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(η^6-Benzene)Ru(II) half-sandwich complexes of pyrazolated chalcogenoethers for catalytic activation of aldehydes to amides transformation

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ABSTRACT

The reaction of $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ with chalcogenoether substituted 1*H*-pyrazole ligands (**L1**-**L3**) in methanol have yielded three novel Ru(II) half-sandwich complexes $[(\eta^6\text{-}C_6H_6)RuCl(\mathbf{L})]PF_6$ (**1**–**3**) in high yield under the ambient reaction conditions. The NMR, MS and FT-IR analytical techniques were used to identify their structures. The molecular structures of the complexes **2** and **3** were established with X-ray crystallographic analysis and revealed a pseudo-octahedral half sandwich piano-stool geometry around ruthenium in each complex. Complexes **1**–**3** are thermally robust and were found to be insensitive towards the air and moisture. All the complexes were found to be catalytically active and produced the excellent yields of amides (up to 95%) from corresponding aldehydes. In contrast to the previous reported catalytic systems for aldehyde to amide transformation, the present complexes **1**–**3** are very efficient and have several advantages in terms of low catalyst loading, reaction time, temperature and wide applicability for various substituted aldehydes. Owing to the stronger σ-donor coordination properties of selenium containing ligands, the complex **2** was found to be more efficient as compare to the sulphur and tellurium analogues.

1. Introduction

Amides are amongst the most important organic compounds which have been extensively explored as synthetic building blocks in various organic transformations [1–3]. The presence of amide functional group [4–9] is a key chemical connection in nitrogen containing biologically active compounds [10], various commercially available pharmaceutical drugs [11–13], and polymers [14,15], show as immense prevalence of amide bond formation in synthetic chemistry. Classically, amides are synthesized by a stoichiometric reaction of carboxylic acid or its derivatives (halides, esters or anhydrides) with amines [16]. The spontaneous formation of the amides is not possible through unifying these two functional groups at ambient temperature, because the essential water elimination step takes place at very high temperature (≥200 °C) [17]. The formation of undesired products and low atom economy in such process restrict their employability in industrial applications. Hence, the development of advance atom-efficient catalytic methods for amide formation are highly desired in modern synthetic chemistry [18,19]. In this context, several metal-catalyzed approaches for amide synthesis have been developed [20]. Many of transition metals including scandium [21], nickel [22], copper [23–25], zinc [26], and palladium [27] based catalysts have been reported for the catalytic transformations of aldehydes [24,25,27–30] or oximes [22,23,28] into corresponding amides. Alumina-supported rhodium [31,32], titanosilicates loaded with rhodium [33], and $[Ir(Cp^*)Cl_2]_2$ [34] have been found to be potential candidates for amide synthesis. However, the prime requisite of an inert atmosphere to handle the air-sensitive metal catalysts and harsh reaction conditions are some of the major disadvantages of these protocols. Moreover, some functional groups do not withstand under such severe ambience and the selectivity of the desire product decreases. Also, the high catalyst loading and stoichiometric amount of additional reagents produce the significant quantity of undesired products. Crabtree and co-workers has developed a ruthenium complex of terpyridine based NNN type pincer ligand which efficiently carry out an additives free one-pot conversion of amides from aldehydes [35]. The prime goal of present work is to develop an elegant and more efficient method for

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one-pot synthesis of amide from aldehyde which can effectively reduced the formation of hazardous wastage and use of detrimental additive reagents. The present ruthenium catalysts are economically better as compare to the reported Rh/Ir/Pd metals based catalysts for amide transformatios. The half sandwich ruthenium(II) complex of tridentate N-heterocycles based organochalcogen ligands had shown promising catalytic activity in various catalytic reactions such as asymmetric catalysis and hydration of nitrile [36,37], transfer hydrogenation of ketones and oxidation of alcohols [38,39]. The promising catalytic potential of various metal complexes of pyrozole containing ligands has been already proven explicitly in various earlier reports [40–48]. The strong donor properties of chalcogen ligands make them suitable candidates for catalysis of organic transformations [49–56]. Apart from efficiency, organochalcogen based catalytic systems are quite attractive due to their insensitivity towards the air and moisture, good solubility in various organic solvents and high stability in organic solutions. The catalytic strength of metal complexes of organochalcogen ligands for this particular transformation has not been investigated so far. Also, to the best in our knowledge, we are the first to report the ruthenium complexes of pyrazole-based organochalcogen ligands. Therefore, moving towards the ligand chemistry and application potential of N-heterocycles containing chalcogenated ligands, we have synthesized three new and novel mononuclear Ru(II) half-sandwich complexes of pyrazole based organochalcogen ligands and investigated their catalytic potential for aldehyde to amide transformations. The comparative study of the catalytic efficiency of these three complexes has been also investigated. Moreover, the present catalytic systems do not require any hazardous additives, and convert the aldehydes into corresponding amides in good to excellent amounts under aerobic reaction conditions.

2. Results and discussion

The systematic methodology adopted for the synthesis of Ru(II) complexes (**1**–**3**) is illustrated in Scheme 1. The previously reported methods [46,57] were used to prepare the pyrazole based thio/seleno/telluro-ether functionalized bidentate ligands (**L1-L3**). Three new half-sandwich (η^6-benzene)ruthenium(II) complexes (**1**–**3**) were synthesized by reacting $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ with a methanolic solution of **L1**/**L2**/**L3** under ambient reaction conditions. All the complexes were characterized by using the NMR, MS, and FT-IR techniques. The NMR and mass spectra of complexes **1**–**3** have been provided in Supplementary data (Figs. S1–S9) which were found to be consistent with their molecular structures illustrated in Scheme 1.

Due to the low solubility of **1**–**3** in $CDCl_3$, their NMR spectra were recorded in CD_3CN. As compared to the corresponding free ligands [46,57], the deshielded NMR signals appeared in ^1H and $^{13}C\{^1H\}$ spectra of **1**–**3** at 0.9 ppm and 8.6 ppm, respectively, corroborating the coordination of ligand with Ru(II) in a bidentate chelate mode. The four methylene protons (each H_5 and H_6 group) of $-N-CH_2-CH_2-E-$ part of chelate ring were recorded as four multiplets in ^1H NMR spectra of complexe **1**–**3**, which confirmed their diastereotopic nature which arised due to the rigid conformation of the coordinated ligand and inherent chirality associated with the asymmetric molecular structure of each of the three Ru complexes. Moreover, in $^{13}C\{^1H\}$ NMR spectra, signals of C_9, C_6 and C_5 were found more deshielded relative to those of other carbon atoms of the complex. The protons attached to these carbons also appeared somewhat more deshielded than other protons present in the complexes. The high magnitude of shift for these carbon atoms and proton is probably due to their closeness to the chalcogen donor atoms (N and S/Se/Te). Additionally, ^1H and $^{13}C\{^1H\}$ NMR of each of the complexes **1**–**3** show a typical resonance (most intense signal) for six protons and carbons of η^6-benzene in the range of 5.59–5.90 ppm and 86.2–87.3 ppm, respectively which is in close agreement with the earlier reported half-sandwich ruthenium complex of η^6-benzene [58]. The intense mass peaks at (m/z) 496.9025, 544.8474 and 624.8472 appeared in mass spectra of **1**, **2** and **3**, respectively, are attributable to $[M-PF_6]^+$ cations in each of the three complexes.

2.1. Crystal structures

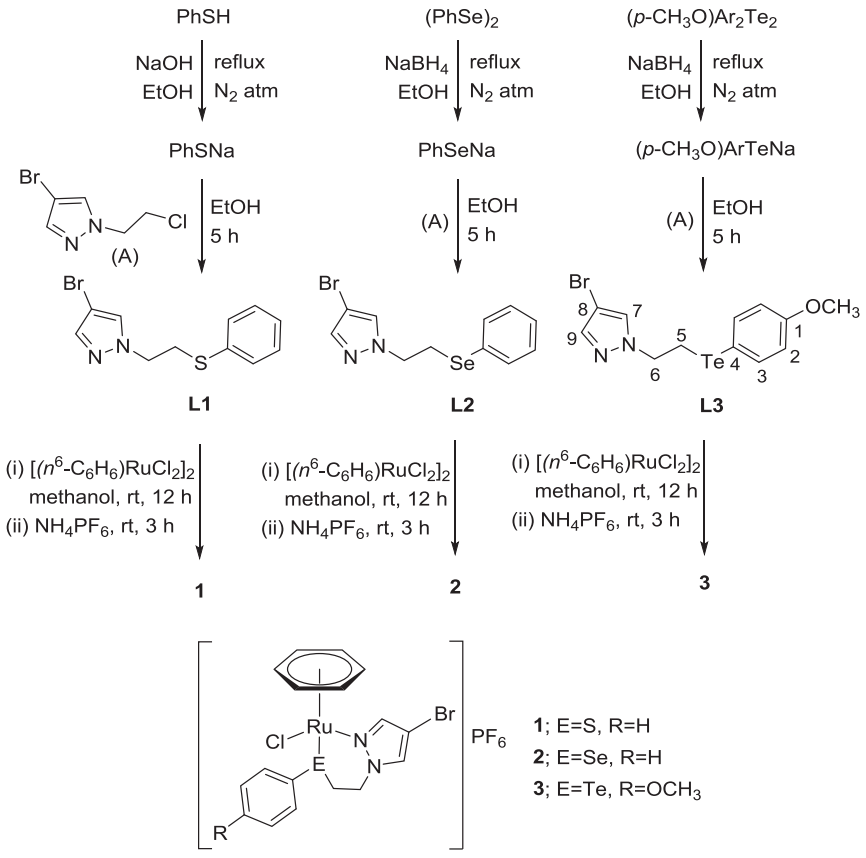
The solubility of complexes **1**–**3** was found to be good in acetonitrile, DMF and DMSO, while close to negligible in dichloromethane, chloroform and methanol, and completely insoluble in diethyl ether and *n*-hexane. The suitable quality single crystals of complexes **2** and **3** were grown by slow evaporation of their saturated solution in acetonitrile/methanol (1:1) and subjected to analysis through single crystal X-ray crystallography. The thermal ellipsoid diagrams of **2** and **3** are depicted in Figs. 1 and 2 with some selected bond lengths and bond angles. Additional parameters are provided in Table 1. The bidentate coordination of ligand through N of pyrazole ring and Se/Te with Ru results in the formation of a six membered chelate ring in each case. In the cation of each complex, Ru adopts a pseudo-octahedral half-sandwich "pianostool" geometry. The observed bond lengths for Ru–Se and Ru–Te bonds in **2** and **3**, are 2.511 Å and 2.648 Å, respectively, which fall in the range of previously reported ruthenium complexes [38,59].

2.2. Evaluation of the catalytic potential of Ru(II) complexes (*1*–*3*) for amide synthesis

Previously, the half-sandwich Ru(II) complexes have been found to be promising candidates for the catalysis of various organic transformations including conversion of aldehyde to amides which were traditionally achieved by the reaction of carboxylic acid or its derivatives (anhydrides, esters or halides) with amines at high temperature [16,17]. In this context, metal-based homogeneous [20–25] as well as heterogeneous [31–33] catalysts have been developed. Most of the methods suffer from several disadvantages like requirement of inert atmosphere, high catalyst loading, a stoichiometric amount of additional reagents, harsh reaction conditions which are detrimental to the integrity of substrate. Therefore, for the employment of the strong σ-donor properties of soft chalcogen donor sites of N-heterocycles based organochalcogen ligands, insensitivity of their metal complexes towards the air and moisture, the catalytic strength of present Ru(II) complexes (**1**–**3**) was explored for catalytic conversion of aryl aldehydes to corresponding amides (Scheme 2).

All three complexes were found to be highly efficient at the 0.1 mol% loading of catalyst at 100 °C temperature under the aerobic conditions. Moreover, the present catalytic reaction does not demand any hazardous additives and produce the amides in good to excellent yields without generating any by-products. For the optimizations of reaction parameters, initially, the benzaldehyde was chosen as a model substrate and a series of the reactions using the ruthenium complexes **1**, **2** and **3** as catalyst were performed (Table 2).

The maximum conversion of aldehyde to amides was obtained with the use of 0.1 mol% amount of the catalyst, while below to 0.1 mol%, the yield of the desired product was significantly reduced. Moreover, the continuous increase in mol% of the catalyst (0.1–0.5) does not help in further improvement of yield of the desire product. Furthermore, during the solvent optimization, the highest yield of product was obtained in toluene (Table 2, Entry 1). The desired product was also produced when solvents including the THF, acetonitrile and 1,4-dioxane were used (Table 2, Entry 2–4), but



Scheme 1. Synthesis of half-sandwich (η^6-benzene)ruthenium(II) complexes **1**–**3**.

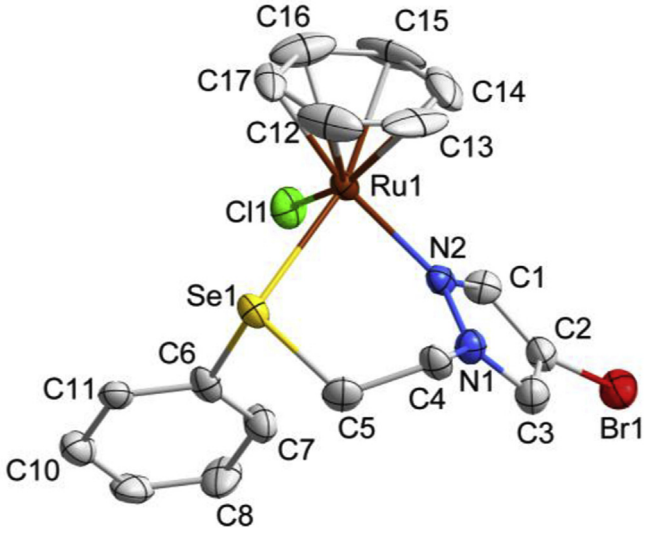


Fig. 1. The molecular structure of **2** with thermal ellipsoids set at the 30% probability level. H atoms and PF_6 counter anion are omitted for clarity. Bond lengths (Å): Ru(1)–N(2) 2.105(11), Ru(1)–Se(1) 2.5106(17); Bond angles (°): N(2)–Ru(1)–Se(1) 87.0(3), Se(1)–Ru(1)–Cl(1) 91.59(11).

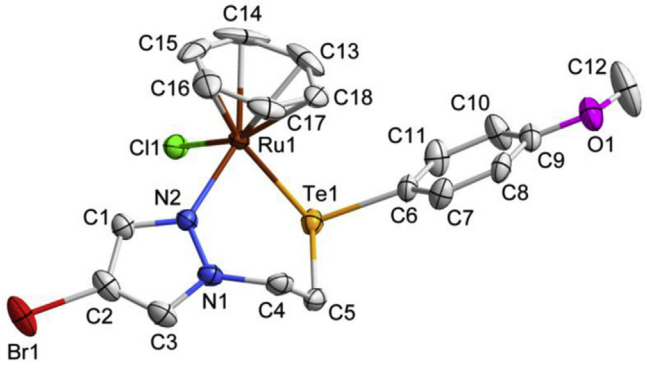


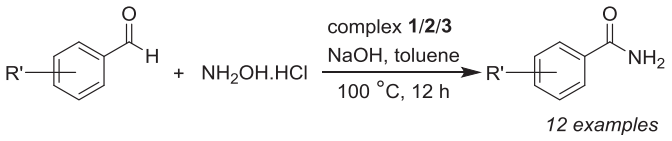
Fig. 2. The molecular structure of **3** with thermal ellipsoids set at the 30% probability level. H atoms and PF_6 counter anion are omitted for clarity. Bond lengths (Å): Ru(1)–N(2) 2.105(5), Ru(1)–Te(1) 2.6486(10); Bond angles (°): N(2)–Ru(1)–Te(1) 86.0(17), Te(1)–Ru(1)–Cl(1) 81.6(6).

yield of the desire product was substantially reduced. Water and DMF were also checked as solvent but the reaction was not initiated and failed to produce the desire product (Table 2, Entry 4–5). The effect of various bases was also investigated, the highest yield (95%) of benzamide was obtained with NaOH (Table 2, Entry 1). Other bases including the $NaHCO_3$, KOH, K_2CO_3 and Cs_2CO_3 afforded relatively low yield of desired product 80%, 40%, 50% and 10%, respectively (Table 2, Entries 7–10). It was also noticed that the reaction did not produce desired product in the absence of base (Table 2, Entry 11). Hence, careful selection of the base is a prime requisite for the present transformation reaction. Furthermore, the highest yield of the amide was obtained at 95–100 °C temperature. The drastic changes in the yield were observed when temperature was reduced to 80 °C (Yield 17%, Table 2, entry 13), and further lowering the temperature of the reaction failed to bring the desired transformations (Table 2, entry 14).

Fig. 3 shown at below, represents the time profile of catalytic reaction of model sustrate producing benzamide under optimized

Table 1
Crystal data and structural refinement parameters for **2** and **3**.

Compound	Complex 2	Complex 3
Empirical formula	$C_{17}H_{17}BrClN_2RuSe.\ PF_6$	$C_{18}H_{19}BrClN_2ORuTe.\ PF_6$
Formula Wt.	689.68	768.34
Crystal size [mm]	0.31 × 0.25 × 0.21	0.29 × 0.28 × 0.22
Crystal system	Triclinic	Monoclinic
Space group	P1	$P2_1/n$
Unit cell dimension	$a = 7.583(2)$Å	$a = 10.808(4)$Å
	$b = 7.862(2)$Å	$b = 10.070(4)$Å
	$c = 9.861(3)$Å	$c = 22.907(9)$Å
	$\alpha = 102.363(5)^\circ$	$\alpha = 90.00^\circ$
	$\beta = 101.494(5)^\circ$	$\beta = 98.559(7)^\circ$
	$\gamma = 91.189(5)^\circ$	$\gamma = 90.00^\circ$
Cell volume [Å^3]	561.5(3)	2465.6(17)
Z	1	4
Density (Calc.) [Mg·m^{-3}]	2.040	2.070
Absorption coeff. [mm^{-1}]	4.344	3.649
$F(000)$	332	1464
θ Range [°]	3.030–24.998	2.21–25.14
Index ranges	$-8 \le h \le 9$	$-12 \le h \le 12$
	$-9 \le k \le 9$	$-11 \le k \le 11$
	$-11 \le l \le 11$	$-27 \le l \le 27$
Reflections collected	5359	19039
Independent reflections ($R_{int.}$)	3964 (0.0319)	4064(0.1195)
Max./Min. transmission	0.405/0.247	0.451/0.331
Data/Restraints/Parameters	3874/0/271	4064/0/290
Goodness-of-Fit on F^2	1.003	1.017
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0525$, w$R_2 = 0.1044$	$R_1 = 0.0524$, w$R_2 = 0.1185$
R Indices (All Data)	$R_1 = 0.0601$, w$R_2 = 0.1083$	$R_1 = 0.0833$, w$R_2 = 0.1331$
Largest diff. peak/Hole [e.Å^{-3}]	0.786/−0.621	1.134/−1.485



Scheme 2. Aldehyde to amide transformation catalyzed with **1**–**3**.

Table 2
Optimization of base, solvent and temperature for aldehyde to amide transformation.

Entry	Base	Solvent	Temp. (℃)	Yield[a] (%)
1	NaOH	toluene	100	95
2	NaOH	THF	100	83
3	NaOH	acetonitrile	100	45
4	NaOH	1,4-dioxane	100	25
5	NaOH	water	100	nd
6	NaOH	DMF	100	nd
7	$NaHCO_3$	toluene	100	80
8	KOH	toluene	100	40
9	K_2CO_3	toluene	100	50
10	Cs_2CO_3	toluene	100	10
11	Base free	toluene	100	nd
12	K^{t}OBu	toluene	100	nd
13	NaOH	toluene	80	17
14	NaOH	toluene	rt	nd

Aldehyde (1.0 mmol, 0.106 g), $NH_2OH.HCl$ (1.0 mmol, 0.064 g), catalyst **2** (0.1 mol%), base (1.0 mmol), solvent (5 ml), time (12 h), nd (not detected), [a] isolated yields after purification.

rection conditions. The initial formation of the desired compound was detected after 4 h in the reaction. The continuous increase in the yield was observed with time and after 12 h the yield of the reaction was found to be constant (95%).

In order to check the wide scope of the reaction, various functionally different aldehydes were used under the optimized reaction conditions and reaction was completely generalized (Table 3). One pot methodology for the synthesis of the primary amides from

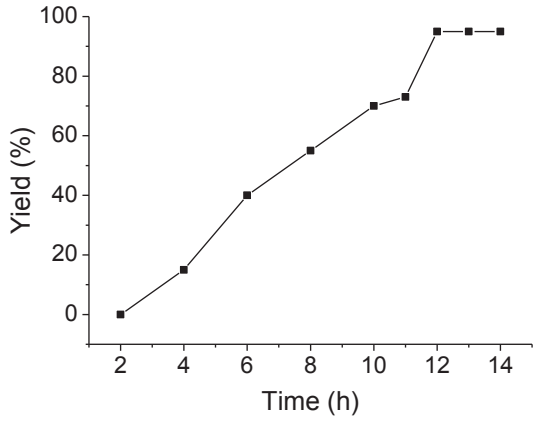
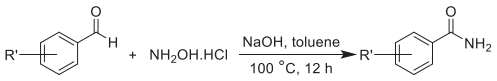


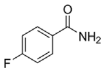
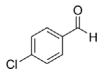
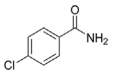
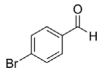
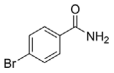
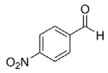
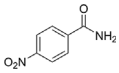
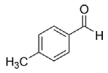
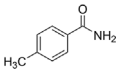
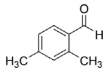
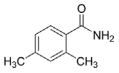
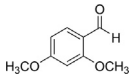
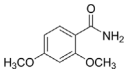
Fig. 3. Time profile of the synthesis of benzamide using complex **2** as catalyst.

various aldehydes was developed by using the Ru(II) complexes (**1**–**3**). It seems that the substituent present on the aromatic ring of benzaldehyde do not affect the formation of product. However, some minor differences in the product's yields were observed.

The catalytic activity of **1**, **2** and **3** was found to be in order of **2** (Se) > **1** (S) > **3** (Te). Such variations are arised due to the difference in the σ-donor properties of S/Se/Te as the other donor sites (N of pyrazole moiety of **L1**-**L3)** are common in all the three complexes. A similar trend of catalytic activity for Pd complexes of S/Se/Te donor analogues ligands towards the C–C coupling reaction has also been reported by Singh and co-workers [60]. An another Pd(II) complex with Te ligand [61] has also been reported which had shown much lower catalytic efficiency than the S/Se analogues [62,63]. The high catalytic activity of the selenium based ligand over the sulphur analogue for transfer hydrogenation has also been established through the experimental as well as the theortical calculations by Singh and co-workers [64]. The catalytic studies on the Se based

Table 3
Aldehyde to amide transformations using **1**, **2** and **3** as catalyst.



Entry	Substrate	Product	Yield[a] (%)		
			1	2	3
1			83	95	56
2			80	89	50
3			86	91	47
4			84	94	59
5			80	93	58
6			85	90	48
7			82	88	45
8			82	85	42
9			81	94	42
10			89	92	41
11			86	94	47
12			84	91	35

Reaction Conditions: Aldehyde (1.0 mmol), $NH_2OH.HCl$ (1.0 mmol), catalyst (0.1 mol %), NaOH (1.0 mmol), toulene (5 ml), time (12 h), temperature (100 °C), [a] Isolated Yield.

systems [63,65,66] have been indicated the excellent reactivity of selenium towards catalytic reactions [63] and sometimes, Se based systems had shown their outperformance to the phosphine based analogue [67]. The lower catalytic activity of present Te containg Ru complex is probably due to the steric effect of large size of Te which causes a lesser electronic charge density accumulation over central metal atom [60].

Based on the available literature evidences for such metal catalyzed reactions [31,68,69], the proposed plausible mechanistic pathway for the present ruthenium catalyzed transformation of aldehyde to amide is depicted in Fig. 4. Here, it is assumed that, the OH group of aldoxime which is generated in situ from the reaction of aldehyde and hydroxyl amine hydrochloride in the presence of base [35], gets coordinated to the ruthenium(II) catalyst (**1**/**2**/**3**) to form (η^6-C_6H_6)Ru(**L**)(−O−N=CHR′) species **I** together with the elimination of HCl (step 1). In the next step, species **I** eliminates the nitrile and resulted the intermediate (**II**) [(η^6-C_6H_6)Ru(**L**)(OH)] [70]. The simultaneous nucleophilic attack of nitrile over the coordinated hydroxide resulted a ruthenium iminolate species (**III**) in step 3 [31,68]. Under the similar reaction conditions, the formation of benzamide was also noted when benzonitrile was directly used as a substrate with Ru catalyst (**2**). This experiment further strengthen and confirmed the reaction proceed through a nitrile intermediate. Finally, in the step 4, the hydrolysis of the ruthenium iminolate species (**III**) leads to regeneration of the catalyst with concomitant formation of the final product.

2.3. Comparison of catalytic efficiency of present Ru catalysts (1–3) with previously reported catalytic systems for aldehyde to amide transformations

The catalytic transformation of aldehydes to amides with the present Ru(II) complexes **1**/**2**/**3** is quite efficient in terms of catalyst loading, reaction time, reaction temperature and use of additives in comparison to reported metal-based catalysts for amide synthesis [22,34,70,71]. The first metal catalyzed transformation of aldoximes to amides was carried out in xylene at high temperature (138 °C) with high catalyst loading of nickel acetate (5.6 mol%). Moreover, the formation of by-products was also observed during the catalytic process [22]. The iridium catalyst [$Ir(Cp^*)Cl_2]_2$ [34] has also been used for the amide synthesis with a higher catalyst loading (2.5 mol %). Williams and co-workers [70] have also reported a Ru catalyst that catalyzed the rearrangement of aldoximes to amides, but *p*-toluenesulfonic acid as an additive was used, and a considerable amount of nitrile was also obtained with amides. Crabtree and co-workers reported the ruthenium catalyst based on NNN pincer ligand [terpyRu(PPh_3)Cl_2], which was found to be effective in the catalysis of aldehyde to amide transformation in 17 h. The maximum yields were observed when an additive $NaHCO_3$ was used with 1.0 mol% of catalyst loading. Moreover, a η^6-arene-ruthenium(II) complex [$RuCl_2$(η^6-C_6Me_6){$P(NMe_2)_3$}] has also been established [71] as an effective catalyst for aldoxime to primary amides in water at 100 °C with high catalyst loading (5 mol%). The present ruthenium half-sandwich complexes (**1**–**3**) show the 95% amide formation in 12 h with 0.1 mol% of Ru catalyst under the aerobic reaction conditions, therefore, can be considered highly effective in the catalysis of aldehyde to amide transformation.

3. Conclusions

Three new Ru(II) half-sandwich complexes have been synthesized in high yield by reacting pyrazole-based chalcogenoethers with [(η^6-C_6H_6)$RuCl(\mu$-$Cl)]_2$ in methanol under ambient reaction conditions and authenticated with ^1H, $^{13}C\{^1H\}$ NMR, mass and FT-IR analytical techniques. Single crystal X-ray diffraction analysis of **2** and **3** revealed pseudo-octahedral half sandwich piano-stool geometry at Ru metal centre in both the complexes. The complexes **1**–**3** have been found efficient, thermally robust and moisture/air insensitive catalysts for the transformation of aldehyde to primary amide in high yield (95%). Complex **2**, consisting the selenium ligand has been found more efficient than their sulphur and tellurium analogues.

4. Experimental section

4.1. Physical measurement

The NMR spectra were recorded on a JEOL ECS-400 spectrometer operating at 400 MHz and 101 MHz for ^1H and ^{13}C nuclei, respectively. FT-IR spectra were recorded on a Perkin-Elmer 10.4.00

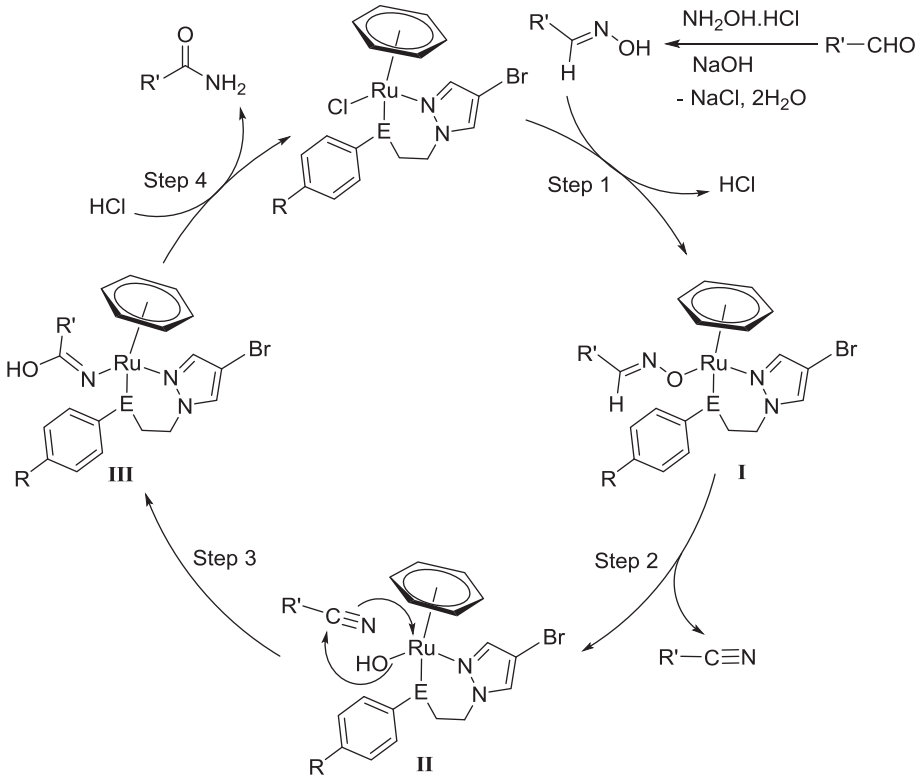


Fig. 4. A plausible mechanism for aldehyde to amide transformation catalyzed with **1**/**2**/**3**. PF_6 Counter anion is omitted for clarity in each step.

FT-IR spectrometer within the range 4000–400 cm^{-1} using KBr pellets of the sample. High-Resolution Electron Impact Mass Spectra (HR-EIMS) were obtained with Xevo G2-S Q-Tof (Waters, USA). The diffraction data on a single crystal of **2** and **3** were collected on a Bruker AXS SMART Apex CCD Diffractometer using Mo-Kα (0.71073 Å) radiation at 298(2) K. The software SADABS [72] was used for absorption correction (if needed) and SHELXTL for space group, structure determination, and refinements. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized position with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached. The least-square refinement cycle on F^2 was performed until the model converged. The melting point of solid compounds were determined in an open capillary and reported as such. The yields given are referred to isolated yields of compounds which have purity ≥95%.

4.2. Chemicals and reagents

4-Bromopyrazole, phenyl diselenide, thiophenol, sodium borohydride, ruthenium chloride, ammonium hexafluorophosphate were procured from Sigma-Aldrich (USA), and used as received. Bis(4-methoxyphenyl) ditelluride, **L1**, **L2** and **L3** were prepared by previously reported methods [46,47]. Prior to their use, all the solvents were dried and distilled by standard procedures [73]. The common chemicals and reagents which are available commercially within the country were used as received.

4.3. Synthesis of complexes [(η^6-C_6H_6)Ru(L1/L2/L3)Cl].PF_6 (1–3)

Brick red solid [Ru(η^6-C_6H_6)Cl_2]$_2$ (0.050 g, 0.1 mmol) was added to a solution of **L1** (0.057 g, 0.2 mmol)/**L2** (0.066 g, 0.2 mmol)/**L3** (0.082 g, 0.2 mmol) made in 25 mL of methanol, and the reaction mixture was stirred for 12 h at ambient temperature. The resulting reaction mixture was filtered, and the volume of the filtrate was reduced to 5 mL at rotary evaporator. It was mixed with solid NH_4PF_6 (0.032 g, 0.2 mmol) and further stirred at rt for 3h. The resulting precipitated solid was filtered, washed with 5 mL of ice-cold methanol, and dried in vacuo. Single crystals of complexes **2** and **3** were obtained by slow evaporation of solution made in methanol.

1. Yellow solid, Yield: 0.096 g, 75%. mp: 195 °C. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 8.08 (s, 1H, H_9), 7.89 (s, 1H, H_7), 7.63–7.46 (m, 5H, $H_{1\text{-}3}$), 5.92 (s, 6H, η^6-$C_6\underline{H}_6$), 4.83–4.78 (m, 1H, H_6), 4.46–4.35 (m, 1H, H_6), 3.45–3.42 (m, 1H, H_5), 2.98–2.92 (m, 1H, H_5). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ (ppm): 148.5 (C_9), 136.7 (C_7), 130.8 (C_3), 130.6 (C_2), 129.7 (C_1), 125.9 (C_4), 93.7 (C_8), 86.2 (η^6-$\underline{C}_6H_6$), 49.9 (C_6), 34.5 (C_5). HR-MS (CH_3CN) [M−PF_6]$^+$ (*m/z*) Found: 496.9025; Calc. value for [$C_{17}H_{17}BrClN_2RuS$]$^+$: 496.9028. FT-IR (KBr, ν_{max}/cm^{-1}): 3093 (m, $\nu_{C-H\ aromatic}$), 2926 (m, $\nu_{C-H\ aliphatic}$), 1579 (m, $\nu_{C=N\ aromatic}$), 1440 (s, $\nu_{C=C\ aromatic}$), 1303 (m, $\nu_{C-N\ aliphatic}$), 823 (s, $\nu_{C-H\ aromatic,\ bending}$).

2. Yellow solid, Yield: 0.099 g, 72%. mp: 190 °C. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 8.08 (s, 1H, H_9), 7.90 (s, 1H, H_7), 7.79–7.76 (m, 2H, H_3), 7.62–7.60 (m, 3H, H_1 and H_2), 5.59 (s, 6H, η^6-$C_6\underline{H}_6$), 5.11–5.05 (m, 1H, H_6), 4.57–4.51 (m, 1H, H_6), 3.34–3.29 (m, 1H, H_5), 3.02–2.95 (m, 1H, H_5). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ (ppm): 148.3 (C_9), 136.8 (C_7), 132.2 (C_3), 130.8 (C_2), 129.1 (C_1), 124.8 (C_4), 93.8 (C_8), 87.3 (η^6-$\underline{C}_6H_6$), 52.0 (C_6), 29.0 (C_5). HR-MS (CH_3CN) [M−PF_6]$^+$ (*m/z*) Found: 544.8474; Calc. value for [$C_{17}H_{17}BrClN_2RuSe$]$^+$: 544.8472. FT-IR (KBr, ν_{max}/cm^{-1}): 3098 (m, $\nu_{C-H\ aromatic}$), 2958 (m, $\nu_{C-H\ aliphatic}$), 1574 (m, $\nu_{C=N\ aromatic}$), 1437 (s, $\nu_{C=C\ aromatic}$), 1299 (m, $\nu_{C-N\ aliphatic}$), 834 (s, $\nu_{C-H\ aromatic,\ bending}$).

3. Yellow solid, Yield: 0.114 g, 74%. mp: 193 °C. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 8.10 (s, 1H, H_9), 7.89 (s, 1H, H_7), 7.72 (d, $^3J_{H-H}$ = 6.6 Hz, 2H, H_3), 7.12 (d, $^3J_{H-H}$ = 6.7 Hz, 2H, H_2), 5.60 (s, 6H,

η^6-$C_6\underline{H}_6$), 5.33–5.29 (m, 1H, H_6), 4.53–4.46 (m, 1H, H_6), 3.85 (s, 3H, $OC\underline{H}_3$), 3.03–2.99 (m, 1H, H_5), 2.92–2.85 (m, 1H, H_5). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN) δ (ppm): 161.9 (C_4), 148.2 (C_9), 136.0 (C_3), 128.4 (C_7), 116.5 (C_2), 103.1 (C_1), 93.5 (C_8), 87.3 (η^6-$\underline{C}_6H_6$), 55.4 ($O\underline{C}H_3$), 53.2 (C_6), 13.0 (C_5). HR-MS (CH_3CN) $[M-PF_6]^+$ (m/z) Found: 624.8472; Calc. value for $[C_{18}H_{19}BrClN_2ORuTe]^+$: 624.8475. FT-IR (KBr, ν_{max}/cm^{-1}): 3087 (m, $\nu_{C-H\ aromatic}$), 2958 (m, $\nu_{C-H\ aliphatic}$), 1580 (m, $\nu_{C=N\ aromatic}$), 1491 (s, $\nu_{C=C\ aromatic}$), 1297 (m, $\nu_{C-N\ aliphatic}$), 822 (s, $\nu_{C-H\ aromatic\ (bending)}$).

4.4. Procedure for the catalytic reaction

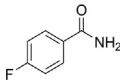
In an oven-dried 100 mL two-neck round bottom flask, a mixture of aryl-aldehyde (1.0 mmol), $NH_2OH.HCl$ (1.0 mmol), NaOH (1.0 mmol), catalyst (0.1 mol%) and solvent (5 ml) were heated at 100 °C with continuous stirring for 12 h in air. The progress of the reaction was continuously monitored by TLC until the maximum conversion of an aldehyde to the desired product observed. After completion, the reaction mixture was cooled to room temperature and extracted in ethyl acetate (2 × 25 mL). This extract was further washed with water and dried over anhydrous Na_2SO_4. The product was purified by column chromatography after removing the solvent on a rotary evaporator under reduced pressure. All the desired product obtained as white solid was authenticated by HR-MS, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy.

^1H and ^{13}C NMR of aldehyde to amides conversion products (Table 3, Entries 1–12).

1. Benzamide [27]

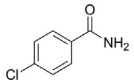
White solid, ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84–7.81 (m, 2H), 7.55–7.51 (m, 1H), 7.46–7.43 (m, 2H), 6.31 (br s, 2H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 169.68, 133.32, 131.95, 128.58, 127.29.

2. 4-Fluorobenzamide [27]



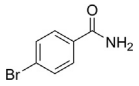
White Solid, ^1H NMR (400 MHz, $CDCl_3$) δ 7.78–7.72 (m, 2H), 6.95–6.88 (m, 2H), 6.39 (br s, 1H), 4.11 (br s, 1H).^{13}C NMR (101 MHz, $CDCl_3$+DMSO-d_6) δ 168.39, 165.82, 163.31, 129.95 (d, J = 8.9 Hz), 129.59, 115.18, 114.97.

3. 4-Chlorobenzamide [27]



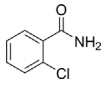
White solid, ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (d, $^3J_{H-H}$ = 8.6 Hz, 2H), 7.99 (d, 8.6 Hz, 2H), 6.13 (br s, 1H), 5.83 (br s, 1H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$+DMSO-d_6) δ (ppm): 167.01, 149.30, 139.22, 128.68, 123.22.

4. 4-Bromobenzamide [27]



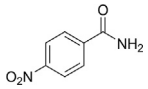
White solid, ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, 2H, $^3J_{H-H}$ = 8.5 Hz), 7.60 (d, 2H, $^3J_{H-H}$ = 8.5 Hz), 6.02 (br s, 1H), 5.81 (br s, 1H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$+DMSO-d_6) δ (ppm) 166.94, 133.40, 131.26, 129.62, 125.04.

5. 2-Chlorobenzamide [27]



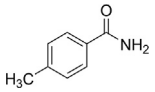
White solid, ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (dd, 1H, $^3J_{H-H}$ = 7.5 Hz, 1.6 Hz), 7.46–7.32 (m, 3H), 6.41 (br s, 2H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 168.24, 133.76, 131.78, 130.77, 130.59, 130.36, 127.12.

6. 4-Nitrobenzamide [34]



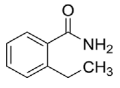
White solid, ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84–7.75 (m, 2H), 7.53–7.43 (m, 2H), 6.03 (br s, 2H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$+DMSO-d_6) δ (ppm): 168.12, 137.42, 131.87, 128.84, 128.24.

7. 4-Methylbenzamide [27]



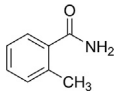
White solid, ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.42 (br s, 1H), 4.19 (br s, 1H), 2.27 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$+DMSO-d_6) δ 169.60, 142.25, 129.92, 128.88, 127.40, 21.22.

8. 2-Ethylbenzamide [74]



^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 7.8, 1.9 Hz, 1H), 7.88 (br s, 1H), 7.40 (ddd, J = 8.4, 7.4, 1.9 Hz, 1H), 7.05–6.977 (m, 2H), 6.90 (d, J = 8.2 Hz, 1H), 4.12 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.83, 157.47, 133.43, 132.39, 121.05, 120.77, 112.39, 64.76, 14.87.

9. 2-Methylbenzamide [75]



White solid, ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (d, 1H $^3J_{H-H}$ = 7.6 Hz), 7.35–7.32 (m, 1H), 7.25–7.19 (m, 2H), 6.20 (br s, 1H), 5.85 (br s, 1H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 172.19, 136.28, 135.15, 131.17, 130.24, 126.91, 125.70, 19.95.

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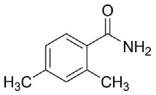
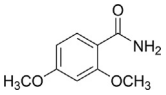
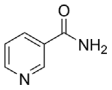
(*continued*)

10. 2,4-Dimethylbenzamide [76] 	White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (d, 1H, $^{3}J_{H-H} = 7.7$ Hz), 7.05 (s, 1H), 7.02 (d, 1H, $^{3}J_{H-H} = 7.8$ Hz), 5.95 (br s, 1H), 5.79 (br s, 1H), 2.47 (s, 3H), 2.34 (s, 3H).^{13}C{^{1}H NMR (101 MHz, $CDCl_3$) δ (ppm): 172.02, 140.51, 136.55, 132.05, 127.14, 126.33, 125.71, 21.23, 20.06.
11. 2,4-Dimethoxybenzamide [77] 	White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, 1H, $^{3}J_{H-H} = 8.8$ Hz), 7.55 (br s, 1H), 6.51 (dd, 1H, $^{3}J_{H-H} = 8.8$ Hz, 2.3 Hz), 6.41 (d, 1H, $^{3}J_{H-H} = 2.2$ Hz 6.25 (br s, 1H), 3.85 (s, 3H), 3.77 (s, 3H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 167.03, 163.72, 159.12, 134.03, 113.70, 105.14, 98.41, 55.78, 55.43.
12. Nicotinamide [34] 	^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6) δ 9.02 (s, 1H), 8.64–8.63 (m, 1H), 8.13 (dt, J = 7.9, 1.8 Hz, 1H), 7.37 (br s, 1H), 7.32–7.28 (m, 1H), 6.36 (br s, 1H).^{13}C NMR (101 MHz, $CDCl_3$+ DMSO-d_6) δ 167.69, 152.24, 148.86, 135.57, 129.46, 123.34.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.09.019.

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