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Introduction

The substituted pyridines are attractive as ligands.¹ The ruthenium(π) complexes of such ligands have also received attention in the recent past.² However, pyridine based ligands explored so far for designing Ru(π) half-sandwich complexes suitable for transfer hydrogenation and oxidation of alcohols are not large in number. Some known examples of Ru(π) half-sandwich complexes having pyridine, its derivatives or related skeleton based ligands are: (i) [π^6 -(C₆H₆)RuCl₂(picoline)],³ (ii)

Half sandwich complexes of chalcogenated pyridine based bi-(N, S/Se) and terdentate (N, S/Se, N) ligands with (η^6 -benzene)ruthenium(μ): synthesis, structure and catalysis of transfer hydrogenation of ketones and oxidation of alcohols†

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The half sandwich complexes $[(\eta^{6}-C_{6}H_{6})Ru(L)CI][PF_{6}]$ (1–5) have been synthesized by the reactions of (2-arylchalcogenomethyl)pyridine [L = L1-L3] and bis(2-pyridylmethyl)chalcogenide [L = L4-L5] (chalcogen = S, Se; Ar = Ph/2-pyridyl for S, Ph for Se) with $[(\eta^{6}-C_{6}H_{6})RuCl_{2}]_{2}$, at room temperature followed by treatment with NH₄PF₆. Their HR-MS, ¹H, ¹³C{¹H} and ⁷⁷Se{¹H} NMR spectra have been found characteristic. The single crystal structures of **1–5** have been established by X-ray crystallography. The Ru has pseudo-octahedral half sandwich "piano-stool" geometry. The complexes **1–5** have been found efficient for catalytic oxidation of alcohols with *N*-methylmorpholine-*N*-oxide (NMO) and transfer hydrogenation of ketones with 2-propanol (at moderate temperature 80 °C) as TON values are up to 9.9 × 10³ and 9.8 × 10³ respectively for the two catalytic reactions. On comparing the required catalyst loading for good conversions and reaction time for the present complexes with those reported in literature for other transfer hydrogenation/oxidation catalysts, it becomes apparent that **1–5** have good promise. The complexes of Se ligands have been found more efficient than their sulphur analogues. The complexes of latter. These orders of efficiency are supported by DFT calculations. The calculated bond lengths/ angles by DFT are generally consistent with the experimental ones.

 $[\eta^{6}-(p-\text{cymene})\text{RuCl}(2-\text{aminomethyl})\text{pyridine}]\text{Cl},^{4}$ (iii) $[\eta^{6}-(\text{arene})]$ RuCl(picolinate ligands]Cl,⁵ (iv) $[\eta^{6}-(C_{6}H_{6})Ru$ (phenylpyridine) NCMe]PF₆,⁶ (v) $[\eta^{6}-(C_{6}H_{6})Ru(2,2'-bipyridyl)(4-vinylpyridine)]$ -(BF₄)₂⁷ and (vi) ruthenium complexes of other related heterocycle based ligands.8 Out of which only (ii) and (iii) have been explored for transfer hydrogenation. The source of ruthenium for all these half-sandwich complexes is a dimer $[(\eta^6-C_6H_6/$ p-cymene)RuCl₂]₂ which undergoes a rich variety of chemistry via intermediary chloro bridge cleavage reaction, leading to the formation of a series of interesting neutral and cationic mononuclear complexes.⁹ Half-sandwich ruthenium(II) complexes have shown in the recent past promise for applications to a variety of catalytic processes, such as asymmetric catalysis in Diels-Alder reactions,¹⁰ asymmetric transfer hydrogenation of ketones,¹¹ hydration of nitriles¹² and 1,3-dipolar cycloaddition reactions of nitrones with methacrolein.13 Our research group has reported that half-sandwich ruthenium (π) complexes of organochalcogen ligands work as efficient catalysts for transfer hydrogenation of ketones and oxidation of alcohols.¹⁴ The ligands incorporating both hard and soft

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[†]Electronic supplementary information (ESI) available: Crystal data and refinement parameters (Table S1), bond lengths and angles (Table S2), HOMO-LUMO energy gap and partial charges (Table S3), distances of non-covalent interactions (Tables S4 and S5), non-covalent interactions (Fig. S1–S9), and NMR spectra (Fig. S10–S21). CCDC 861152, 861154, 861153, 918663 and 918664 (for 1 to 5 respectively). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt00126a



donors (which sometimes may be hemilabile) are important for catalysis¹⁵ as properties of metal complexes can be finetuned by such a combination. However, there is no report on mononuclear half-sandwich ruthenium(II) complexes with (N, S/Se) and (N, S/Se, N) ligands based on pyridine skeleton. Such complexes are of further importance to understand that out of bidentate and terdentate ligands having similar donor sites, which is superior to design catalysts for transfer hydrogenation of ketones and oxidation of alcohols. Herein, we report the synthesis of complexes of η^6 -(benzene)ruthenium(II) with chalcogenated pyridine ligands (L1-L5; see Chart 1) and their single crystal structural aspects. The applications of these ruthenium(II) complexes 1-5 in catalyzing transfer hydrogenation of ketones with 2-PrOH and oxidation of alcohols with N-methylmorpholine-N-oxide (NMO) have been found promising. Bidentate (Se, N) type ligand gives complexes of better efficiency. All these results are given in the present paper. Density functional theory (DFT) calculations have been made and appear to support experimental results (both catalysis and structural aspects).

Results and discussion

The syntheses of L1–L5 and their complexes have been summarized in Scheme 1. The L1–L3 have been prepared by



Scheme 1

synthetic procedures reported earlier.¹⁶ The procedures used for synthesis of L4 and L5 are distinct from those known earlier¹⁷ and give relatively high yields, up to 95%. All the ligands stable in air and moisture show good solubility in common organic solvents *viz.*, CHCl₃, CH₂Cl₂, CH₃OH and CH₃CN. The complexes 1–5 (Yield 87–90%), have been synthesized by reacting $[(\eta^6-C_6H_6)RuCl_2]_2$ at room temperature in methanol with L1–L5 in a 1:2 molar ratio, respectively (Scheme 1). The complexes (1–5) are moderately soluble in CHCl₃, CH₂Cl₂ and CH₃OH, but their solubility is good in CH₃CN. The solutions of complexes 1–5 made in CH₃CN remain stable for several months under ambient conditions.

NMR spectra

NMR spectra of ligands L1-L5 and complexes 1-5 are consistent with their structures shown in Scheme 1 and single-crystal structures of 1-5 determined with X-ray diffraction. The signal in 77 Se{ 1 H} NMR spectrum of 2 appears shifted to a higher frequency by ~ 25 ppm in comparison to that of free L2 as Se is coordinated to Ru center. In the case of complex 5 the signal in ⁷⁷Se{¹H} NMR spectrum has been observed shifted to a lower frequency by ~32 ppm with respect to that of free L5. This may be due to its pincer type strong binding resulting shorter Ru-Se bond than that of 2 (see crystal structure below). In ¹H and ¹³C 1 H NMR spectra of 1–5 signals of protons and carbon atoms generally appear at higher frequency relative to those of free ligands which coordinate with Ru in a bidentate (N, S/Se) (1-3) or terdentate (N, S/Se, N) (4-5) mode. The magnitude of shift to higher frequency is high for $CH_2(E)$ (E = S/Se) up to 10.6 ppm in ${}^{13}C{}^{1}H$ NMR and 0.87 ppm for protons attached to them. These observations imply that there is a dispersion of electron density from ligands L1-L5 to ruthenium. In ¹H and ¹³C{¹H} NMR spectra of **1–5** the signals (singlet) of n^6 -benzene appear to be shifted to lower frequency (up to 0.3) and 3.3 ppm respectively) with respect to those of $[\eta^6-(C_6H_6)]$ RuCl₂]₂. This occurs due to substitution of Cl with S and Se, which have relatively lower electronegativity and are stronger donors.

Crystal structures

Crystals of 1-5 suitable for X-ray crystallographic diffraction were obtained by slow diffusion of diethyl ether into concentrated solutions of the complexes made in a methanol-acetonitrile mixture (1:3 v/v). The crystallographic and refinement data for 1-5 are summarized in Table S1 of ESI.[†] The L1, L2 and L3 exhibit a similar bonding mode in all complexes 1-3. The five member ring is formed by their coordination to the metal center through pyridine nitrogen and chalcogen. The L4 and L5 form two five member rings on their coordination with Ru centre, via Se/S and N donor sites of two pyridine rings. The ORTEP diagrams of cations of 1-5 are given in Fig. 1-5 with selected bond lengths and angles. In each cation of these complexes there is a pseudo-octahedral half-sandwich "pianostool" type disposition of donor atoms around Ru center. The centroid of the η^6 -benzene ring occupies the center of three octahedral sites. The nitrogen and chalcogen atoms of L1-L5

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Fig. 1 ORTEP diagram of the cation of **1** with ellipsoids at the 30% probability level. Hydrogen atoms and the PF_6^- anions have been omitted for clarity. Bond lengths (Å): Ru–S(1) 2.3771(18), Ru–N(1) 2.095(5), Ru(1)–Cl(1) 2.3876(19). Bond angles (°): S(1)–Ru(1)–N(1) 80.49(15), S(1)–Ru(1)–Cl(1) 93.39(6).



Fig. 2 ORTEP diagram of the cation of **2** with ellipsoids at the 40% probability level. Hydrogen atoms and the PF_6^- anions have been omitted for clarity. Bond lengths (Å): Ru–Se(1) 2.4879(7), Ru–N(1) 2.101(5), Ru(1)–Cl(1) 2.3955(15). Bond angles (°): Se(1)–Ru(1)–N(1) 81.49(12), Se(1)–Ru(1)–Cl(1) 92.78(4).



Fig. 3 ORTEP diagram of the cation of **3** with ellipsoids at the 50% probability level. Hydrogen atoms and the PF_6^- anions have been omitted for clarity. Bond lengths (Å): Ru–S(1) 2.3740(9), Ru–N(1) 2.096(3), Ru(1)–Cl(1) 2.3989(9). Bond angles (°): S(1)–Ru(1)–N(1) 80.82(8), S(1)–Ru(1)–Cl(1) 93.09(3).

and chlorine complete the coordination sphere. The half sandwich Ru(n)-complexes of selenoether ligands are less investigated than their sulphur analogues. The complexes of



Fig. 4 ORTEP diagram of the cation of **4** with ellipsoids at the 30% probability level. Hydrogen atoms and the PF_6^- anions have been omitted for clarity. Bond lengths (Å): Ru–S(1) 2.3133(15), Ru–N(1) 2.098(4), Ru(1)–N(2) 2.111(5). Bond angles (°): N(1)–Ru(1)–S(1) 83.02(13), N(2)–Ru(1)–S(1) 83.13(14).



Fig. 5 ORTEP diagram of the cation of **5** with ellipsoids at the 30% probability level. Hydrogen atoms and the PF_6^- anions have been omitted for clarity. Bond lengths (Å): Ru(1)–Se(1) 2.4252(9) N(1)–Ru(1) 2.123(6) N(2)–Ru(1) 2.105(5). Bond angles (°): N(1)–Ru(1)–Se(1) 83.88(16) N(2)–Ru(1)–Se(1) 83.70(15).

 $(\eta^{6}\text{-benzene})Ru(\pi)$ and $(\eta^{6}\text{-}p\text{-cymene})Ru(\pi)$ with selenated pyrrolidine/morpholine derivative have been reported by our research group recently in which Ru is coordinated through Se and N forming a five membered chelate ring.¹⁴ The 2 and 5 are new additions to the small family of Ru-selenoether complexes. The Ru-C distances in the cations of 1-5 are normal.^{14,18} The Ru-S bond lengths of 1 and 3 are within the range [2.3548(15)-2.4156(9) Å] in which such a bond length of several species has been reported.^{14,19} The Ru-Se bond length of cation of 2 [2.4879(7) Å] also falls in the range 2.4756(10)-2.5240(9) Å in which such a bond length of Ru(II)-complexes¹⁴ and Ru-Se clusters²⁰ has been reported. The Ru-S [2.3133(15) Å] and Ru–Se [2.4252(9) Å] bond lengths in complex 4 and 5 are comparatively shorter than those of 1 and 2 due to a strong pincer type bonding mode of L4 and L5. The PF₆⁻ has been found to be involved in C-H…F secondary interactions resulting in chains in complexes 1-5. In Fig. 6 and 7 these are shown for complex 2 and 5 along with the distances respectively. The secondary interactions for other complexes are shown in the ESI (Fig. S1 and S2⁺). More C–H…F distances (Å) of 1-5 are given in Table S4 (ESI⁺). The crystals of 1-3 also have C-H···Cl and C-H···π secondary interactions (For details see ESI Table S5 and Fig. S3-S8[†]).



Fig. 6 Non-covalent C–H…F interactions in 2.



Fig. 7 Non-covalent C-H····F interactions in 5.

Catalytic transfer hydrogenation

Transfer hydrogenation reactions involve transfer of hydrogen from one organic molecule to another and are very important in organic synthesis because the use of inflammable molecular hydrogen is avoided.²¹ Such catalytic reactions many times necessitate high temperature and inert atmosphere.²² Therefore catalysts working under mild conditions continue to be of current interest. Transfer hydrogenation reactions of ketones (Scheme 2) can be catalyzed with the present complexes (0.01 mol% for 1-3 and 0.1 mol% for 4-5) at a moderate temperature 80 °C. The KOH known as best inorganic base for such transformations²³ with 2-propanol as hydrogen donor has been used in the present catalytic transfer hydrogenation. The control reactions carried out in the absence of catalyst for 2-3 h result in 5-8% conversions only. The most efficient conversions (up to 98%) were found in the case of acetophenone with all the catalysts; while in the case of aliphatic ketones the conversions were up to 93%. The values of percent conversions and TONs are given in Table 1. The complex 2 is the most



efficient catalysts among the five complexes. The 77Se{1H} NMR spectra were recorded in the course of transfer hydrogenation reactions catalyzed with 2 and 5. The signals in the spectra were found shifted to higher frequency (~25 and \sim 21 ppm for 2 and 5 respectively), indicating that probably the Ru-Cl/N bond (2/5) is cleaved or weakened very significantly to make a coordination site on metal centre available so that formation of an intermediate having a Ru-H bond can take place.²⁴ The ¹H NMR spectra were also recorded during transfer hydrogenation reactions catalyzed with 2. After 1 h a broad singlet was noticed around $\delta -10.5/\delta -8.9$ ppm (2/5) which being characteristic of metal-hydrides, indicates the formation of a Ru-H bond.²⁵ Thus catalytic reactions with the present complexes probably proceed via formation of metal-hydride complex intermediate as suggested for conventional mechanism.26

The catalytic efficiency generally varies with chalcogen ligands in the order of Se > S, when other co-ligands and substituent on donor atoms are same. It may be ascribed to a stronger electron-donating tendency of Se towards the metal centre than sulfur, thus promoting the formation of hydride with it. This order of catalytic reactivity was supported by DFT calculation as HOMO-LUMO energy gap is lower for 2 than 1 and 3. When catalytic efficiencies of 1 and 2 were compared with those of 4 and 5, it was found that the complexes of bidentate ligands were better than terdentates. In case of bidentate ligands probably the easy cleavage of Ru-Cl bond facilitates the catalysis. The DFT calculations also support this reactivity order as HOMO-LUMO energy gap for 1 and 2 is lower than that of 4 and 5 (see below DFT studies). The performance of 2, best among the five present complexes has been compared with the earlier reported ruthenium(II) based homogeneous catalysts for transfer hydrogenation. The temperature used in all cases is around 80 °C. For three other parameters important to judge catalyst performance viz., catalyst loading required, conversion (%) and reaction time, the complex 2 gives a very good combination. The air-sensitive [RuR(η^6 -*p*-cymene) phosphine-anilido complexes (P, N-Ph₂PAr⁻)] (R = H, Et; Ar⁻ = o-C₆H₄NMe⁻)²⁷ for 0.01 mol% loading give less than 50% conversions even in 2 h for acetophenone which generally gives the highest conversion among ketones. The catalysis with complex of pincer ligand Ru $(SNS^{tBu})Cl_2(MeCN)$ $[SNS^{tBu} = 2,6-bis(tert-butylthiomethyl)pyri$ dine] takes shorter time but for a catalyst loading of 0.1 mol%. For a related complex Ru(SNS^{tBu})Cl₂(PPh₃), 7 h reaction time gives only 85% conversion.²⁸ Ruthenium(II) complexes bearing pyridine-based tridentate ligands and 2-(aminomethyl)pyridine show good conversions in lower reaction time^{4a} than that of complex 2 but catalyst loading required is 0.1-1.0 mol%. Several other Ru-complexes have been reported for catalysis of transfer hydrogenation but in comparison with 2 either they require higher catalyst loading or reaction time. The $[(\eta^6-arene)-$ Ru(N,N)ClCl (arene = p-cymene, C_6Me_6 ; N,N = bipyridyl with OH, OMe, or H at the 6- and 6'-positions) is reported²⁹ to give 100% conversion in 24 h and at 1 mol% catalyst loading. The Ru(II) complexes with piperidine based ligands^{4b} have been

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Table 1 Transfer hydrogenation of ketones^a

		TON (% conversion)					
Substrate	Catalyst mol%	1	2	3	4	5	
	0.01/0.1	8.9×10^3 (89)	$9.3 \times 10^3 (93)$	8.8×10^3 (88)	$9.0 imes 10^2$ (90)	9.4×10^2 (94)	
	0.01/0.1	8.8×10^3 (88)	$9.2 \times 10^3 (92)$	8.6×10^3 (86)	$8.5 \times 10^2 (85)$	9.2×10^2 (92)	
	0.01/0.1	$9.5 \times 10^3 (95)$	$9.8 \times 10^3 (98)$	$9.2 \times 10^3 (92)$	$9.4 \times 10^2 (94)$	9.8×10^2 (98)	
	0.01/0.1	$9.0 \times 10^3 (90)$	$9.6 \times 10^3 (96)$	$9.0 \times 10^3 (90)$	$9.2 \times 10^2 (92)$	$9.6 \times 10^2 (96)$	
Ph	0.01/0.1	$9.1 \times 10^3 (91)$	$9.6 \times 10^3 (96)$	$9.0 \times 10^3 (90)$	$9.2 \times 10^2 (92)$	9.6×10^2 (96)	
	0.01/0.1	9.0×10^3 (90)	9.4×10^3 (94)	8.5×10^3 (85)	8.8×10^2 (88)	$9.4 \times 10^2 (94)$	
	0.01/0.1	9.0×10^3 (90)	9.6×10^3 (96)	8.8×10^3 (88)	9.0×10^2 (90)	$9.5 \times 10^2 (95)$	
O V S	0.01/0.1	8.2×10^3 (82)	8.6×10^3 (86)	8.0×10^3 (80)	8.0×10^2 (80)	8.5×10^2 (85)	
	0.01/0.1	8.5×10^3 (85)	8.8×10^3 (88)	8.1×10^3 (81)	8.6×10^2 (86)	8.8×10^2 (88)	

^{*a*} Catalyst: 0.01 mol% for **1**, **2** and **3**; 0.1 mol% for **4** and **5**; conversion in control reactions (in absence of catalyst and under optimum conditions) 5–8%.

explored to catalyze transfer hydrogenation and for good conversions 4 h reaction time with 1 mol% catalyst loading are required. Half sandwich complexes^{14*a*} of arenes with chalcogenated Schiff bases and related ligands require lower catalyst loading but with 7 h reaction time only. [Ru(arene)-Cl(N,N)]-BPh₄ (arene = benzene, *p*-cymene, N,N = bis(pyrazol-1-yl)-methane)³⁰ can give more than 95% conversions but require a reaction time of 24 h at 0.004 mol% loading.

Oxidation of alcohols

The complexes 1-5 have been studied for the catalytic oxidation of primary and secondary alcohols with *N*-methylmorpholine-*N*-oxide (NMO). Maximum conversions were reached in 2 h with 2 and in 3 h with 1 or 3-5 (Scheme 3). However, in the absence of catalyst the conversions were low. When reactions were carried out for the time found optimum in the presence of the catalyst, the conversions noticed were <5%. The

percent conversions and TON values are given in Table 2. On the basis of earlier work³¹⁻³⁹ and some of the observations made by us, the mechanism of the catalytic oxidation appears to involve Ru^{IV}=O species that seems to be formed by oxygen free radicals (generated by heterolytic cleavage of NMO). The addition of AIBN [azobis(isobutyronitrile), a free radical initiator] to the oxidation of benzyl alcohol in the presence of 2 (most efficient catalyst) with NMO under optimized reaction conditions resulted in enhanced conversion (up to 94%). Further addition of AIBN to the same oxidation reaction in the absence of 2 did not result in any oxidation. In the presence of benzoquinone (a free-radical inhibitor) the conversion was minimal. These observations are consistent with those made by Goldstein and Drago with H2O2 and OCl in the oxidation of alkanes.³⁹ When NMO was added to the solution of 2 or 5, the signals in their ⁷⁷Se{¹H} NMR spectra were found shifted to a higher frequency (473 and 454 ppm respectively). The signal in



the $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of L2 or L5 on other hand remains unshifted on addition of NMO. This rules out that the reason of this high frequency shift as selenoxide formation. Therefore, the ruthenium center is most probably oxidized to Ru(IV). A new shoulder at 390–394 nm, which is reported $^{36-41}$ to be due to Ru IV =O species appears in the UV/Vis spectra of

1–5 on addition of NMO to their solutions made in dichloromethane. This further supports that Ru(IV) species is most probably responsible for the transfer of oxygen atom to the alcohol substrates resulting in their oxidation. IR spectra of the residues left after evaporating the solvent from the mixtures of NMO with complexes 1–5 exhibit very strong bands at 844–857 cm⁻¹. As ν_{P-F} band at 837–845 cm⁻¹ is of medium intensity only, the strong overlapping band due to the formation of Ru^{IV}=O species^{36,37,41} is probably responsible for the enhancement of intensity as well as the minor shift. Thus in present catalytic oxidation of alcohols Ru^{IV}=O species are likely to be involved. The fact that catalytic activities of Ru^{IV}=O species towards oxidation have been reported earlier^{35–39,42} further strengthens their involvement in the present case. The ¹H NMR spectra of present ruthenium

Substrate		TON (% conversion)				
	Catalyst mol%	1	2	3	4	5
ОН	0.01/0.1	$9.1 \times 10^3 (91)$	$9.4 \times 10^3 (94)$	$8.6 \times 10^3 (86)$	$9.0 \times 10^2 (90)$	$9.4 \times 10^2 (94)$
ОН	0.01/0.1	$9.2 \times 10^3 (92)$	$9.6 \times 10^3 (96)$	$8.8 \times 10^3 (88)$	$9.2 \times 10^2 (92)$	9.6×10^2 (96)
ОН	0.01/0.1	8.3×10^3 (83)	8.7×10^3 (87)	7.8×10^3 (78)	$8.5 \times 10^2 (85)$	$8.8 imes 10^2$ (88)
OH OH	0.01/0.1	$9.0 \times 10^3 (90)$	$9.3 \times 10^3 (93)$	$8.4 \times 10^3 (84)$	$9.0 \times 10^2 (90)$	$9.4 \times 10^2 (94)$
OH Ph	0.01/0.1	$9.3 \times 10^3 (93)$	$9.6 \times 10^3 (96)$	$8.8 \times 10^3 (88)$	9.2×10^2 (92)	$9.6 \times 10^2 (96)$
OH OH	0.01/0.1	$8.8 \times 10^3 (88)$	$9.1 \times 10^3 (91)$	8.0×10^3 (80)	$8.8 \times 10^2 (88)$	$9.2 \times 10^2 (92)$
ОН	0.01/0.1	9.0×10^3 (90)	9.2×10^3 (92)	$8.5 \times 10^3 (85)$	9.0×10^2 (90)	$9.4 \times 10^2 (94)$
OH OH	0.01/0.1	8.5×10^3 (85)	$8.9 \times 10^3 (89)$	$8.0 \times 10^3 (80)$	$8.2 \times 10^2 (82)$	8.9×10^2 (89)
OH OH	0.01/0.1	8.6×10^3 (86)	$9.0 imes 10^3$ (90)	8.2×10^3 (82)	8.6×10^2 (86)	9.1×10^2 (91)
ОН	0.01/0.1	9.6×10^3 (96)	9.9×10^3 (99)	9.1×10^3 (91)	$9.5 \times 10^2 (95)$	$9.9 \times 10^2 (99)$

^a Catalyst: 0.01 mol% for 1, 2 and 3; 0.1 mol% for 4 and 5; conversion in control reactions (in absence of catalyst and under optimum conditions) <5%.

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complexes recorded after the addition of NMO were found broadened, indicating the formation of paramagnetic species and supporting indirectly the involvement of Ru^{IV}=O species in the present catalytic oxidation. Like transfer hydrogenation, Se ligand containing complexes are more efficient in catalyzing oxidation than their S analogues containing similar coligands, as Se being softer than S facilitates the formation of Ru^{IV}=O species. On other hand bidentate complexes have been found more efficient than the corresponding terdentate complexes. It is probably due to facile cleavage of Ru-Cl bond, needed to form oxo species. This order has been corroborated by DFT calculation as given below. It is interesting to compare the promising ruthenium(II) based catalysts reported in literature for oxidation of alcohols with the present ones. Ruthecomplexes of tetraphenylimidodiphosphinate43 nium(II) explored for catalysis of oxidation of alcohols with NMO have carried out good conversions at 1 mol% of catalyst, while 0.01 mol% of 2 is sufficient for this purpose with a comparable reaction time. Similarly for many other ruthenium based catalysts explored for oxidation of alcohols, the catalyst loading or reaction time required for good conversion is higher than that of 2. Iodide-bridged diruthenium complexes, $[(\eta^5-2,5-R_2-3,4 Ph_2C_4COH)(CO)_2Ru-(\mu-I)-Ru(CO)_2(\eta^4-2,5-R_2-3,4-Ph_2C_4CO)]$ (R = Ph or Me)⁴⁴ when used as catalyst, 97% conversion required its 2 mol%. It is reported that 1 mol% of $[Ru(\eta^6-p-cymene)(AsPh_3)-$ (L)] [L = pyridine-2-thiocarboxamide ligand] catalyzes oxidation of alcohols with NMO resulting good conversion.45 In case of catalyst $[(\eta^6-p-cymene)RuCl(L)]$ (where L = monoanionic 2-(naphthylazo) phenolato ligands) also, catalyst loading of 1 mol% is required and that too with a reaction time of 8 h. However, 0.001 mol% of half sandwich complexes of Ru(II)¹⁴ with morpholine based ligands or Schiff bases and related

ligands is enough to catalyze conversion of alcohols to ketones. In their comparison the reaction time of present complexes is somewhat short. Thus efficiencies of 2 and 5 can be considered promising when comparison is made with Ru(II) based catalysts reported in the literature.

Density functional theory calculations

In an attempt to understand further the nature of bonding within these complexes and their reactivity the density functional theory (DFT) calculations (see Experimental for details) were performed on all complexes 1-5. The accuracy of such calculations for molecules of late transition metals is insufficient to warrant a detailed discussion of MO energy levels. However, an analysis of lowest energy configurations and frontier orbitals can provide a qualitative insight into the bonding characteristics of the complexes. The HOMOs (highest occupied molecular orbital) of all complexes are essentially identical and are positioned primarily over the metal centre and benzene ring, with some contribution towards chalcogen, nitrogen, and Cl donors (see Fig. 8). The agreement between the experimentally observed bonding parameters and the calculated one is good for Ru-E (E = S or Se), Ru-Cl, Ru-N and Ru-benzene (centroid). The calculated and experimentally found bond angles are generally consistent (Table 3). Some of the calculated bond distances and angles differ from those experimentally found but such differences are not unusual and have been reported earlier also.16,46

As mentioned earlier the absolute values for the HOMO energy levels cannot be reliably determined for complexes of heavy metals, but relative energies of the levels are quite informative. It has been reported that there is a correlation between the HOMO-LUMO energy gap of a complex and its chemical



Fig. 8 Frontier molecular orbitals of 1–5.

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Table 3 Selected bond lengths (Å) and angles (°) for **1–5** and the values calculated by DFT^a

	nd angle DFT gth value 252(9) 2.505 2.516) 2.140 05(5) 2.140 05(5) 2.158 82(1) 1.852 88(16) 83.45	70(15) 82.71 60(2) 83.98
5	DFT Bor value leny 2.429 2.4. 2.143 2.11 2.143 2.11 1.842 1.7 82.66 83.1	82.31 83.7 82.31 83.0
	Bond angle length 2.313(15) 2.098(3) 2.111(5) 1.795(1) 8.3.02(13)	83.13(14) 83.46(18)
4	Ru-E(1) Ru-N(1) Ru-N(2) Ru-C ^a E1-Ru-N1	E1-Ru-N2 N1-Ru- N2
	DFT value 2.407 2.389 2.130 1.755 80.61	92.04 84.15
3	Bond angle length 2.3740(9) 2.3989(9) 2.096(3) 1.685(1) 80.82(8)	93.09(3) 84.34(8)
	DFT value 2.502 2.394 2.140 1.758 82.02	93.51 84.48
2	Bond angle length 2.4879(7) 2.3955(15) 2.101(5) 1.687(1) 81.49(12)	92.78(4) 84.97(13)
	DFT value 2.402 2.389 2.135 1.756 81.41	93.51 84.08
1	Bond angle length 2.3771(18) 2.3876(19) 2.095(5) 1.685(1) 80.49(15)	93.39(6) 85.33(15)
	Ru-E(1) Ru-Cl(1) Ru-N(1) $Ru-C^{a}$ E1-Ru- N1	E1-Ru-Cl Cl-Ru-N1

reactivity.47 The chemical reactivity of a system is related with chemical hardness defined as the resistance to perturbation in the electron distribution in a molecule.^{47b} In terms of frontier orbitals, chemical hardness corresponds to the energy gap between the HOMO and LUMO, and is approximated by $(\varepsilon_{\text{HOMO}} - \varepsilon_{\text{LUMO}})/2$, where $\varepsilon_{\text{LUMO}}$ and $\varepsilon_{\text{HOMO}}$ are the LUMO and HOMO energies.^{47a} The large the HOMO-LUMO energy gap, makes the deformation of the electron cloud hard, which in turn results less reactivity. Its vice versa that lower the energy gap, higher the reactivity is also true, as in such a case electron cloud is easily perturbed by an external field.⁴⁷ Thus a larger gap reflects lower reactivity and vice versa. Therefore among the two catalysts, the one having low HOMO-LUMO energy gap is supposed to be better as catalyst. The HOMO-LUMO energy gaps in 1-5 differ sufficiently, lower in the case of 2/5 relative to their sulfur analogues 1 and 4 respectively (see Fig. 8, Table S3 in ESI⁺).

This indicates that reactivity of Se complexes is greater than those of the corresponding S analogues. In the assessment of bidentate vs. terdentate complexes, the HOMO-LUMO energy gaps (lower in case of bidentate, see Fig. 8, Table S3 in ESI⁺) suggest more efficiency of bidentate complexes over the terdentate ones. This is consistent with the experimentally observed order of catalytic efficiencies of complexes: Se > Sand bidentate > terdentate. The magnitude of HOMO-LUMO energy gaps is not unusual and has been reported of the same order i.e. ~4 eV for complexes of group VIII metal ions containing chalcogen donors.^{16,47a} Mulliken partial atomic charge analyses for 1-5, show that the charge on Ru center of 2/5 is greater than those of the corresponding sulfur complexes (Fig. 9, Table S3 in ESI[†]). This makes easier the formation of Ru^{IV}=O species needed in catalytic oxidation, with 2/5 in comparison to their sulfur analogues, and in turn makes them more efficient. The more charge on Ru also facilitates the formation of ruthenium hydride needed in the case of transfer hydrogenation. Thus Se containing species are expected to be more efficient for the transfer hydrogenation catalysis as well.



Fig. 9 Mulliken partial charges of 1–5.

The charges on the other atoms are given in Fig. 9 and Table S3 (ESI \dagger).

Experimental

Physical measurements

The ¹H, ¹³C{¹H}, and ⁷⁷Se{¹H} NMR spectra have been recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, and 57.24 MHz respectively and chemical shifts are reported in ppm relative to normal standards. IR spectra in the range 4000-400 cm⁻¹ were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 Series II C, H, and N analyzer. For single crystal structures the data were collected on a Bruker AXS SMART Apex CCD diffractometer using Mo Kα (0.71073 Å) radiation at 298(2) K. The software SADABS⁴⁸ was used for absorption correction (if needed) and SHELXTL for space group, structure determination, and refinements.49 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 least-squares refinement cycles on F^2 were performed until the model converged. High resolution mass spectral measurements were performed with electron spray ionization (10 eV, 180 °C source temperature, sodium formate as reference compound) on a Bruker MIcroTOF-Q II, taking sample in CH₃CN. The commercial nitrogen gas was used after passing it successively through traps containing solutions of alkaline anthraquinone, sodium dithionite, alkaline pyrogallol, concentrated H₂SO₄ and KOH pellets. Nitrogen atmosphere if required was created using Schlenk techniques. Yields refer to isolated yields of compounds which have purity $\geq 95\%$ [established by ¹H NMR]. All reactions were carried out in glassware dried in an oven, under ambient conditions except the syntheses of L1-L5 which were carried in nitrogen atmosphere.

Chemicals and reagents

Diphenyldiselenide, thiophenol, bis(2-pyridyl)disulfide, NaBH₄, (2-chloromethyl)pyridine hydrochloride and ammonium hexafluorophosphate procured from Sigma-Aldrich (USA) were used as received. The ligands **L1**, **L2**, and **L3** were synthesized as reported earlier.¹⁶ The $[(\eta^6-C_6H_6)RuCl_2]_2$ was prepared according to literature method.⁵⁰ All the solvents were dried and distilled before use by standard procedures.⁵¹ The common reagents and chemicals available locally were used.

DFT calculations

All DFT calculations were carried out at the Department of Chemistry, Supercomputing Facility for Bioinformatics and Computational Biology, IIT Delhi, using GAUSSIAN-03⁵² program with an immediate objective of identifying the reactivity in the present series of compounds. The geometry of complex **1** to **5** was optimized at the B3LYP⁵³ level using a LANL2DZ basis set for Ru atom and 6-31G* basis sets for C, N, H, Cl, and chalcogen. Geometry optimizations were carried out

without any symmetry restriction with X-ray coordinates of the molecule. Harmonic force constants were computed at the optimized geometries to characterize the stationary points as minima. The molecular orbital plots were made using the Chemcraft program package (http://www.chemcraftprog.com).

Synthesis of L4 and L5

Sulphur (0.064 g, 2 mmol)/selenium powder (0.156 g, 2 mmol) dissolved in 30 cm³ of ethanol was treated with a solution (made in 5% NaOH) of NaBH₄ (0.149 g, 4.0 mmol) (added drop wise) under nitrogen atmosphere until the reaction mixture became colorless due to the formation of Na₂Se/Na₂S. (2-Chloromethyl)pyridine hydrochloride (0.656 g, 4.0 mmol) dissolved in 5 cm³ of ethanol was mixed to this colorless solution with constant stirring The mixture was stirred further for 3–4 h and poured into 100 cm³ of ice-cold distilled water and extracted into CHCl₃ (5 × 40 cm³). The extract was washed with water (3 × 50 cm³) and dried over anhydrous sodium sulfate. Its solvent was evaporated off under reduced pressure on a rotary evaporator, resulting in L4/L5 as pale yellow oil.

L4: Yield: 0.410 g, 95%. ¹H NMR (CDCl₃, 25 °C, vs Me₄Si): δ (ppm): 3.83 (s, 4H, H_{1, 7}), 7.13–7.17 (m, 2H, H_{5, 11}), 7.36–7.38 (m, 2H, H_{3, 9}), 7.60–7.66 (m, 2H, H_{4, 10}), 8.54 (d, ³*J*_{H–H} = 4.8 Hz, 2H, H_{6, 12}). ¹³C{¹H} NMR (CDCl₃, 25 °C, vs Me₄Si): δ (ppm): 37.5 (C_{1, 7}), 121.9 (C_{5, 11}), 123.3 (C_{3, 9}), 136.7 (C_{4, 10}), 149.3 (C_{6, 12}), 158.4(C_{2, 8}). IR (KBr, cm⁻¹): 3085 (m; $\nu_{C-H (aromatic)})$, 2915 (s; $\nu_{C-H (aliphatic)})$, 1591 (m; $\nu_{C=N}$), 1421 (m; $\nu_{C=C (aromatic)})$, 752 (m; $\nu_{C-H (aromatic)})$.

L5: Yield: 0.450 g, 95%. ¹H NMR (CDCl₃, 25 °C, vs Me₄Si): δ (ppm): 3.92 (s, 4H, H_{1, 7}), 7.07–7.11 (m, 2H, H_{5, 11}), 7.29–7.31 (m, 2H, H_{3, 9}), 7.55–7.60 (m, 2H, H_{4, 10}), 8.49 (m, 2H, H_{6, 12}). ¹³C{¹H} NMR (CDCl₃, 25 °C, vs Me₄Si): δ (ppm): 28.9 (C_{1, 7}), 121.5 (C_{5, 11}), 123.1 (C_{3, 9}), 136.5 (C_{4, 10}), 149.3 (C_{6, 12}), 159.6 (C_{2, 8}). ⁷⁷Se{¹H} NMR (CDCl₃, 25 °C, vs Me₂Se): δ (ppm): 328. IR (KBr, cm⁻¹): 3083 (m; ν_{C-H} (aromatic)), 2920 (s; ν_{C-H} (aliphatic)), 1590 (m; $\nu_{C=N}$), 1421 (m; $\nu_{C=C}$ (aromatic)), 755 (m; ν_{C-H} (aromatic)).

Synthesis of complexes 1-5

The solid $[(\eta^6-C_6H_6)RuCl_2]_2$ (0.05 g, 0.1 mmol) and L1, L2, L3, L4 or L5 (0.2 mmol) dissolved in CH₃OH (15 cm³) were stirred together for 8 h at room temperature. The resulting yellow solution was filtered and the volume of the filtrate was reduced to ~7 cm³ with a rotary evaporator. The concentrate was mixed with solid NH₄PF₆ (0.032 g, 0.2 mmol) and the resulting yellow colored microcrystalline solid 1–5 was filtered, washed with ice-cold 10 cm³ CH₃OH and dried *in vacuo*. The single crystals of 1–5 were obtained by diffusion of diethyl ether into their solutions (1 cm³) made in a mixture of CH₃OH and CH₃CN (1:3).

1: Yield: 0.097 g, 87%, Anal. Calcd for $C_{18}H_{17}CINRuS \cdot [PF_6]$: C, 38.54; H, 3.05; N, 2.50. Found: C, 38.69; H, 3.03; N, 2.39. Mp 204 °C. NMR (¹H, CDCl₃, 25 °C, TMS) (δ : ppm): 4.40–4.68 (m, 2H, H₅), 5.79 (s, 6H, Ru-Ar-H), 7.27–7.64 (m, 5H, H₁₋₃), 7.78–8.08 (m, 3H, H₇₋₉), 9.46 (d, ³J_{H-H} = 5.7 Hz, 1H, H₁₀); (¹³C {¹H}, CDCl₃, 25 °C, TMS) (δ : ppm): 48.3 (C₅), 88.9 (RuAr-C), 125.0 (C₇), 126.5 (C₉), 130.0 (C₃), 130.7 (C₂), 131.3 (C₁), 135.7 (C₄), 141.4 (C₈), 158.0 (C₁₀), 161.0 (C₆). HR-MS (CH₃CN) [M]⁺ (*m/z*) = 415.9797; calculated value for C₁₈H₁₇ClNRuS = 415.9809 (δ : 3.0 ppm). IR (KBr, cm⁻¹): 3093 (m; ν _{C-H (aromatic)}), 2939 (s; ν _{C-H (aliphatic)}), 1605 (m; ν _{C=N}), 1438 (m; ν _{C=C (aromatic)}), 845 (s; ν _{P-F}), 772 (m; ν _{C-H (aromatic)}).

2: Yield: 0.109 g, 90%. Anal. Calcd for $C_{18}H_{17}ClNRuSe\cdot[PF_6]$: C, 35.57; H, 2.82; N, 2.30. Found: C, 35.59; H, 2.89; N, 2.11 Mp 196.0 °C. NMR (¹H, CDCl₃, 25 °C, TMS) (δ : ppm): 4.34–4.65 (m, 2H, H₅), 5.85 (s, 6H, RuAr-H), 7.20–7.62 (m, 5H, H₁₋₃), 7.70–8.03 (m, 3H, H₇₋₉), 9.50 (d, ³J_{H-H} = 5.7 Hz 1H, H₁₀); (¹³C{¹H}, CDCl₃, 25 °C, TMS) (δ : ppm): 41.5 (C₅), 88.4 (RuAr-C), 125.8 (C₇), 126.1 (C₉), 130.0 (C₁), 131.3 (C₂), 131.9 (C₄), 132.2 (C₃), 140.9 (C₈), 158.7 (C₁₀), 161.5 (C₆); (⁷⁷Se{¹H}, CDCl₃, 25 °C, Me₂Se) (δ : ppm): 389.8; HR-MS (CH₃CN) [M]⁺ (*m*/*z*) = 463.9246; calculated value for C₁₈H₁₇ClNRuSe = 463.9257 (δ : 2.4 ppm). IR (KBr, cm⁻¹): 3093 (m; ν_{C-H} (aromatic)), 2965 (s; ν_{C-H} (aliphatic)), 1610 (m; $\nu_{C=N}$), 1438 (m; $\nu_{C=C}$ (aromatic)), 838 (s; ν_{P-F}), 770 (m; ν_{C-H} (aromatic)).

3: Yield: 0.100 g, 90%. $C_{17}H_{16}ClN_2RuS \cdot [PF_6]$: C, 36.34; H, 2.87; N, 4.99. Found: C, 36.14; H, 2.97; N, 5.03. Mp 186 °C. NMR (¹H, CDCl₃, 25 °C, TMS) (δ : ppm): 4.60–5.20 (m, 2H, H₆), 6.10 (s, 6H, RuAr-H), 7.21–8.19 (m, 6H, H_{2–4} + H_{8–10}), 8.77–8.86 (m, 1H, H₁), 9.32 (d, ³J_{H–H} = 5.5 Hz, 1H, H₁₁); (¹³C{¹H}, CDCl₃, 25 °C, TMS) (δ : ppm): 46.4 (C₆), 88.4 (RuAr-C), 124.3 (C₄), 125.4 (C₂), 126.0 (C₈), 127.7 (₁₀), 137.5 (C₃), 140.6 (C₉), 150.9 (C₁₁), 152.4 (C₁), 157.3 (C₇), 161.8 (C₅); HR-MS (CH₃CN) [M]⁺ (*m*/*z*) = 416.9763; calculated value for C₁₇H₁₆ClN₂RuS = 416.9761 (δ : –0.4 ppm). IR (KBr, cm⁻¹): 3096 (m; ν _{C-H (aromatic)}), 2928 (s; ν _{C-H (aliphatic)}), 1608 (m; ν _{C=N}), 1444 (m; ν _{C=C (aromatic)}), 837 (s; ν _{P-F}), 766 (m; ν _{C-H (aromatic)}).

4: Yield: 0.123 g, 90%. $C_{18}H_{18}N_2RuS\cdot2[PF_6]$: C, 31.54; H, 2.65; N, 4.09. Found: C, 31.28; H, 2.87; N, 4.13. Mp 225 °C. ¹H NMR (CDCl₃, 25 °C, vs Me₄Si): δ (ppm): 3.42–4.60 (m, 4H, H₁, 7), 6.30 (s, 6H, RuAr-H), 7.39 (m, 2H, H_{5, 11}), 7.50–7.53 (m, 2H, H_{3, 9}), 7.86–7.89 (m, 2H, H_{4, 10}), 9.26 (d, ³J_{H-H} = 5.7 Hz, 2H, H₆, 12). ¹³C{¹H} NMR (CDCl₃, 25 °C, vs Me₄Si): δ (ppm): 46.9 (C_{1, 7}), 90.7 (RuAr-C), 124.5 (C_{5, 11}), 125.9 (C_{3, 9}), 140.4 (C_{4, 10}), 156.2 (C_{6, 12}), 160.5(C_{2, 8}). IR (KBr, cm⁻¹): 3095 (m; ν_{C-H} (aromatic)), 2935 (s; ν_{C-H} (aliphatic)), 1601 (m; $\nu_{C=N}$), 1430 (m; $\nu_{C=C}$ (aromatic)), 845 (s; ν_{P-F}), 761 (m; ν_{C-H} (aromatic)).

5: Yield: 0.135 g, 92% $C_{18}H_{18}N_2RuSe\cdot[PF_6]$: C, 29.52; H, 2.48; N, 3.83. Found: C, 29.84; H, 2.26; N, 3.73. Mp 210 °C. ¹H NMR (CDCl₃, 25 °C, vs Me₄Si): δ (ppm): 3.31–4.51 (m, 4H, H_{1, 7}), 6.30 (s, 6H, RuAr-H), 7.34–7.39 (m, 2H, H_{5, 11}), 7.50–7.53 (m, 2H, H_{3, 9}), 7.85–7.90 (m, 2H, H_{4, 10}), 9.37 (d, ³J_{H-H} = 5.4 Hz, 2H, H_{6, 12}). ¹³C{¹H} NMR (CDCl₃, 25 °C, vs Me₄Si): δ (ppm): 38.6 (C_{1, 7}), 89.5 (RuAr-C), 125.0 (C_{5, 11}), 125.3 (C_{3, 9}), 139.7 (C_{4, 10}), 156.7 (C_{6, 12}), 161.4 (C_{2, 8}). ⁷⁷Se{¹H} NMR (CDCl₃, 25 °C, vs Me₂Se): δ (ppm): 295.1 IR (KBr, cm⁻¹): 3098 (m; ν_{C-H} (aromatic)), 2945 (s; ν_{C-H} (aliphatic)), 1604 (m; $\nu_{C=N}$), 1438 (m; $\nu_{C=C}$ (aromatic)), 839 (s; ν_{P-F}), 767 (m; ν_{C-H} (aromatic)).

Procedure for catalytic transfer hydrogenation of ketones

A solution of a ketone (1 mmol) made in 2-propanol (15 cm³), KOH (2 cm³ of a 0.2 M solution in 2-propanol), and a complex from 1 to 5 (0.01 mol% in case of 1-3 and 0.1 mol% for 4-5

dissolved in CH₃CN) were mixed and refluxed (80 °C) for appropriate time (2 h for 2 and 3 h for others). The reaction was followed by ¹H NMR spectroscopy. After completion of the reaction, the reaction mixture was cooled at room-temperature, 2-propanol was removed on a rotary evaporator and resulting semi-solid was extracted with diethyl ether ($3 \times 20 \text{ cm}^3$). The extract was passed through a short column (~8 cm in length) of silica gel. The column was washed with ~50 cm³ of diethyl ether. All the eluates from the column were mixed and solvent from the mixture was evaporated off on a rotary evaporator. The resulting residue was subjected to the ¹H NMR. The final conversions are reported as an average of two runs of each catalytic reaction.

Procedure for catalytic oxidation of alcohols

A typical reaction for catalytic oxidation of primary alcohols to corresponding aldehydes and secondary ones to ketones with N-methylmorpholine-N-oxide (NMO) and complex 1, 2, 3, 4, or 5 is as follows. A solution of a complex among 1, 2, 3 (0.01 mol %) 4, and 5 (0.1 mol%) in 20 cm³ of CH_2Cl_2 was mixed with neat alcohol substrate (1 mmol) and solid NMO (3 mmol). The mixture was refluxed for 2 h with 2 and 3 h for remaining four complexes. The reaction was followed by ¹H NMR spectroscopy. On completion of reaction the reaction mixture was cooled at room-temperature and its solvent was evaporated off using a rotary evaporator. The residue having an oxidized product was extracted with 20 cm³ of petroleum ether. The complex-catalyst undissolved in petroleum ether was recovered almost quantitatively for the next catalytic cycle. The oxidized product present in petroleum ether was analyzed by the ¹H NMR spectra.

Conclusions

Five half-sandwich "piano-stool" ruthenium(π) complexes, [(η^6 - C_6H_6 Ru(L)Cl [PF₆] (1-5) with bi and terdentate chalcogenated pyridine ligands (L = L1-L5), have been synthesized and characterized by multinuclei NMR, HR-MS and X-ray crystallography. These half-sandwich complexes of ruthenium(II) have been explored for transfer hydrogenation of ketones at moderate temperature of 80 °C and oxidation of alcohols. The TON values are promising, up to 9.9×10^3 for transfer hydrogenation reactions of ketones, and 9.8×10^3 for oxidation of alcohols. Air and moisture stability of these complexes are their additional advantages. The catalytic activities follow the orders: Ru-Se donor complexes > Ru-S donor complexes and bidentate > terdentate, which are corroborated by DFT calculations. The catalytic transfer hydrogenation with the present complexes probably proceeds via formation of rutheniumhydride as an intermediate. The Ru^{IV}=O species appears to be involved in the oxidation. The comparison of required catalyst loading for good conversions and reaction time for 1-5 with those reported in literature for other transfer hydrogenation/ oxidation catalysts, suggests that the present complexes have good promise. Generally there is a reasonably good matching between experimentally determined bond distances/angles and those calculated by DFT. The difference between them is noticed in some cases but is not unusual.

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