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Reactions of benzene based half sandwich ruthenium(II) complex with 2,6-bis((phenylseleno)methyl)pyridine: Preferential substitution of ring resulting in a catalyst of high activity for oxidation of alcohols

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ABSTRACT

[2,6-Bis((phenylseleno)methyl)pyridine] (**L**) a (Se, N, Se) pincer ligand synthesized by reacting $PhSe^-$ (in situ generated) with 2,6-bis(chloromethyl)pyridine reacts with $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ (2:1 molar ratio) by preferential substitution of ring resulting in the first Ru-(Se, N, Se) pincer ligand complex, *mer*-$[Ru(CH_3CN)_2Cl(\mathbf{L})][PF_6]$(**1**).$H_2O$. Similar reaction in 4:1 molar ratio results in *mer*-$[Ru(\mathbf{L})_2][ClO_4]_2$(2). The ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra of **L**, **1** and **2** were found characteristic. The single crystal structures of **1** and **2** were studied by X-ray crystallography. The geometry of Ru in both the complexes is distorted octahedral. The Ru–Se distances are in the ranges 2.4412(16)–2.4522(16) and 2.4583(14)–2.4707(15) Å respectively for **1** and **2**. The structural solutions from the crystal data in case of **2**, due to inferior quality of its crystals, are suitable for supporting bonding mode of **L** with Ru(II) only. The **1** shows high catalytic activity for oxidation of primary and secondary alcohols (TON up to 9.7×10^4).

Ruthenium(II) complexes of pincer ligands of (N, N, N), (P, N, N), (P, N, P), (C, N, N) and (P, C, P) types have been investigated in the recent past [1–9] due to their potential catalytic applications. Recently ruthenium(II) complexes with (N, N, N) pincer ligand 2,6-bis (pyrazolyl)pyridine have been used as effective catalysts for hydrogen transfer reaction of ketones [1,10–12]. The (P, N, P) pincer ligand [2,6-bis(di-*tert*-butylphosphinomethyl)pyridine] and (P, N, N) pincer [2-(di-*tert*-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine] form ruthenium(II) complexes which have been found efficient for catalytic dehydrogenative coupling of alcohols [2], hydrogenation of esters to alcohols [4] and reaction of alcohols with amines to form amides with liberation of H_2 [13]. The complex formed by acridine-based (P, N, P) pincer ligand with Ru(II), [RuHCl(A-*i*PrPNP)(CO)] [A-*i*PrPNP = 4,5-bis-(di-*iso*-propylphosphinomethyl)acridine] has been used for selective synthesis of primary amines directly from alcohols and ammonia [3]. Ruthenium(II) complex of a (C, N, N) pincer ligand has been explored successfully for catalytic asymmetric reduction of alkyl aryl ketones [7]. The (P, C, P) pincer-arylruthenium(II) complex has been used to catalyze the asymmetric hydrogen transfer reaction [8]. However Ru(II) complexes with selenium containing pincer ligands are not in our knowledge. Recently (Se, N, Se) pincer ligand and its palladium(II) complexes have been reported from our group [14]. The palladium complexes are efficient for catalytic heck coupling reactions [14]. It was therefore thought worthwhile to study reactions of half sandwich species $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ (**a**) with (Se, N, Se) type pincer ligand **L** (Scheme 1). The reactions in 2:1 and 4:1 molar ratios (**L:a**) give *mer*-$[Ru(CH_3CN)_2Cl(\mathbf{L})][PF_6]$(**1**).$H_2O$ and *mer*-$[Ru(\mathbf{L})_2][ClO_4]_2$(**2**) respectively. The formation of **1** takes place due to preferential substitution of benzene ring with pincer ligand reported scantly. Only one example is in our knowledge [15]. The **1** has been explored for its catalytic activity for oxidation of alcohols and found efficient. The results of these investigations are the subject of present paper.

The ligand **L** was synthesized by the reported procedure [14] summarized in Scheme 1 and its NMR data required for comparison with those of the present complexes are given in online Supplementary material. The syntheses of both ruthenium(II) complexes **1** and **2** using precursor $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ synthesized by reported procedure [16] are also summarized in Scheme 1. The ligand **L** was soluble in common organic solvents. The complexes (**1**/**2**) also have good solubility in common organic solvents except hexane and petroleum ether in which they were found sparingly soluble. The solutions of both complexes in DMSO showed the sign of decomposition after 20–24 h.

The complexes (**1**/**2**) show characteristic ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR [17,18] and IR spectra (online Supplementary material). These spectra of ligand **L** are also characteristic (see online Supplementary material for detail). The molar conductance of complex **1** is close to the value expected for an 1:1 electrolyte [17] while that of **2** is close to that of an 1:2 electrolyte [18]. The signal in $^{77}Se\{^1H\}$ NMR spectrum of **L** (δ, 351.2 ppm) shifts to a high frequency by 41.8 and 40.3 ppm respectively, on the formation of complexes **1** and **2**, implying the

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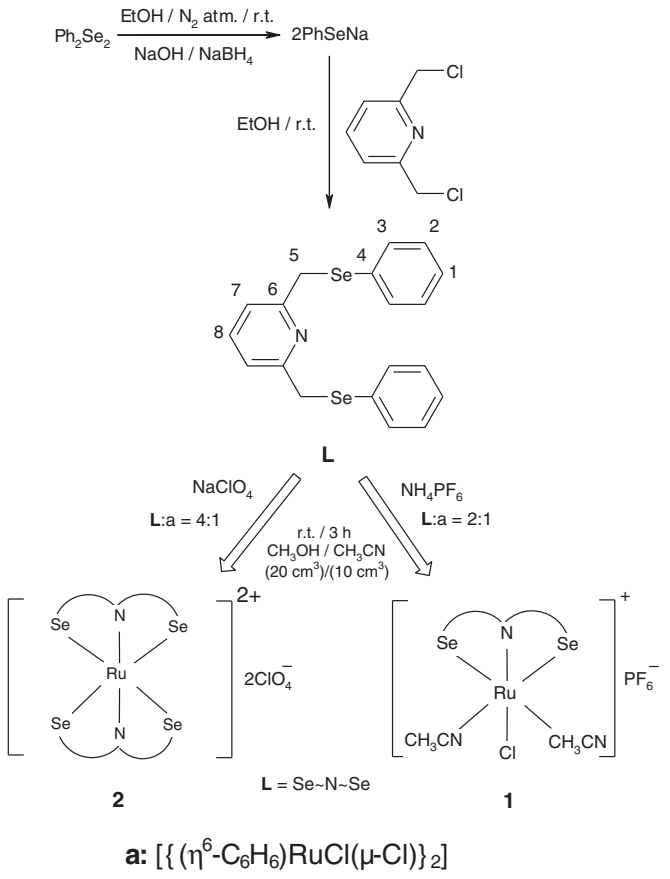

Scheme 1. Synthesis of **L** and its ruthenium complexes **1** and **2**.

coordination of ruthenium with Se of **L**. The presence of only one signal in $^{77}Se\{^1H\}$ NMR spectra of complexes indicates the equivalence of bonding of all Se donor sites to ruthenium. In ^1H NMR spectrum of **1** signals of H_5 and H_7 appear shifted to higher frequency by 0.87 and 0.76 ppm respectively while in case of complex **2** by 1.07 and 0.79 ppm respectively, relative to those of free ligands, corroborating with the coordination of **L** through Se donor sites as inferred from $^{77}Se\{^1H\}$ NMR spectral data [17,18]. In $^{13}C\{^1H\}$ NMR spectra of complex **1** the signals of C_5, C_6 and C_7 appear shifted to higher frequency by 8.9, 6.1 and 2.4 ppm respectively while in complex **2** by 7.8, 7.0 and 1.8 ppm respectively relative to those of free ligand, corroborating with the ^1H NMR spectra [17,18].

The single crystal structure of **1** has been solved [19a]. The crystals of **2** were not of good quality [19b] and therefore some disorders were observed in the structural data of carbon atoms of phenyl rings and oxygen atom of anion ClO_4^-. However, they are not of much significance in the context of inference related to the binding of two pincer ligands with ruthenium(II) (see Supplementary material), which is very much supported by the results of X-ray crystallographic study of **2**. In Figs. 1 and 2 molecular structures of **1** and **2** with some bond lengths are given. The geometries of ruthenium in **1** and **2** are distorted octahedral as revealed by bond angles [20a–b]. More details of crystal data, structural refinements, bond lengths and angles are available in online Supplementary material (Tables S1–S2). The Ru–Se bond lengths of **1** are in the range 2.4412(16)–2.4522(16) and of **2** in 2.4583(14)–2.4707(15) Å and do not differ much. The bond distances of **1** are shorter than the values 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 $[Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)]$ [21]. Probably this is may be due to the fact that (Se, N, Se) pincer ligand **L** behaves as a strong donor for Ru(II). In $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}SeR)_3Ru(\eta^5\text{-}C_5Me_5)]Cl$

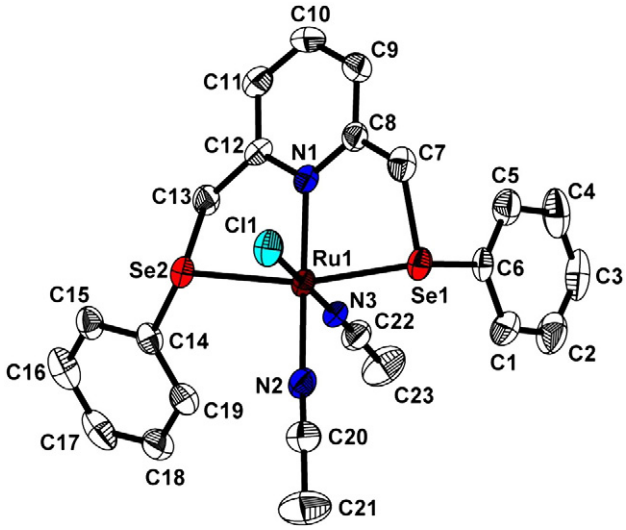

Fig. 1. ORTEP diagram of cation of **1** with 30% probability ellipsoids; H_2O, PF_6^- and H atoms are omitted for clarity; Selected bond lengths(Å): Ru(1)–N(3) 2.016(8), Ru(1)–N(2) 2.029(8), Ru(1)–N(1) 2.067(7), Ru(1)–Cl(1) 2.411(3), Ru(1)–Se(1) 2.4412(16), Ru(1)–Se(2) 2.4522(16).

(R = Tol) Ru–Se bond distances are in the range 2.446(4)–2.466(4) Å [22] and consistent with those of **1** and **2**.

The Ru–Se bond lengths of complex **1**/**2** are shorter than the value 2.480(11) Å reported for $[(\eta^6\text{-}C_6H_6)RuCl(N\text{-}\{2\text{-}(phenylseleno)ethyl\}pyrrolidine)]$ [23]. The Ru–N bond lengths of **1** are between 2.016(8) and 2.067(7) Å while that of **2** between 2.091(10) and 2.095(8) Å. Both are somewhat shorter than the Ru–N bond distance (2.163(10) Å) reported for $[(\eta^6\text{-}p\text{-cymene})Ru(2\text{-}MeSC_6H_4CH_2NH(CH_2)_2TeC_6H_4\text{-}4\text{-}OMe)][PF_6]_2.CHCl_3$ [24]. The Ru–Cl bond distance of **1**, 2.411(3) Å is consistent with the values 2.416(2) Å reported for $[(\eta^6\text{-}p\text{-cymene})RuCl(1\text{-}(phenylselenomethyl)\text{-}1H\text{-}benzotriazole)][PF_6]$ [25]. In the crystal of **1** weak O···H interactions (3.433(30)–3.600(29) Å) which may be due to packing effects have been observed (Fig. S1 in online Supplementary material).

The complex **1** shows high activity for catalyzing oxidation of primary alcohols to aldehydes and secondary ones to ketones, with *N*-

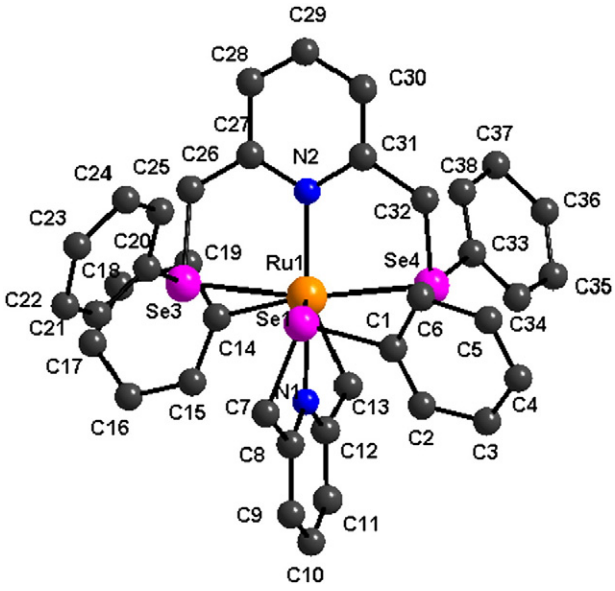

Fig. 2. Molecular structure of cation **2**; ClO_4^- and H atoms are omitted for clarity; Selected bond lengths(Å): N(1)–Ru(1) 2.091(10), N(2)–Ru(1) 2.095(8), Ru(1)–Se(2) 2.4583(14), Ru(1)–Se(4) 2.4587(13), Ru(1)–Se(3) 2.4640(13), Ru(1)–Se(1) 2.4707(15).