 32.3 (C_5), 54.0 (C_7), 55.5 (C_6), 125.7 (C_1), 128.7 (C_2), 128.8 (C_3), 132.4 (C_4).

2.7. Synthesis of [$PdCl_2$(**L2**)] (**7**) and [$PtCl_2$(**L2**)] (**8**)

The solution of **L2** (0.052 g, 0.25 mmol) made in 10 cm^3 of acetone was reacted with Na_2PdCl_4 (0.08 g, 0.25 mmol) or K_2PtCl_4 (0.1 g, 0.25 mmol) dissolved in 10 cm^3 of deoxygenated water as described in Section 2.1 for **1/2**. The resulting **7** or **8** was filtered, washed with hexane and dried in vacuo.

7: Yield: 0.072 g (~75%). m.p. 140.9 °C. Λ_M = 8.1 S cm^2 mol^{-1}. *Anal.* Calc. for $C_{12}H_{17}Cl_2NPdS$: C, 37.47; H, 4.45; N, 3.64%. Found: C, 37.12; H, 4.65; N, 3.35%. NMR: (^{1}H, CD_3CN, 25 °C versus TMS) δ (ppm): 1.93–1.98 (m, 4H, H_8), 2.75–3.06 (m, 4H, H_7), 3.12–3.37 (m, 2H, H_5), 3.73–4.01 (m, 2H, H_6), 7.57–7.61 (m, 3H, H_1, H_2), 8.23–8.26 (m, 2H, H_3). (^{13}C {^{1}H}, CD_3CN, 25 °C versus TMS) δ (ppm): 22.6 (C_8), 41.8 (C_5), 59.8 (C_7), 63.0 (C_6),130.7 (C_1), 130.8 (C_2), 132.0 (C_3), 134.2 (C_4).

8: Yield: 0.083 g (~70%). m.p. 156.8 °C. Λ_M = 11.4 S cm^2 mol^{-1}. *Anal.* Calc. for $C_{12}H_{17}Cl_2NPtS$: C, 30.46; H, 3.62; N, 2.96%. Found: C, 29.97; H, 3.39; N, 2.75%. NMR: (^{1}H, DMSO-d_6, 25 °C versus TMS): (δ, ppm): 1.69–1.87 (m, 4H, H_8), 2.41–2.51 (m, 4H, H_7), 2.77–2.97 (m, 2H, H_5), 3.07–3.34 (m, 2H, H_6), 7.51–7.61 (m, 3H, H_1, H_2), 8.14–8.19 (m, 2H, H_3), (^{13}C{^{1}H}, DMSO-d_6, 25 °C versus TMS) δ (ppm): 22.2 (C_8), 33.9 (C_5), 62.2 (C_7), 64.6 (C_6), 125.8 (C_1), 130.1 (C_2), 130.8 (C_3), 133.4 (C_4).

2.8. Synthesis of [RuCl(η^6-C_6H_6)(**L2**)][PF_6] (**9**) and[RuCl(η^6-p-Cymene)(**L2**)][PF_6] (**10**)

The ligand **L2** (0.042 g, 0.2 mmol) dissolved in CH_3OH (15 cm^3) was reacted with solid [{(η^6-C_6H_6)RuCl(μ-Cl)}$_2$] (0.05 g, 0.1 mmol) or [{(η^6-*p*-cymene)RuCl(μ-Cl)}$_2$] (0.06 g, 0.1 mmol) as described for **3** and **4** in Section 2.4. The **9** and **10** including their single crystals were obtained in a similar fashion (Section 2.4).

9: Yield 0.09 g, (~85%); m.p. 167 °C. Molecular conductance Λ_M = 150.1 S cm^2 mol^{-1}. *Anal.* Calc. for $C_{18}H_{23}ClNRuSPF_6$: C, 38.14; H, 4.09; N, 2.47%. Found: C, 37.97; H, 3.99; N, 2.45%. NMR: (^{1}H, CD_3CN, 25 °C versus TMS) δ (ppm): 1.93–1.96 (m, 4H, H_8), 2.53–2.95 (m, 4H, H_7), 3.06–3.58 (m, 2H, H_5), 3.71–3.91 (m, 2H, H_6), 5.55 (s, 6H, RuAr–H), 7.42 (m, 1H, H_1), 7.67 (m, 2H, H_2), 7.87 (m, 2H, H_3), (^{13}C{^{1}H}, CD_3CN, 25 °C versus TMS) δ (ppm): 40.1 (C_8), 55.4 (C_5), 65.2 (C_7), 67.6 (C_6), 88.0 (RuAr–C), 129.9 (C_1), 131.5 (C_2), 132.3 (C_3), 132.6 (C_4).

10: Yield 0.1 g, (~80%) m.p. 179 °C. Λ_M = 144.8 S cm^2 mol^{-1}. *Anal.* Calc. For $C_{22}H_{31}ClNRuS{\cdot}PF_6$: C, 42.42; H, 5.02; N, 2.25%. Found: C, 42.46; H, 5.09; N, 2.27%. NMR: (^{1}H, CD_3CN, 25 °C TMS) δ (ppm): 1.30 (d, ^3J = 6.6 Hz, 6H, CH_3 of *i*-Pr), 1.95–2.10 (m, 4H, H_8), 2.23 (s, 3H, CH_3 *p* to *i*-Pr), 2.52–2.75 (m, 4H, H_7), 2.89 (sp, ^3J = 6.9 Hz, 1H, CH of *i*-Pr), 3.02–3.20 (m, 2H, H_5), 3.39–3.53 (m, 2H, H_6), 5.30–5.85 (m, 4H, Ar–H of *p*-cymene), 7.41–7.60 (m, 5H, H_1, H_2, H_3), (^{13}C{^{1}H}, CD_3CN, 25 °C versus TMS): δ (ppm): 18.0 (CH_3, *p* to *i*-Pr), 22.2, 22.3 (CH_3 of *i*-Pr), 30.9 (CH of *i*-Pr), 31.8 (C_8), 55.1 (C_5), 64.7 (C_7), 66.5 (C_6), 82.1–106.0 (Ar–C of *p*-cymene), 128.0 (C_1), 128.4 (C_2), 129.9 (C_3), 130.7 (C_4).

2.9. Synthesis of **L3**

Selenium powder (0.40 g, 5 mmol) and sodium borohydride (0.38 g, 10.0 mmol) solution (made in 10 cm^3 of 2.0 M NaOH) were stirred in 50 cm^3 of water for 1 h under nitrogen atmosphere at room temperature. To the resulting thin slurry of Na_2Se, was added dropwise with constant stirring, (2-chloroethyl) pyrrolidine hydrochloride (1.7 g, 10.0 mmol) dissolved in 5 cm^3 of ethanol. The mixture was stirred further for 2–3 h and poured into 100 cm^3 of distilled water. The **L3** was extracted into diethyl ether (3 × 20 cm^3) from the aqueous phase. The ether extract was washed with distilled water (2 × 10 cm^3) and dried over anhydrous sodium sulfate. On evaporating off ether under reduced pressure on rotary evaporator **L3** was obtained as a yellow liquid, unstable under ambient conditions. Yield: 1.78 g (~65%). NMR: (^{1}H, $CDCl_3$, 25 °C versus TMS) δ (ppm): 1.78–1.83 (m, 4H, H_4), 2.54–2.56 (m, 4H, H_3), 2.69–2.78 (m, 4H, H_1, H_2), (^{13}C{^{1}H}, $CDCl_3$, 25 °C versus TMS) δ (ppm): 22.3 (C_4), 23.1 (C_1), 53.7 (C_3), 56.9 (C_2), (^{77}Se {^{1}H}, ($CDCl_3$, 25 °C versus Me_2Se) δ (ppm): 143.1.

2.10. Procedure for catalytic Suzuki reaction

Bromobenzene or its derivative (1 mmol), benzeneboronic acid (0.183 g, 1.5 mmol), K_2CO_3 (0.276 g, 2 mmol), distilled water (0.5 cm^3), DMF (4 ml) and catalyst (complex **1**/**7**) (0.001 mol%) were mixed and stirred under reflux over an oil bath for 24 h at

100 °C under ambient conditions. After cooling to room temperature, 20 cm^3 of distilled water was added to reaction mixture. The product was extracted with a mixture of hexane–diethyl ether (25–50 cm^3). The solvent of extract was partly evaporated on a rotary evaporator to get white crystalline solid product, which was filtered, washed with 3–4 cm^3 of hexane and authenticated by NMR (^1H and $^{13}C\{^1H\}$) spectra and m.p.

2.11. Procedure for catalytic Heck reaction

A mixture of alkene (1.5 mmol), aryl halide (1 mmol), Na_2CO_3 (0.212 g, 2.0 mmol), DMF (4.0 cm^3) and catalyst (complex **1**/**7**) (0.001 mol%) was stirred under reflux on oil bath for 24 h at 100 °C under nitrogen atmosphere. After cooling the reaction mixture to room temperature, 20 cm^3 of water was added to it. The product was extracted into dichloromethane (40 cm^3) and the extract filtered. To obtain (*E*)-1-(4-chloro/nitrophenyl)-2-phenylethene, the filtrate was washed with water (3×25 cm^3) and evaporated on a rotary evaporator. The residue was purified by silica gel column chromatography using hexane–ethylacetate mixture (9:1). In case of (*E*)-3-(4-chloro/nitrophenyl)acrylic acid, the cooled reaction mixture was mixed with $NaHCO_3$ (0.50 g) and water (30 cm^3). It was stirred for 1 h at room temperature and filtered. The filtrate was washed with CH_2Cl_2 (3×20 cm^3). The aqueous phase was acidified with 5 N HCl and cooled to 0 °C. The resulting solid precipitate of the product was filtered, washed with cold water and air dried. The NMR (^1H and $^{13}C\{^1H\}$) spectra and m.p. authenticated the product.

2.12. Procedure for catalytic oxidation of alcohols

Oxidations of primary alcohols to aldehydes and secondary ones to ketones with *N*-methylmorpholine-*N*-oxide (NMO) were catalyzed by the presence of half sandwich compounds [RuCl(η^6-C_6H_6)(**L1**)][PF_6] (**3**) and [RuCl(η^6-C_6H_6)(**L2**)][PF_6] (**9**). A typical reaction using the complexes **3** or **9** as catalyst is as follows. A solution of complex **3** or **9** (0.001 mol%) in 20 cm^3 of CH_2Cl_2 was added to the mixture of substrate (1 mmol) and NMO (3 mmol). The mixture was refluxed for 3 h and the solvent was evaporated under reduced pressure with a rotary evaporator resulting in a solid mass, which contained the complex **3** or **9** and the oxidized product. It was shaken with petroleum ether (60–80 °C) (20 cm^3). The complex **3** or **9** remained as precipitate was recovered almost quantitatively. The oxidized product extracted into petroleum ether was analyzed by GC.

3. Results and discussion

The syntheses of **L1**–**L3** and their complexes (**1**–**10**) are summarized in Scheme 1. There is no reference in literature for the synthesis of **L2** except the registry number 398472-84-9, indicating its commercial availability. The bridge-cleavage reactivity of chloro bridged dimers [((η^6-C_6H_6)RuCl(μ-Cl))$_2$] and [((η^6-*p*-cymene)RuCl(μ-Cl))$_2$] with **L1** and **L2** and subsequent treatment with NH_4PF_6 have resulted in the formation of **3**, **4**, **9** and **10**. The **6** was formed by substitution of Cl with CH_3CN. The formation of **5** resulted due to reaction of unreacted chlorobridged dimeric compound of Ru with NH_4PF_6. The **L3** is unstable and therefore its complexes of good purity could not be isolated. On contrary its tellurium analoge is stable [30]. All the ligands were found soluble in common organic solvents. The **L1** and **L2** were found stable for a week in referigerator (~5 °C). The solid complexes **1**–**10** were found stable and could be stored for six months easily under ambient conditions. They exhibit solubility in common organaic solvents except hexane or petroleum ether in which they were found only sparingly soluble. The solutions of all the complexes in DMSO showed the sign of decomposition after 1–2 days. The molar conductance values of half sandwich ruthenium(II) complexes **3**, **4**, **5**, **9** and **10** are close to the values expected for a 1:1 electrolyte. In case of **6** the molar conductance value concurrs with its 1:2 electrolytic nature. In IR spectra of **3**–**6** and **9**–**10** the band around 850 cm^{-1} may be assigned to P–F vibrations. IR data are further detailed in supplementry material.

3.1. NMR spectra

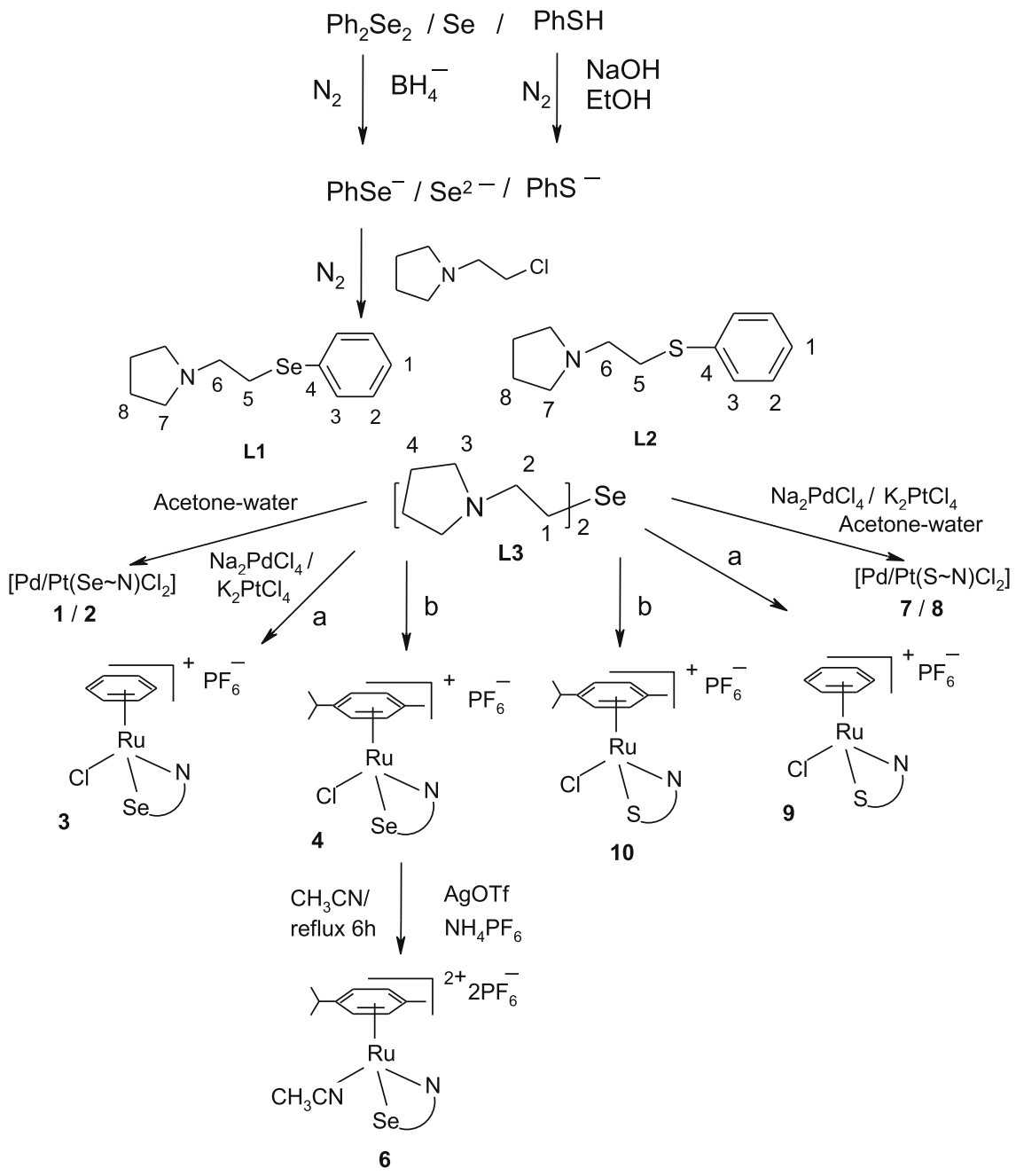
The characteristic signal in $^{77}Se\{^1H\}$ NMR spectra of **L1** shifts to a high frequency on complex formation (Shift: ~191, 147, 103.2–104.5 and 79.5 ppm for **1**, **2**, **3**/**4** and **6** respectively), implying the coordination of Pd, Pt or Ru through Se of **L1**. The signals at almost similar frequency in the spectra of **3** and **4** indicate that electronic effects on selenium of *p*-cymene and benzene ligands are not much different.

On complexation of **L1** with metal ions the signals of H_3, H_5, H_6 and H_7 in ^1H NMR spectra shift to higher frequency (0.41–1.24 ppm) relative to those of free **L1**, implying the coordination of **L1** through Se and N donor sites. In $^{13}C\{^1H\}$ NMR spectra of complexes of **L1** the signals of C_3, C_5, C_6 and C_7 appear at higher frequency (up to ~19 ppm) relative to those of free **L1**, corroborating with the proton NMR spectra. The ^1H NMR spectra of complexes of **L2** exhibit signals of H_3, H_5, H_6 and H_7 at higher frequency (up to 0.91 ppm) with respect to those of free **L2**. Thus **L2** appears to coordinate with Pd, Pt and Ru like **L1**. This is corroborated by $^{13}C\{^1H\}$ NMR spectra of complexes of **L2** as the signals of C_3, C_4, C_5, C_6 and C_7 are shifted to higher frequency (up to ~22.8 ppm) with respect to those of free ligand. These observations suggest that **L1** and **L2** in all the complexes behave as (S/Se, N) donors, as revealed by single crystal structures (Section 3.3).

The cyclic voltammetric (CV) experiments performed at 298 K in CH_3CN (0.01 M NBu_4ClO_4 as supporting electrolyte) for both **3** and **9** at scan rate 100 mV s^{-1} (anodic sweep) show two metal centered voltammetric responses (Fig. 1). A quasi-reversible oxidation with $E_{1/2}$ values +0.452 and +0.612 V (versus Ag/AgCl) respectively for **3** and **9** has been observed. The higher value of $E_{1/2}$ for **9** in comparison to that of **3** suggests that substitution of (N, S) ligand with a (N, Se) at ruthenium centre leads to a less thermodynamically favorable oxidation. However these $E_{1/2}$ values indicate that **3** and **9** are expected to be reasonably efficient catalyst for the redox process [36].

3.2. Crystal structures

The data of single crystals of **1**, **3**–**6**, **9** and **10** and structural refinement parameters are given in Supplementary material (Table S1 and S2). The molecular structure of **1** is shown in Fig. 2 along with important bond lengths and angles. More bond lengths and angles are given in Supplementary material (Table S3). The geometry around Pd is slightly distorted square planar. The Pd–Se, Pd–N and Pd–Cl bond distances 2.353(2), 2.085(14) and 2.340(5)/2.303(5) Å, respectively are consistent with values 2.3669(11), 2.003(7) and 2.305(2) Å, respectively reported recently [37] for Pd(II) complex of a tridentate selenated Schiff base. In Figs. 3–5 molecular structures of complexes **3**, **4** and **6** are given along with selected bond lengths and angles (see Table S3 in Supplementary material for further details). The molecular structure of **5** is shown in Supplementary material (Fig S3). In all complexes **3**–**6** the cation exhibits the pseudo-octahedral half sandwich "piano-stool" disposition around Ru. The benzene ring or ring of *p*-cymene occupies one face of octahedron. The Ru–C distances (2.170(8)–2.215(8) Å for **3**, 2.165(6)–2.235(7) Å for **4** and 2.164(3)–2.208(3) Å for **5** are normal and consistent with the earlier reports [38,39]. The **6** has



a: $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$; NH_4PF_6; MeOH; r.t; 10 h

b: $[((\eta^6\text{-}p\text{-}Cymene)RuCl(\mu\text{-}Cl))_2]$; NH_4PF_6; MeOH; r.t; 14 h

Scheme 1. Synthesis of ligands and complexes.

some what longer Ru–C bond lengths (2.190(4)–2.253(4) Å) in comparison to those of **3**, **4** or **5**. The *trans* influence of MeCN appears to contribute partly to this elongation. The formation of hydrogen bond by anion PF_6^- in the crystals of **3**–**6** (Figs. S1, S2, S4 and S6 and Table S4 in Supplementary material) results in extended solid state structures. In the crystals of **4** and **5** intra and inter molecular hydrogen bonds between Cl and various H atoms have also been observed (Table S4 and Fig. S5 in Supplementary material). The Ru–N bond lengths of **3** and **4** (2.201(5) Å) are some what longer than those of **5** (2.146(3)/2.154(3) Å, partly due to steric effects of bidentate **L1** in **3** and **4**. However, Ru–N bond lengths of **3**–**5** are consistent with the recent literature reports (2.0511(17)–2.163(10) Å) [38–39]. We are unaware of any crystallographic study carried out on a Ru-complex of a selenoether ligand. Therefore, comparisons of present Ru–Se bond distances are made with those present in cluster or bimetallic species having bridging selenide or diselenide ligand(s). The Ru–Se bond lengths of **3** and **4** [2.4918(9) and 2.480(11) Å, respectively] fall within the 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 $[Ru_3(\mu_3\text{-}Se)$

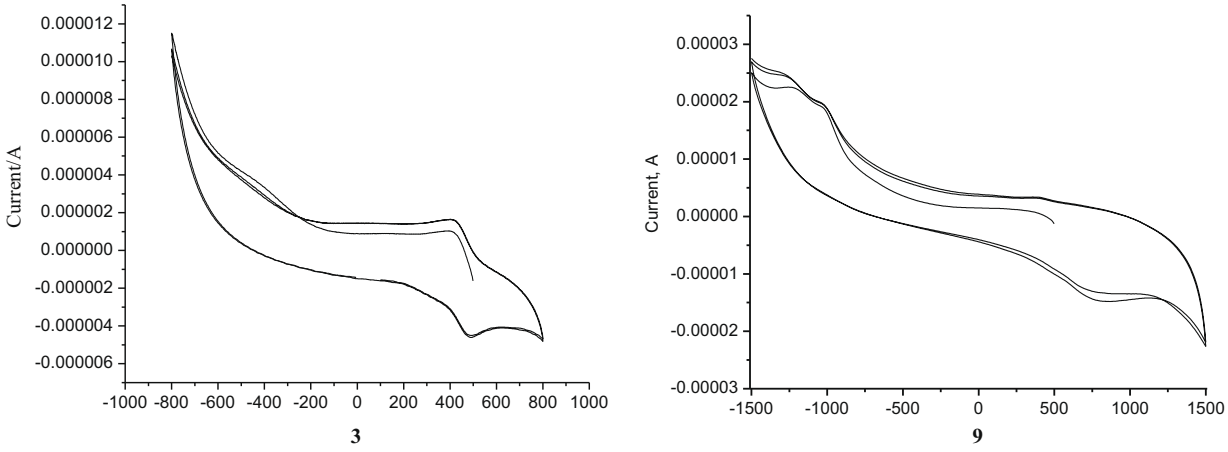


Fig. 1. Cyclic voltammogram of **3** and **9**.

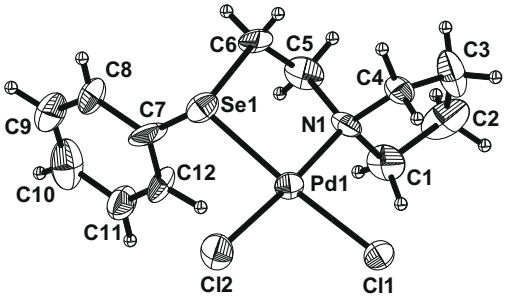


Fig. 2. ORTEP diagram of **1** with 50% probability ellipsoids; bond length (Å): Pd(1)–Se(1) 2.353(2), Pd(1)–N(1) 2.085(14), Pd(1)–Cl(1) 2.340(5), Pd(1)–Cl(2) 2.303(5); bond angle (°): Cl(1)–Pd(1)–Se(1)169.2(17), Cl(2)–Pd(1)–Se(1) 86.6(15), N(1)–Pd(1)–Se(1) 89.2(4), N(1)–Pd(1)–Cl(1) 93.4(4), N(1)–Pd(1)–Cl(2) 173.7(4), Cl(2)–Pd(1)–Cl(1) 91.6(19).

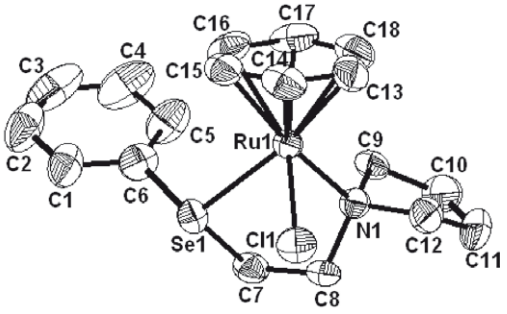


Fig. 3. ORTEP diagram of **3** with 50% probability ellipsoids; hydrogen atoms and PF_6 are omitted due to clarity. bond length (Å): Ru(1)–Se(1) 2.480(11), Ru(1)–N(1) 2.201(5), Ru(1)–Cl(1) 2.406(2), Ru(1)–C 2.170(8)–2.215(8); bond angle (°): Cl(1)–Ru(1)–Se(1) 80.87(6), N(1)–Ru(1)–Se(1) 83.81(15), N(1)–Ru(1)–Cl(1) 85.73(15).

(μ_3-S)(CO)$_7$(μ-dppm)] [40]. For Ru(IV) complex [Cp*Ru{η^2-Se$_2$P(*i*-Pr)$_2$}{η^2-SeP(*i*-Pr)$_2$}][PF$_6$] the Ru–Se bond lengths [41] are reported in the range 2.538(2)–2.590(2) Å, longer than those of **3** and **4** due to steric crowding. The Ru–Se and Ru–N (**L1**) bond distances of **6** (2.4770(5) and 2.190(3) Å, respectively) are somewhat shorter than those of **3**/**4**. The Ru–Se bond distance found in bimetallic species [CpRu(CO)(C≡CPh)(μ-Se)ZrCp$_2$] 2.494(1) Å [42], is closer to that of **3**. In [(η^5-C$_5$Me$_5$)Ru(μ_2-SeR)$_3$Ru(η^5-C$_5$Me$_5$)]Cl (R = Tol) Ru–Se bond distances are in the range 2.446(4)–2.466(4) Å [43] and shorter than those of **3** and **4**, because RSe$^-$

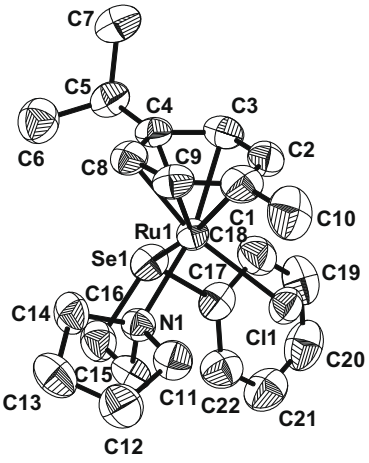


Fig. 4. ORTEP diagram of **4** with 50% probability ellipsoids; hydrogen atoms and PF_6 are omitted due to clarity. bond length (Å): Ru(1)–Se(1) 2.4918(9), Ru(1)–N(1) 2.201(5), Ru(1)–Cl(1) 2.3815(17), Ru(1)–C 2.165(6)–2.235(7); bond angle (°): Cl(1)–Ru(1)–Se(1) 90.00(5), N(1)–Ru(1)–Se(1) 84.12(13), N(1)–Ru(1)–Cl(1) 86.37(13).

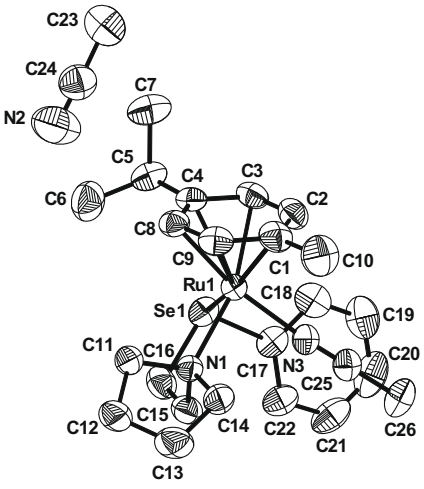


Fig. 5. ORTEP diagram of **6** with 50% probability ellipsoids; hydrogen atoms and PF_6 are omitted due to clarity. bond length (Å): Ru(1)–Se(1) 2.4770(5), Ru(1)–N(1) 2.190(3), Ru(1)–N(3) 2.041(4), Ru(1)–C 2.190(4)–2.253(4); bond angle (°): N(1)–Ru(1)–Se(1) 84.96(9), N(3)–Ru(1)–Se(1) 88.99(9), N(3)–Ru(1)–N(1) 84.70(13).

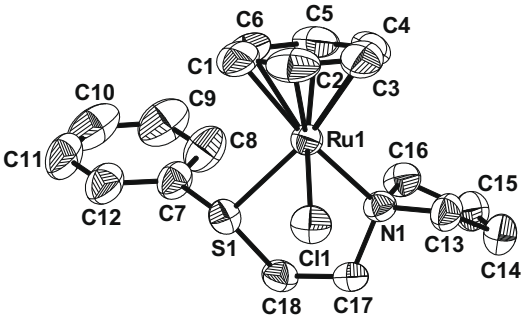


Fig. 6. ORTEP diagram of **9** with 50% probability ellipsoids; hydrogen atoms and PF_6 are omitted due to clarity. bond length (Å): Ru(1)–S(1) 2.3649(13), Ru(1)–N(1) 2.187(3), Ru(1)–Cl(1) 2.3914(12), Ru(1)–C 2.168(5)–2.193(5); bond angle (°): Cl(1)–Ru(1)–S(1) 82.39(4), N(1)–Ru(1)–S(1) 83.08(10), N(1)–Ru(1)–Cl(1) 85.56(9).

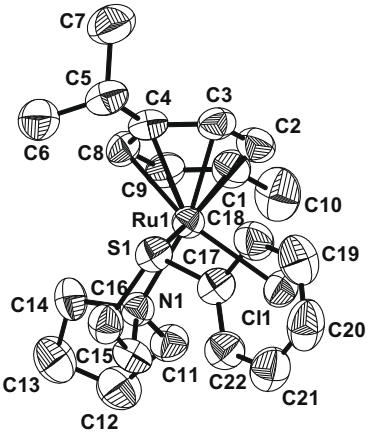


Fig. 7. ORTEP diagram of **10** with 50% probability ellipsoids; hydrogen atoms and PF_6 are omitted due to clarity. bond length (Å): Ru(1)–S(1) 2.389(16), Ru(1)–N(1) 2.192(4), Ru(1)–Cl(1) 2.383(16), Ru(1)–C 2.184(6)–2.228(5); bond angle (°): Cl(1)–Ru(1)–S(1) 89.78(6), N(1)–Ru(1)–S(1) 83.87(12), N(1)–Ru(1)–Cl(1) 86.79(11).

is expected to be bonded strongly in comparison to a selenoether. In a diselenide bridged complex $[(MeCp)Ru(PPh_3)]_2(\mu\text{-}Se_2)_2(Otf)_2$. Ru–Se bond distances are 2.518(1) and 2.556(1) Å [44], somewhat longer than those of **3** and **4**. The molecular structures of **9** and **10** are shown in Fig. 6 and 7 whereas secondary interactions observed in their crystals are shown in Figs. S7–S10 of Supplementary material. The Ru–S and Ru–N bond distances of **9** and **10** are nearly similar (see Figs. 6 and 7). For $[Cp^*Ru(PMe_3)_2(SC_6F_4H)]$ and $[Cp^*Ru(NO)(SC_6F_4H)_2]$ [41] the Ru–S bond distances are reported as 2.4104(9)/2.4156(9) and 2.3899(6)/2.3880(6) Å, respectively. These values are closer to the value 2.389(16) Å observed for **10** in comparison to 2.3649(13) Å found for **9**. The Ru–S bond distance in case $[\{RuCl_2(p\text{-cymene})\{\mu\text{-}o\text{-}C_5H_4\text{-}(CH_2SMe)_2\}\}]$ is reported as 2.4021(10) Å, longer than those of **9** and **10** both. The formation of chelate ring in **9** and **10** appears to be responsible for short Ru–S distances.

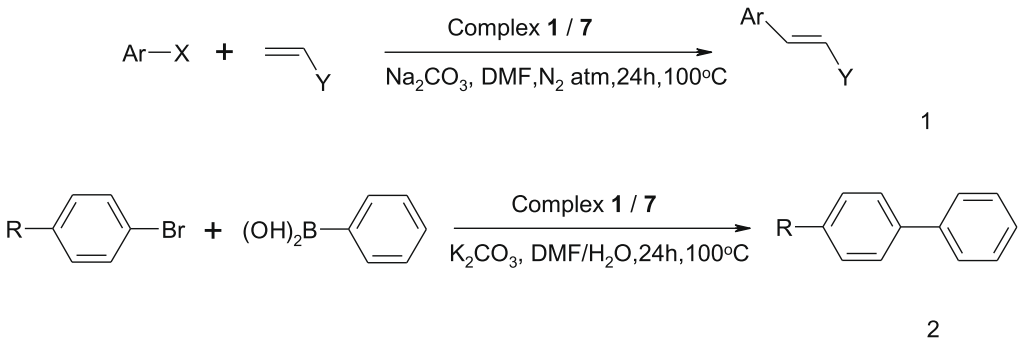
3.3. Catalytic Heck and Suzuki–Miyaura reactions

One of the most important facets of electronic properties of selenium is its strong electron donating ability which has been responsible for the efficiency of Pd(II)–selenium ligand complex for Heck reaction [31]. There is current interest in phosphine-free catalysts for Heck coupling [45–46]. Thus palladium complex **1** having Se–ligand has been explored for Heck reactions given in Scheme 2 (Eq. (1)). The palladium complex **7**, which is sulfur analog of **1** has been explored for comparison and found to be only marginally less efficient than **1**. In Table 1 substrates, percentage conversions and values of turnover number (TON) are given. The TOF values are in the ranges 1.46×10^3–$3.46 \times 10^3\ h^{-1}$ and 1.04×10^3–$3.13 \times 10^3\ h^{-1}$, respectively for **1** and **7**. The air stability of **1** and **7** is the major advantage of using them. The conversions are higher for ArI in comparison to ArBr. The TON values of **1** and **7** (up to 83 000) for many substrates are comparable to those reported for Pd-complex of Se–C–Se pincer ligand [31].

Suzuki–Miyaura reaction given in Scheme 2 (Eq. (2)), is also among the most important palladium-catalyzed cross-coupling reactions of both academic and industrial interest. In view of air and moisture sensitivity of complexes of phosphorus ligands, there is a current interest in palladium complexes of phosphine-free ligands for the Suzuki–Miyaura reaction [47–49] as well. Complexes **1** and **7** have been explored for Suzuki–Miyaura reaction as they offer the advantage of stability under ambient conditions. In Table 1 substrates, percentage conversions and values of turnover number (TON) are given. The TOF values are in the range 1.46×10^3–$3.54 \times 10^3\ h^{-1}$ for **1** and 1.04×10^3–$3.42 \times 10^3\ h^{-1}$ for **7**. The TON values dependent on R have been found up to 85000 and better for some substrates than those reported earlier [47–49]. The Se containing complex is some what more efficient than its sulfur analog.

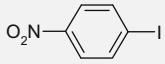
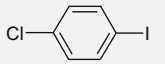
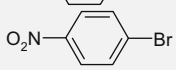
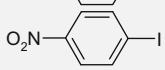
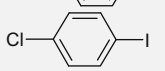
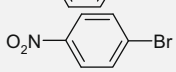
3.4. Catalytic oxidation of alcohols

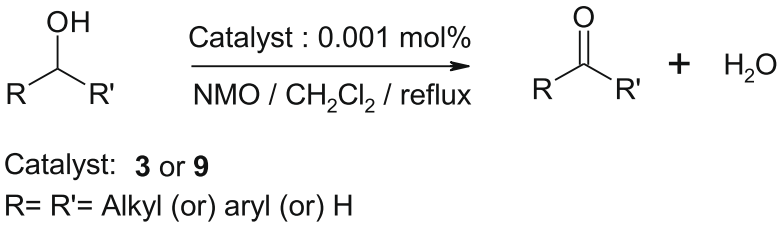
The catalytic performances of Ru-complexes **3** and **9** have been explored for oxidation of primary and secondary alcohols in a classical oxidation system developed in CH_2Cl_2 in the presence of NMO (Scheme 3). In Table 2 percentage conversions and values of turn over number (TON) are given. The conversion is between 80% and 97%, whereas TON value varies between 8.0×10^4 and 9.7×10^4. These values commensurate with the redox potentials derived by CV studies. The TOF values in case of **3** are in the range



Scheme 2. Heck and Suzuki reactions.

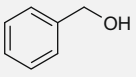
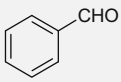
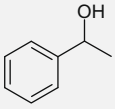
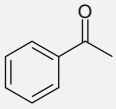
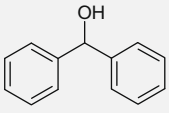
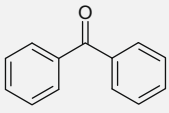
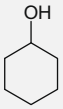
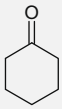
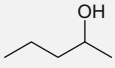
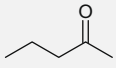
Table 1
Yields (%) in Suzuki and Heck reactions.

Substituents on reactants		Complex	
		1	**7**
Ar–X	Y	TON (yield of trans product %)	
Heck reaction			
	COOH	8.3×10^4 (83)	7.5×10^4 (75)
	COOH	8.0×10^4 (80)	7.2×10^4 (72)
	COOH	3.7×10^4 (37)	2.5×10^4 (25)
	Ph	8.0×10^4 (80)	7.2×10^4 (72)
	Ph	7.8×10^4 (78)	7.0×10^4 (70)
	Ph	3.5×10^4 (35)	2.8×10^4 (28)
R		TON (yield %)	
Suzuki reaction			
OMe		3.5×10^4 (35)	2.5×10^4 (25)
H		6.0×10^4 (60)	5.0×10^4 (50)
NO_2		8.5×10^4 (85)	8.2×10^4 (82)



Scheme 3. Catalytic oxidation of alcohols.

Table 2
Oxidation of alcohols to corresponding aldehydes and ketones with NMO catalyzed by complexes **3** and **9**.

Entry	Substrate	Product	TON (% conversion)	
			3	**9**
1			8.5×10^4 (85)	8.0×10^4 (80)
2			9.2×10^4 (92)	8.9×10^4 (89)
3			9.6×10^4 (96)	9.2×10^4 (92)
4			9.3×10^4 (93)	9.0×10^4 (90)
5			9.4×10^4 (94)	9.1×10^4 (91)
6			9.8×10^4 (98)	9.6×10^4 (96)
7			9.7×10^4 (97)	9.4×10^4 (94)

2.84×10^4–$3.27 \times 10^4\ h^{-1}$, whereas for **9** the range is 2.67×10^4–$3.20 \times 10^4\ h^{-1}$. It has been observed that neither **3**/**9** nor NMO alone causes these organic transformations under identical reaction conditions. The **3** and **9** both effectively catalyze the oxidation of benzyl alcohol with maximum selectivity to aldehyde, importantly, with no further oxidation to carboxylic acid. It appears that probably NMO reacts with Ru-complex to yield ruthenium(IV)-oxo species, which in turn oxidizes the alcohols. On addition of NMO to a dichloromethane solution of **3** or **9** a new shoulder at 391 nm in UV–Vis spectrum appears, which supports the formation of Ru(IV)═O species. The IR of residue left after evaporating solvent from the mixture of **3** or **9** with NMO exhibits a very strong band at 856 cm^{-1} which appears to have contribution from Ru(IV)═O species [50]. The band of moderate intensity around this position due to PF_6 is also present therefore unequivocal assignment of this band is not possible but the occurrence of more intense band is an indication of contribution by Ru(IV)═O species. The earlier reports on the oxidation of various substrates including alcohols by oxo-ruthenium species [51–53] further support our proposition. The complex **3** is somewhat more efficient catalyst than **9**.

4. Conclusion

Selenated pyrrolidines *N*-{2-(phenylseleno)ethyl}pyrrolidine (**L1**), *N*-{2-(phenylthio)ethyl}pyrrolidine (**L2**), and bis{2-pyrrolidene-*N*-yl)ethyl selenide (**L3**) have been synthesized for the first time. The NMR spectral and crystallographic studies on complexes $[PdCl_2$(**L1/L2**)**]** (**1**/**7**), $[PtCl_2$(**L1/L2**)**]** (**2**/**8**), $[RuCl(\eta^6$-$C_6H_6)$(**L1/L2**)$][PF_6]$ (**3/9**), $[RuCl(\eta^6$-*p*-cymene)(**L1/L2**)$][PF_6]$ (**4/10**), $[RuCl(\eta^6$-*p*-cymene)$(NH_3)_2][PF_6]$ (**5**) and $[Ru(\eta^6$-*p*-cymene)(**L1**)$(CH_3CN)]$-$[PF_6]_2{\cdot}CH_3CN$ (**6**) reveal that **L1** and **L2** both behave as bidentate ligands. The CV data reveal the potential of **3** and **9** for catalytic oxidation. The TON value varying between 8.0×10^4 and 9.7×10^4 for this oxidation are promising. For Heck and Suzuki–Miyaura coupling reactions TON values found up to 85000 with the advantage of catalyst's stability in air are reasonably good. The selenium analogs are more efficient than sulfur ones for catalytic C–C coupling as well as oxidation.

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Appendix A. Supplementary material

CCDC 735502, 699208, 735503, 735504, 735505, 735506 and 735507 contain the supplementary crystallographic data for **1**, **3**, **5**, **9**, **10**, **4**, and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.08.004.

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