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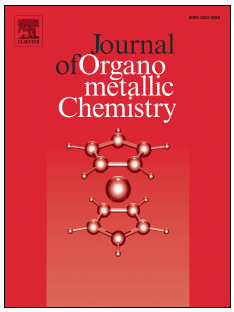

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(η^6-Benzene)Ru(II) half-sandwich complexes of pyrazolated chalcogenoethers for catalytic activation of aldehydes to amides transformation

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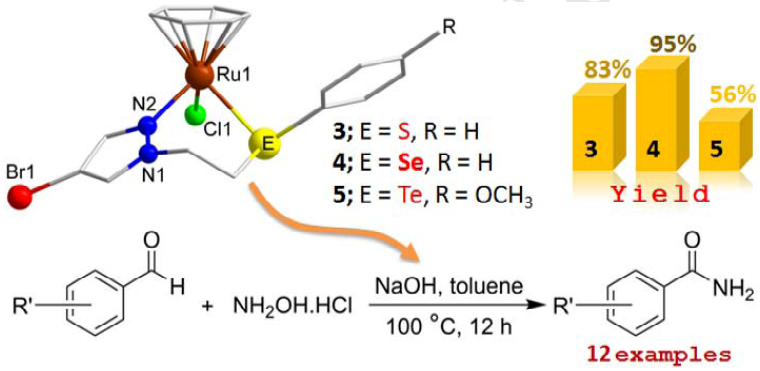
Keywords: Thioether • selenoether • telluroether • half-sandwich complexes • aldehyde to amide transformation

TOC Graphic



ABSTRACT

The reactions of $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ with chalcogenoether substituted 1*H*-pyrazole ligands (**L1**-**L3**) in methanol has endowed 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 spectral techniques were used to acquaint with their structures. The molecular structures of the complexes **2** and **3** was established with X-ray crystallographic analysis and revealing a pseudo-octahedral half sandwich piano-stool geometry around ruthenium in each case. Complexes **1-3** are thermally robust and found insensitive towards the air and moisture. All the complexes were found catalytically active and produce the excellent conversion of aldehyde to amide (up to 95%). In contrast to previously reported complexes, complexes **1-3** have several advantages in term of catalyst loading, time of reaction, temperature and optimum reaction conditions. Owing to the stronger soft donor properties of the selenium, the complex **2** was found to be more efficient than the sulphur and tellurium analogues.

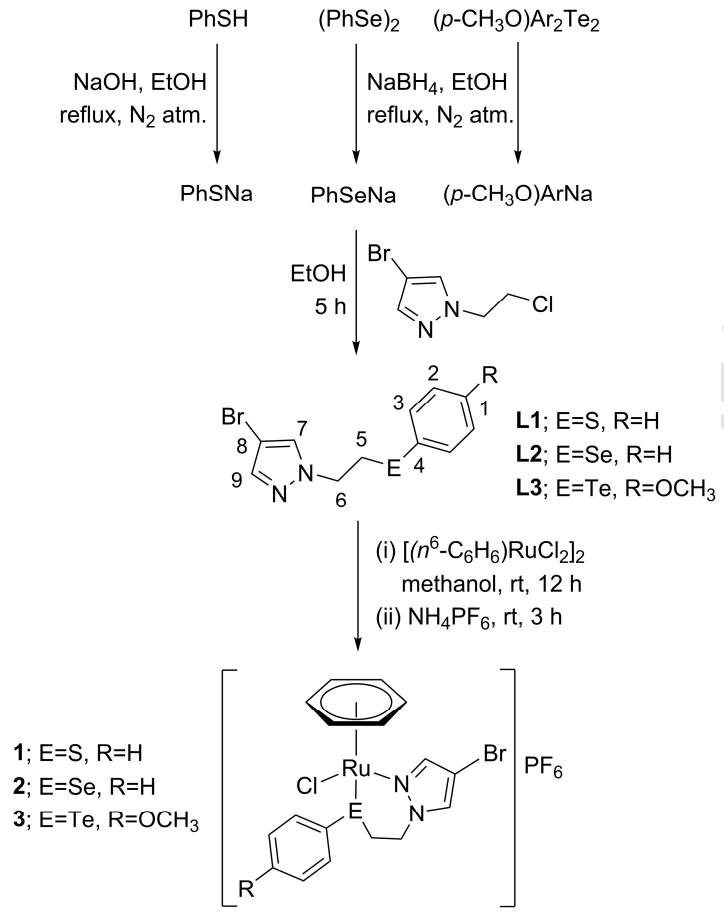
1. Introduction

Amides are amongst the most important organic compounds which have been extensively explored as synthetic modules in various organic transformations [1-3]. The presence of amide functional group [4-9] as a key chemical connection in nitrogen containing biologically active compounds [10], various commercially available pharmaceutical drugs [11-13], and polymers [14, 15], shows the immense prevalence of amide bond formation in synthetic chemistry. Classically, amides are synsthesized by the stoichiometric reaction of carboxyilic acids and derivatives (halides, esters or anhydrides) with amines [16]. The spontaneous formation of amide is not possible through unifying these two functional groups at ambient temperature, the essential water elimination requires high temperature ≥200 °C [17]. The formation of undesired products and low atom economy in such process curtails their employability in industrial applications. Hence, the development of advanced atom-efficient catalytic methods for amide formation becomes desirable in modern synthetic chemistry [18, 19]. In this context, several metal-catalysed approaches have been developed for amide bond formation [20]. Many transition metals including the 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 promising candidates for amide synthesis. However, the requirement of an inert atmosphere to handle the air-sensitive metal catalysts and harsh reaction conditions which are typically detrimental to the integrity of the substrates are some of the major disadvantages of these protocols. Moreover, some functional groups do not withstand under such severe ambiance and the selectivity of the desired product decreases. In addition, high catalyst loading and stoichiometric amount of additional reagents, produces the significant quantity of undesired products. Crabtree and co-workers developed a ruthenium complex of terpyridine based NNN type pincer ligand that could efficiently catalyzed the one-pot conversion of aldehydes into amides without the use of additives [35]. The prime goal of current work is the development of an elegant and more efficient method for the one-pot synthesis of amide from aldehyde which can effectively reduced the formation of hazardous wastage. Moreover, the present ruthenium based catalysts are less expensive as compare to the reported methods in which very precious Rh/Ir/Pd metals based catalytic systems were used. The half sandwich ruthenium(II) complex of terdentate 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 potential of various metal complexes of pyrozole containing ligands has been already proven in various earlier reports [40-48]. The strong donor properties of chalcogen donor sites present within the organochalocogen ligands make the resulting complexes suitable catalysts [49-56]. Apart from efficiency, organochalcogen ligand based catalytic systems are attractive due to their insensitivity to air and moisture, solubility in various organic solvents and stability in solution. The catalytic strength of metal complexes of organochalcogen ligands for this particular transformation is not investigated yet. Also, to the best in our knowledge, we are the first to report the ruthenium complex of pyrazole based organochalcogen ligands. Therefore, moving towards the ligand chemistry and application of N-heterocycles based chalcogenated ligands and keeping all these facts in mind, we have synthesised three new and novel mononuclear Ru(II) complexes of pyrazole based organochalcogen ligand and investigated them for catalytic transformation of aldehyde to amide. The comparative study of the catalytic efficiency of these three complexes is investigated for the one-pot synthesis of primary amides from a wide range of aryl aldehydes in the presence of $NH_2OH.HCl$ and a base. Present catalytic system does not require any hazardous additives and convert aldehyde into amides in good to excellent yield under the aerobic reaction conditions without forming any by-products.

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 methanolic solution of **L1**/**L2**/**L3** under ambient reaction conditions. The characterization techniques such as NMR, MS, and FT-IR were used to determine the structures of newly synthesized complexes **1-3**. The NMR and mass spectra of complexes **1-3** are provided in Supplementary data (Figures S1-S9) which were found consistent with their molecular structures illustrated in Scheme 1.



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

Due to the inadequate solubility of **1**-**3** in $CDCl_3$, their NMR spectra were recorded in CD_3CN. The signals in ^1H and $^{13}C\{^1H\}$ spectra of **1**-**3** appeared deshielded up to 0.9 ppm and 8.6 ppm, respectively, with relative to those of corresponding free ligands [46, 57], corraborating the coordination of ligand with Ru(II) in a bidentate chelate mode. 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 the fact that they are very close to donor sites (N and S/Se/Te). Additionally, ^1H and $^{13}C\{^1H\}$ NMR of each of the complexes **1**-**3** how 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, and match with the earlier reported half-sanwich ruthenium complex of η^6-benzene [58]. In mass spectra of **1**, **2** and **3**, the intense peak at (*m*/*z*) 496.9025, 544.8474 and 624.8472 appeared respectively, is attributable to $[M-PF_6]^+$.

Crystal structures

The 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 analyse through single crystal X-ray crystallography. The thermal ellipsoid diagrams of **2** and **3** are depicted in figures 1 and 2 with some selected bond length and bond angles, while the details parameters are provides in Table S1 of SI. The bidentate coordination of ligand through N of pyrazol ring and Se/Te with Ru results the formation of a six membered chelate ring. In the cation of each complex, Ru adopt a pseudo-octahedral half-sandwich "pianostool" geometry. The distances for Ru-Se and Ru-Te bonds in **2** and **3**, was obtained at 2.511 Å and 2.648 Å, respectively, and fall in the range of previously reported ruthenium complexes [38, 59].

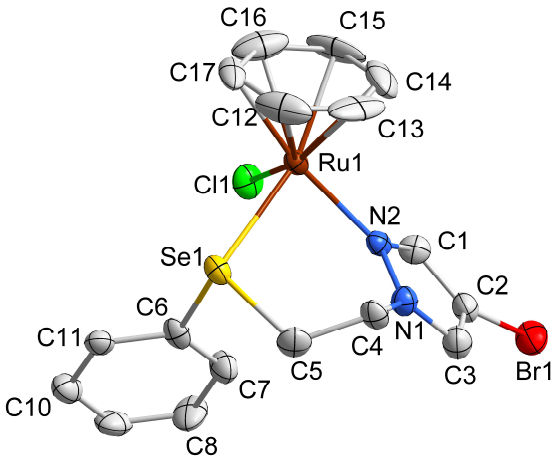


Fig. 1. Molecular structure of **2** with thermal ellipsoids set at the 30% probability level. H atoms and PF_6 counter anion are omitted for clarity. Bond lengths (Å): Ru(1)–N(2) 2.105(11), Ru(1)–Se(1) 2.5106(17); Bond angles (°): N(2)–Ru(1)–Se(1) 87.0(3), Se(1)–Ru(1)–Cl(1) 91.59(11).

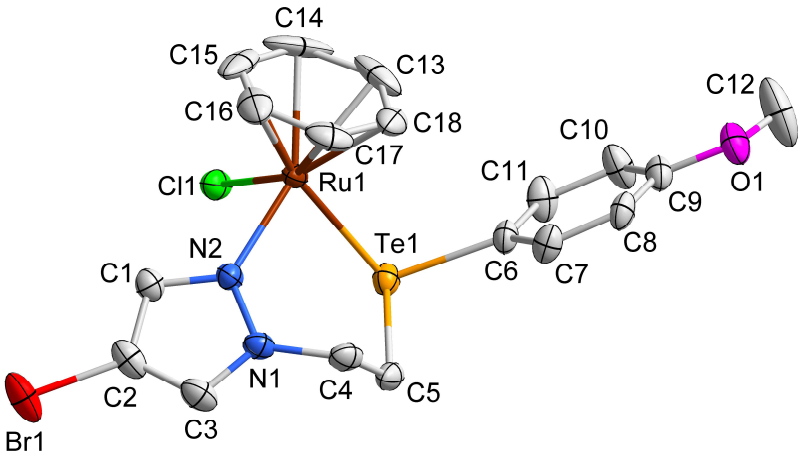


Fig. 2. Molecular structure of **3** with thermal ellipsoids set at the 30% probability level. H atoms and PF_6 counter anion are omitted for clarity. Bond lengths (Å): Ru(1)–N(2) 2.105(5), Ru(1)–Te(1) 2.6486(10); Bond angles (°): N(2)–Ru(1)–Te(1) 86.0(17), Te(1)–Ru(1)–Cl(1) 81.6(6).

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	*P* 1	*P* 2(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
	α = 102.363(5)°	α = 90.00°
	β = 101.494(5)°	β = 98.559(7)°
	γ = 91.189(5)°	γ = 90.00°
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	$-8 \leq h \leq 9$	$-12 \leq h \leq 12$
	$-9 \leq k \leq 9$	$-11 \leq k \leq 11$
	$-11 \leq l \leq 11$	$-27 \leq l \leq 27$
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	R_1 = 0.0525,	R_1 = 0.0524,
[$I > 2\sigma(I)$]	wR_2 = 0.1044	wR_2 = 0.1185
R Indices (All Data)	R_1 = 0.0601,	R_1 = 0.0833,
	wR_2 = 0.1083	wR_2 = 0.1331
Largest Diff. Peak/Hole [e.Å^{-3}]	0.786/–0.621	1.134/–1.485

Evaluation of catalytic potential of Ru(II) complexes (1-3) for aldehyde to amide transformation

Previously, the half-sandwich Ru(II) complexes have been found to be promising candidates in the catalysis of various organic transformations including conversion of aldehyde into amides which was traditionally achieved by the reaction of carboxylic acid or its derivatives *i.e.* 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 conditions, high catalyst loading, stoichiometric amount of additional reagents and harsh reaction conditions, those are not advisable for the substrate's integrity. Therefore, for the employment of the attractive soft donor properties of chalcogen donor sites of N-heterocycles based organochalcogen ligands, insensitivity of their metal complexes to air and moisture, the catalytic strength of present Ru(II) complexes (**1**-**3**) were explored for catalytic conversion of a series of aryl aldehydes into corresponding amides. All three complexes were found highly efficient at 0.1 mol% of catalyst loading at 100 °C temperature in inert free conditions. Moreover, the current reaction does not demand any hazardous additives and produced the amides in good to excellent yield without generating any by-products. For the optimization of reaction parameters, initially, benzaldehyde was chosen as model substrate and a series of the reactions using the ruthenium complexes **1**, **2** and **3** as catalyst was performed (Table 2).

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

Entry	Base	Solvent	Temp. (˚C)	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^tOBu	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.

For maximum conversion of aldehyde to amides, 0.1 mol% amount of the catalyst was found suitable. Below 0.1 mol%, the yield of the desired product was significantly reduced, while a continuously increasing the mol% from 0.1 to 0.5 does not bring any significant change in yield of product. Further, during the solvent optimization, the highest yield of product was obtained in toluene (Table 2, Entry 1), the THF, acetonitrile and 1,4-dioxane also produced the desire product (Table 2, Entry 2-4), but yield is drastically reduced. Water and DMF were also checked as solvent but the reaction was not initiated and failed to produce the desire products (Table 2, Entry 4-5). The effect of various bases was also investigated and 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 lower yields 80%, 40%, 50% and 10%, respectively (Table 2, Entries 7-10). It was also observed that reaction did not produce any

product in the absence of base (Table 2, Entry 11), hence, careful selection of the base is a prime requisite to initiate the present catalytic transformation. Furthermore, the highest yield of the amide was obtained in between 95-100 ˚C temperature, while drastic changes in the yield were observed when temperature was reduced at 80 ˚C (Yield 17%, Table 2, entry 13), and furthermore lowering the temperature of the reaction failed to bring the desired transformations (Table 2, entry 14)

Below, the Figure 3 shows the reaction time profile of representative reactions for the synthesis of benzamide under optimized rection conditions. The initial formation of the desired product 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 reaction was found to be constant (95%).

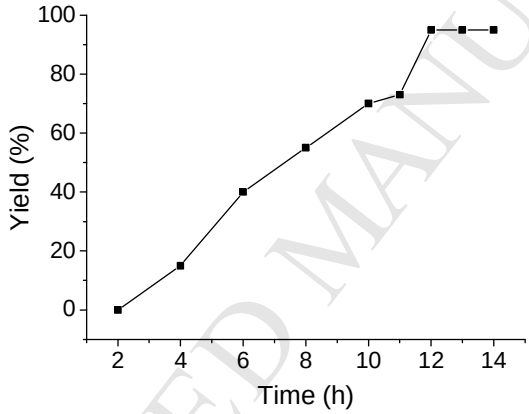
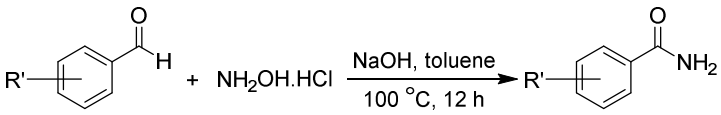


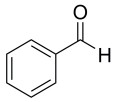
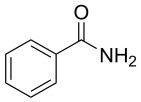
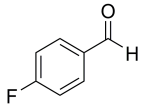
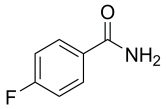
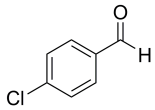
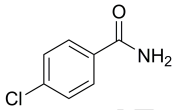
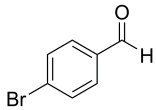
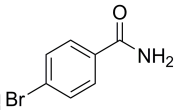
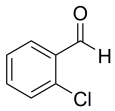
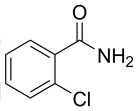
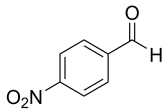
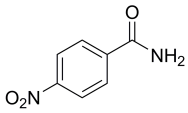
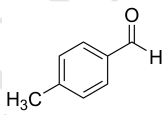
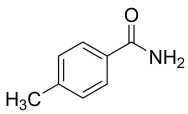
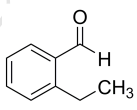
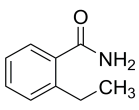
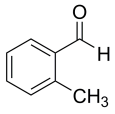
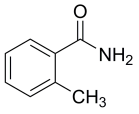
Fig. 3. Time profile of the synthesis of benzamide using complex **2** as catalyst.

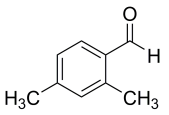
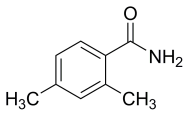
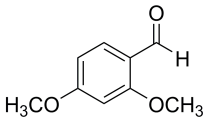
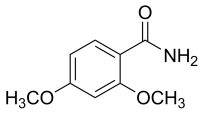
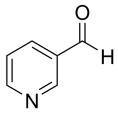
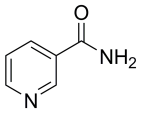
In order to check the wide scope of the reaction, various functionally different aldehydes were used under the optimized reaction conditions and reaction was completely generalized (Table 3). One pot methodology for the synthesis of the primary amides from various aldehydes was developed by using the 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 products yield were observed. The catalytic activity of **1**, **2** and **3** was found in order of **2** > **1** > **3**. The variation observed in catalytic efficiency with chalcogen ligands (**L1**-**L3**) may be arises due to the difference in the donor properties of S/Se/Te as the other donor site *i.e.*, N of pyrazole moiety is common in the three complexes. It was found that the catalytic activity of **2** is best among the three complexes. Moreover, similar trend of catalytic activity (Se > S) of

the previously reported[40] Ru(II) complexes was found for transfer hydrogenation of ketones and oxidation of alcohols.

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.

The plausible reaction mechanistic for present ruthenium catalyzed transformation of aldehyde into amide, based on the previous reports on such metal catalyzed reactions [31, 60, 61], is depicted in figure 4. Most probably, the active catalytic species (**I**) is generated *in situ* from the catalyst in presence of NaOH. Thereafter, the aldoxime which is produced by the reaction [35] of aldehyde and hydroxyl amine hydrochloride in the presence of base), gets coordinated to Ru(II) catalyst through OH group (**1**/**2**/**3**) to form (η^6-C_6H_6)Ru(**L**)(−O−N=CHR) species (**II**) together with the elimination of a water molecule (step 1). In the next step, species **II** eliminates (η^6-C_6H_6)Ru(**L**)(OH) species (**I**) to give nitrile intermediate [62] which probably again binds to the metal centre of **I** with the simultaneous nucleophilic attack of coordinated hydroxide on the nitrile to form a ruthenium iminolate species (**III**) in the step 3 [31, 60]. 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.

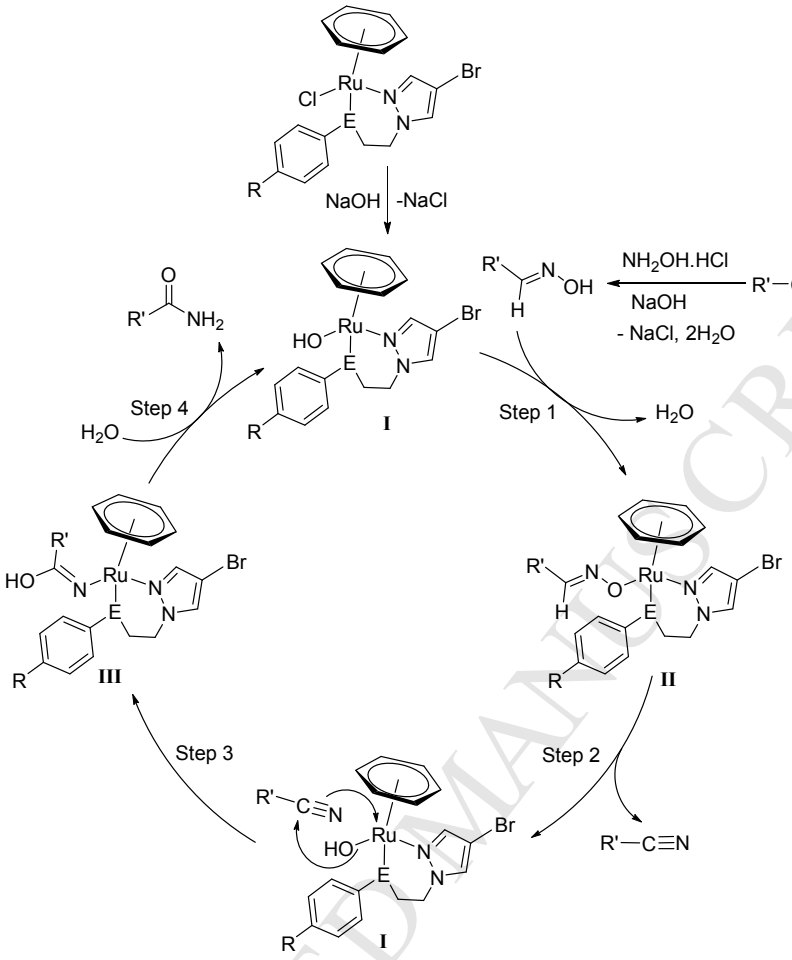


Fig. 4. Plausible mechanism for aldehyde to amide transformation catalyzed with **1**/**2**/**3**. PF_6 Counter anion is omitted for clarity in each step.

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, 63, 64]. The first metal catalyzed transformation of aldoximes to amides was carried out in xylene at high temperature (138 °C) and high catalyst loading (5.6 mol% nickel acetate), moreover, it also associated formation of by-products [22]. The iridium catalyst $[Ir(Cp^*)Cl_2]_2$ [34] has been used for the amide synthesis but required loading is again high (2.5 mol %). Furthermore, the reaction temperature needed was 111 °C, more than the present catalysis by **1/2/3**. Williams and co-

workers [63] have reported a Ru catalyst that efficiently catalyzed the rearrangement of aldoximes to amides but this system also requires *p*-toluenesulfonic acid as additives and formed amide with considerable amount of nitrile. Crabtree and co-workers reported ruthenium catalyst based on NNN pincer ligand [terpyRu(PPh_3)Cl_2], however, it was found very effective for aldehyde to amide conversion in good yields with using $NaHCO_3$ as additive at 1.0 mol% loading, but long reaction time (17 h) is again a drawback. An η^6-arene-ruthenium(II) complex [$RuCl_2$(η^6-C_6Me_6){$P(NMe_2)_3$}] has also been established as an effective catalyst for aldoxime to primary amides in water at 100 °C but high catalyst loading of 5 mol% put this catalyst on inferior side with respect to those **1**/**2**/**3** [64]. Thus, the present ruthenium half-sandwich complexes (**1**-**3**) may be labeled as efficient catalyst for aldehyde to amide transformation as the yields were up to 95% in 12 h under aerobic reaction conditions.

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(μ-Cl)]$_2$ in methanol under ambient reaction conditions and authenticated with ^{1}H, ^{13}C{^{1}H} NMR, mass and FT-IR spectroscopic 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 transformation of aldehyde to primary amide in high yield (95%) in 12 h, with 0.1 mol% catalyst loading and 100 °C reaction temperature. Complex **2**, consisting the selenium ligand has been found more efficient than their sulphur and tellurium analogues.

4. Experimental section

Physical measurement. The NMR spectra were recorded on a JEOL ECS-400 spectrometer operating at 400 MHz and 101 MHz for ^{1}H and ^{13}C nuclei, respectively. FT-IR spectra were recorded on a Perkin-Elmer 10.4.00 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 [65] was used for absorption correction (if

needed) and SHELXTL for space group, structure determination, and refinements. All nonhydrogen 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 solids were determined in an open capillary and reported as such. The yields given are refered as isolated yields of compounds which have purity ≥95%.

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 use, all the solvents were dried and distilled by standard procedures [66]. The common chemicals and reagents which were available commercially within the country were used as received.

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, $\nu_{C–H\ aromatic,\ bending}$).

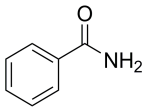
3. Yellow solid, Yield: 0.114 g, 74%. mp: 193 °C. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 8.10 (s, 1H, H_9), 7.89 (s, 1H, H_7), 7.72 (d, $^{3}J_{H–H}$ = 6.6 Hz, 2H, H_3), 7.12 (d, $^{3}J_{H–H}$ = 6.7 Hz, 2H, H_2), 5.60 (s, 6H, η^6-$C_6\underline{H}_6$), 5.33-5.29 (m, 1H, H_6), 4.53-4.46 (m, 1H, H_6), 3.85 (s, 3H, $OC\underline{H}_3$), 3.03-2.99 (m, 1H, H_5), 2.92-2.85 (m, 1H, H_5). $^{13}C\{^{1}H\}$ 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, $\nu_{C–H\ aromatic\ (bending)}$).

General 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 (0.5 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, ^{1}H, and $^{13}C\{^{1}H\}$ NMR spectroscopy.

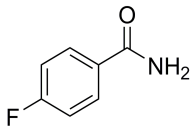
^{1}H and ^{13}C NMR of Aldehyde to Amides Conversion Products (Table 3, Entries 1-12)

1. Benzamide[67]



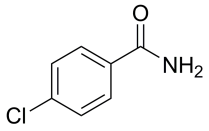
White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 – 7.81 (m, 2H), 7.55 – 7.51 (m, 1H), 7.46 – 7.43 (m, 2H), 6.31 (br s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 169.68, 133.32, 131.95, 128.58, 127.29.

2. 4-Fluorobenzamide[67]



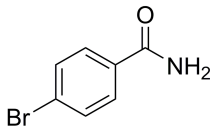
White Solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 6.95 – 6.88 (m, 2H), 6.39 (br s, 1H), 4.11 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$+DMSO-d_6) δ 168.39, 165.82, 163.31, 129.95 (d, J = 8.9 Hz), 129.59, 115.18, 114.97.

3. 4-Chlorobenzamide[67]



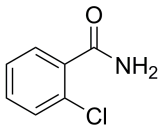
White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (d, $^{3}J_{H–H}$ = 8.6 Hz, 2H), 7.99 (d, 8.6 Hz, 2H), 6.13 (br s, 1H), 5.83 (br s, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$+DMSO-d_6) δ (ppm): 167.01, 149.30, 139.22, 128.68, 123.22.

4. 4-Bromobenzamide[67]



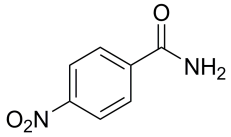
White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, 2H, $^{3}J_{H–H}$ = 8.5 Hz), 7.60 (d, 2H, $^{3}J_{H–H}$ = 8.5 Hz), 6.02 (br s, 1H), 5.81 (br s, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$+DMSO-d_6) δ (ppm) 166.94, 133.40, 131.26, 129.62, 125.04.

5. 2-Chlorobenzamide[67]



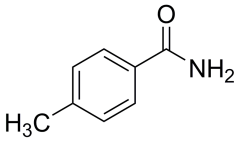
White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (dd, 1H, $^{3}J_{H–H}$ = 7.5 Hz, 1.6 Hz), 7.46 – 7.32 (m, 3H), 6.41 (br s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 168.24, 133.76, 131.78, 130.77, 130.59, 130.36, 127.12.

6. 4-Nitrobenzamide[68]



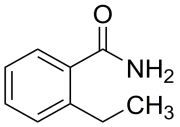
White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 – 7.75 (m, 2H), 7.53 – 7.43 (m, 2H), 6.03 (br s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$+DMSO-d_6) δ (ppm): 168.12, 137.42, 131.87, 128.84, 128.24.

7. 4-Methylbenzamide[67]



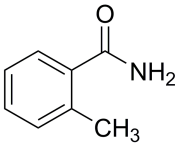
White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.42 (br s, 1H), 4.19 (br s, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$+DMSO-d_6) δ 169.60, 142.25, 129.92, 128.88, 127.40, 21.22.

8. 2-Ethylbenzamide[69]



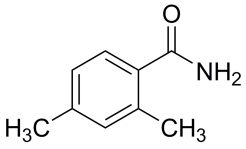
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 7.8, 1.9 Hz, 1H), 7.88 (br s, 1H), 7.40 (ddd, J = 8.4, 7.4, 1.9 Hz, 1H), 7.05 – 6.977 (m, 2H), 6.90 (d, J = 8.2 Hz, 1H), 4.12 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.83, 157.47, 133.43, 132.39, 121.05, 120.77, 112.39,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

9. 2-Methylbenzamide[70]



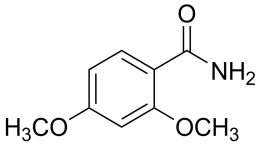
White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (d, 1H $^{3}J_{H–H}$ = 7.6 Hz), 7.35 – 7.32 (m, 1H), 7.25 – 7.19 (m, 2H), 6.20 (br s, 1H), 5.85 (br s, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 172.19, 136.28, 135.15, 131.17, 130.24, 126.91, 125.70, 19.95.

10. 2,4-Dimethylbenzamide[71]



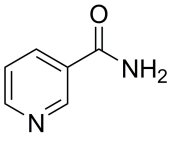
White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (d, 1H, $^{3}J_{H–H}$ = 7.7 Hz), 7.05 (s, 1H), 7.02 (d, 1H, $^{3}J_{H–H}$ = 7.8 Hz), 5.95 (br s, 1H), 5.79 (br s, 1H), 2.47 (s, 3H), 2.34 (s, 3H). ^{13}C{^{1}H NMR (101 MHz, $CDCl_3$) δ (ppm): 172.02, 140.51, 136.55, 132.05, 127.14, 126.33, 125.71, 21.23, 20.06.

11. 2,4-Dimethoxybenzamide[72]



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[68]



^{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.

5. Appendix A. Supplementary data

NMR spectra, mass spectra, crystal and refinement data, bond lengths and angles, copy of ^{1}H and ^{13}C NMR of all catalytic conversion products and CIFs of **2** (CCDC No. 1829142) and **3** (CCDC No. 1829143) are available.

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References

[1] E.L. Baker, M.M. Yamano, Y. Zhou, S.M. Anthony, N.K. Garg, A two-step approach to achieve secondary amide transamidation enabled by nickel catalysis, Nat. Commun. 7 (2016) 11554.

[2] S.A. Ruider, N. Maulide, Strong Bonds Made Weak: Towards the General Utility of Amides as Synthetic Modules, Angew. Chem. Int. Ed. Engl. 54(47) (2015) 13856-13858.

[3] P.-Q. Huang, Y.-H. Huang, H. Geng, J.-L. Ye, Metal-Free C–H Alkyliminylation and Acylation of Alkenes with Secondary Amides, Sci. Rep. 6 (2016) 28801.

[4] A. Greenberg, C.M. Breneman, J.F. Liebman, The Amide Linkage: Structural Significance in Chemistry, Biochemistry, and Materials Science, Wiley-Interscience: New York2000.

[5] J.M. Humphrey, A.R. Chamberlin, Chemical Synthesis of Natural Product Peptides: Coupling Methods for the Incorporation of Noncoded Amino Acids into Peptides, Chem. Rev. 97(6) (1997) 2243-2266.

[6] P.S. Chaudhari, S.D. Salim, R.V. Sawant, K.G. Akamanchi, Sulfated tungstate: a new solid heterogeneous catalyst for amide synthesis, Green Chem. 12(10) (2010) 1707-1710.

[7] H. Lundberg, F. Tinnis, N. Selander, H. Adolfsson, Catalytic amide formation from non-activated carboxylic acids and amines, Chem. Soc. Rev. 43(8) (2014) 2714-2742.

[8] A. Ojeda-Porras, D. Gamba-Sánchez, Recent Developments in Amide Synthesis Using Nonactivated Starting Materials, J. Org. Chem. 81(23) (2016) 11548-11555.

[9] E. Valeur, M. Bradley, Amide bond formation: beyond the myth of coupling reagents, Chem. Soc. Rev. 38(2) (2009) 606-631.

[10] T. Wieland, M. Bodanszky, The World of Peptides: A Brief History of Peptide

Chemistry, Springer1991.

[11] B.D. Roth, 1 The Discovery and Development of Atorvastatin, A Potent Novel Hypolipidemic Agent, in: F.D. King, A.W. Oxford, A.B. Reitz, S.L. Dax (Eds.), Progress in Medicinal Chemistry, Elsevier2002, pp. 1-22.

[12] A.A. Patchett, Excursions in drug discovery, J. Med. Chem. 36(15) (1993) 2051-2058.

[13] V.S. Ananthanarayanan, S. Tetreault, A. Saint-Jean, Interaction of calcium channel antagonists with calcium: spectroscopic and modeling studies on diltiazem and its Ca2+ complex, J. Med. Chem. 36(10) (1993) 1324-1332.

[14] B.L. Deopura, 2 - Polyamide fibers, Polyesters and Polyamides, Woodhead Publishing2008, pp. 41-61.

[15] A.K. Agrawal, M. Jassal, 4 - Manufacture of polyamide fibres, Polyesters and Polyamides, Woodhead Publishing2008, pp. 97-139.

[16] F.A. Carey, Organic Chemistry, McGraw-Hill, New York, NY 2005.

[17] B.S. Jursic, Z. Zdravkovski, A Simple Preparation of Amides from Acids and Amines by Heating of Their Mixture, Synth. Commun. 23(19) (1993) 2761-2770.

[18] V.R. Pattabiraman, J.W. Bode, Rethinking amide bond synthesis, Nature 480 (2011) 471.

[19] J.S. Carey, D. Laffan, C. Thomson, M.T. Williams, Analysis of the reactions used for the preparation of drug candidate molecules, Org. Biomol. Chem. 4(12) (2006) 2337-2347.

[20] C.L. Allen, J.M.J. Williams, Metal-catalysed approaches to amide bond formation, Chem. Soc. Rev. 40(7) (2011) 3405-3415.

[21] B.K. Allam, K.N. Singh, Highly efficient one-pot synthesis of primary amides catalyzed by scandium(III) triflate under controlled MW, Tetrahedron Lett. 52(44) (2011) 5851-5854.

[22] L. Field, P.B. Hughmark, S.H. Shumaker, W.S. Marshall, Isomerization of Aldoximes to Amides under Substantially Neutral Conditions1, J. Am. Chem. Soc. 83(8) (1961) 1983-1987.

[23] S.K. Sharma, S.D. Bishopp, C. Liana Allen, R. Lawrence, M.J. Bamford, A.A. Lapkin, P. Plucinski, R.J. Watson, J.M.J. Williams, Copper-catalyzed rearrangement of oximes into primary amides, Tetrahedron Lett. 52(33) (2011) 4252-4255.

[24] N.C. Ganguly, S. Roy, P. Mondal, An efficient copper(II)-catalyzed direct access to primary amides from aldehydes under neat conditions, Tetrahedron Lett. 53(11) (2012) 1413-1416.

[25] A. Martínez-Asencio, M. Yus, D.J. Ramón, Copper(II) acetate-catalyzed one-pot conversion of aldehydes into primary amides through a Beckmann-type rearrangement, Tetrahedron 68(21) (2012) 3948-3951.

[26] C.L. Allen, C. Burel, J.M.J. Williams, Cost efficient synthesis of amides from oximes with indium or zinc catalysts, Tetrahedron Lett. 51(20) (2010) 2724-2726.

[27] M.A. Ali, T. Punniyamurthy, Palladium-Catalyzed One-Pot Conversion of Aldehydes to Amides, Adv. Synth. Catal. 352(2-3) (2010) 288-292.

[28] J.F. Hull, S.T. Hilton, R.H. Crabtree, A simple Ru catalyst for the conversion of aldehydes or oximes to primary amides, Inorg. Chim. Acta 363(6) (2010) 1243-1245.

[29] A. Kanchanadevi, R. Ramesh, D. Semeril, Synthesis of Ru(II) pyridoxal thiosemicarbazone complex and its catalytic application to one-pot conversion of aldehydes to primary amides, Inorg. Chem. Commun. 56(Supplement C) (2015) 116-119.

[30] W. Wang, X.-M. Zhao, J.-L. Wang, X. Geng, J.-F. Gong, X.-Q. Hao, M.-P. Song, Transition metal-free synthesis of primary amides from aldehydes and hydroxylamine hydrochloride, Tetrahedron Lett. 55(20) (2014) 3192-3194.

[31] H. Fujiwara, Y. Ogasawara, K. Yamaguchi, N. Mizuno, A One-Pot Synthesis of Primary Amides from Aldoximes or Aldehydes in Water in the Presence of a Supported Rhodium Catalyst, Angew. Chem. Int. Ed. 46(27) (2007) 5202-5205.

[32] H. Fujiwara, Y. Ogasawara, M. Kotani, K. Yamaguchi, N. Mizuno, A Supported Rhodium Hydroxide Catalyst: Preparation, Characterization, and Scope of the Synthesis of Primary Amides from Aldoximes or Aldehydes, Chem. Asian J. 3(8-9) (2008) 1715-1721.

[33] L. Xu, N. Li, H.-g. Peng, P. Wu, Clean Synthesis of Amides over Bifunctional Catalysts of Rhodium-Loaded Titanosilicates, ChemCatChem 5(8) (2013) 2462-2470.

[34] N.A. Owston, A.J. Parker, J.M.J. Williams, Iridium-Catalyzed Conversion of Alcohols into Amides via Oximes, Org. Lett. 9(1) (2007) 73-75.

[35] D. Gnanamgari, R.H. Crabtree, Terpyridine Ruthenium-Catalyzed One-Pot Conversion of Aldehydes into Amides, Organometallics 28(3) (2009) 922-924.

[36] A.J. Davenport, D.L. Davies, J. Fawcett, D.R. Russell, Arene-ruthenium complexes with salicyloxazolines: diastereoselective synthesis, configurational stability and applications as asymmetric catalysts for Diels-Alder reactions, Dalton Trans. (9) (2004) 1481-1492.

[37] H. Joshi, K.N. Sharma, A.K. Sharma, O. Prakash, A. Kumar, A.K. Singh, Magnetite nanoparticles coated with ruthenium via SePh layer as a magnetically retrievable catalyst for the selective synthesis of primary amides in an aqueous medium, Dalton Trans. 43(32) (2014) 12365-12372.

[38] P. Singh, A.K. Singh, Transfer Hydrogenation of Ketones and Catalytic Oxidation of Alcohols with Half-Sandwich Complexes of Ruthenium(II) Designed Using Benzene and Tridentate (S, N, E) Type Ligands (E = S, Se, Te), Organometallics 29(23) (2010) 6433-6442.

[39] P. Singh, A.K. Singh, “Piano-Stool” Complexes of Ruthenium(II) Designed with Arenes and N-[2-(Arylchalcogeno)ethyl]morpholines: Highly Active Catalysts for the Oxidation of Alcohols with N-Methylmorpholine N-Oxide, tert-Butyl Hydroperoxide and Sodium Periodate and Oxychloride, Eur. J. Inorg. Chem. 2010(26) (2010) 4187-4195.

[40] O. Prakash, K.N. Sharma, H. Joshi, P.L. Gupta, A.K. Singh, Half sandwich complexes of chalcogenated pyridine based bi-(N, S/Se) and terdentate (N, S/Se, N) ligands with ([small eta]6-benzene)ruthenium(ii): synthesis, structure and catalysis of transfer hydrogenation of ketones and oxidation of alcohols, Dalton Trans. 42(24) (2013) 8736-8747.

[41] O. Prakash, K.N. Sharma, H. Joshi, P.L. Gupta, A.K. Singh, (η5-Cp*)Rh(III)/Ir(III) Complexes with Bis(chalcogenoethers) (E, E′ Ligands: E = S/Se; E′ = S/Se): Synthesis, Structure, and Applications in Catalytic Oppenauer-Type Oxidation and Transfer Hydrogenation, Organometallics 33(4) (2014) 983-993.

[42] K. Nomura, H. Okumura, T. Komatsu, N. Naga, Ethylene/Styrene Copolymerization by Various (Cyclopentadienyl)(aryloxy)titanium(IV) Complexes−MAO Catalyst Systems, Macromolecules 35(14) (2002) 5388-5395.

[43] A.A. Tregubov, K.Q. Vuong, E. Luais, J.J. Gooding, B.A. Messerle, Rh(I) Complexes Bearing N,N and N,P Ligands Anchored on Glassy Carbon Electrodes: Toward Recyclable Hydroamination Catalysts, J. Am. Chem. Soc. 135(44) (2013) 16429-16437.

[44] S. Kotha, K. Lahiri, D. Kashinath, Recent applications of the Suzuki–Miyaura cross-coupling reaction in organic synthesis, Tetrahedron 58(48) (2002) 9633-9695.

[45] J. García-Álvarez, Deep Eutectic Mixtures: Promising Sustainable Solvents for Metal-Catalysed and Metal-Mediated Organic Reactions, Eur. J. Inorg. Chem. 2015(31) (2015) 5147-5157.

[46] K.N. Sharma, H. Joshi, V.V. Singh, P. Singh, A.K. Singh, Palladium(ii) complexes of pyrazolated thio/selenoethers: syntheses, structures, single source precursors of Pd4Se and PdSe nano-particles and potential for catalyzing Suzuki-Miyaura coupling, Dalton Trans. 42(11) (2013) 3908-3918.

[47] K.N. Sharma, H. Joshi, A.K. Sharma, O. Prakash, A.K. Singh, Single source precursor routes for synthesis of PdTe nanorods and particles: solvent dependent control of shapes, Chem. Commun. 49(81) (2013) 9344-9346.

[48] K. Nayan Sharma, H. Joshi, O. Prakash, A.K. Sharma, R. Bhaskar, A.K. Singh, Pyrazole-Stabilized Dinuclear Palladium(II) Chalcogenolates Formed by Oxidative Addition of Bis[2-(4-bromopyrazol-1-yl)ethyl] Dichalcogenides to Palladium(II) – Tailoring of Pd–S/Se Nanoparticles, Eur. J. Org. Chem. 2015(29) (2015) 4829-4838.

[49] G.K. Rao, A. Kumar, B. Kumar, D. Kumar, A.K. Singh, Palladium(ii)-selenated Schiff base complex catalyzed Suzuki-Miyaura coupling: Dependence of efficiency on alkyl chain length of ligand, Dalton Trans. 41(7) (2012) 1931-1937.

[50] D.V. Aleksanyan, V.A. Kozlov, Y.V. Nelyubina, K.A. Lyssenko, L.N. Puntus, E.I. Gutsul, N.E. Shepel, A.A. Vasil'ev, P.V. Petrovskii, I.L. Odinets, Synthesis, catalytic activity, and photophysical properties of 5,6-membered Pd and Pt SCS[prime or minute]-pincer complexes based on thiophosphorylated 3-amino(hydroxy)benzoic acid thioanilides, Dalton Trans. 40(7) (2011) 1535-1546.

[51] D. Yuan, H.V. Huynh, Dinuclear and Tetranuclear Palladium(II) Complexes of a Thiolato-Functionalized, Benzannulated N-Heterocyclic Carbene Ligand and Their Activities toward Suzuki−Miyaura Coupling, Organometallics 29(22) (2010) 6020-6027.

[52] G.K. Rao, A. Kumar, J. Ahmed, A.K. Singh, Palladacycle containing nitrogen and selenium: highly active pre-catalyst for the Suzuki-Miyaura coupling reaction and unprecedented conversion into nano-sized Pd17Se15, Chem. Commun. 46(32) (2010) 5954-5956.

[53] V.A. Kozlov, D.V. Aleksanyan, Y.V. Nelyubina, K.A. Lyssenko, A.A. Vasil’ev, P.V. Petrovskii, I.L. Odinets, Cyclopalladation of meta-(Diphenylthiophosphoryloxy)benzaldimines: NCS and Unexpected NCO 5,6-Membered Pincer Palladium Complexes, Organometallics 29(9) (2010) 2054-2062.

[54] V.V. Singh, G.K. Rao, A. Kumar, A.K. Singh, Palladium(ii)-selenoether complexes as new single source precursors: First synthesis of Pd4Se and Pd7Se4 nanoparticles, Dalton Trans. 41(4) (2012) 1142-1145.

[55] K.N. Sharma, H. Joshi, A.K. Sharma, O. Prakash, A.K. Singh, Selenium-Containing N-Heterocyclic Carbenes and Their First Palladium(II) Complexes: Synthesis, Structure, and Pendent Alkyl Chain Length Dependent Catalytic Activity for Suzuki–Miyaura Coupling, Organometallics 32(8) (2013) 2443-2451.

[56] N.S. Kamal, S. Naveen, K.J. Raj, Thioether–NHC-Ligated PdII Complex for Crafting a Filtration-Free Magnetically Retrievable Catalyst for Suzuki–Miyaura Coupling in Water, Eur. J. Org. Chem. 2018(16) (2018) 1743-1751.

[57] H. Joshi, K.N. Sharma, A.K. Sharma, O. Prakash, A.K. Singh, Graphene oxide grafted with Pd17Se15 nano-particles generated from a single source precursor as a recyclable and efficient catalyst for C-O coupling in O-arylation at room temperature, Chem. Commun. 49(68) (2013) 7483-7485.

[58] A.K. Sharma, H. Joshi, K.N. Sharma, P.L. Gupta, A.K. Singh, 2-Propanol vs Glycerol as Hydrogen Source in Catalytic Activation of Transfer Hydrogenation with (η6-Benzene)ruthenium(II) Complexes of Unsymmetrical Bidentate Chalcogen Ligands, Organometallics 33(13) (2014) 3629-3639.

[59] F. Saleem, G.K. Rao, S. Kumar, M.P. Singh, A.K. Singh, Complexes of ([small eta]6-benzene)ruthenium(ii) with 1,4-bis(phenylthio/seleno-methyl)-1,2,3-triazoles: synthesis, structure and applications in catalytic activation of oxidation and transfer hydrogenation, Dalton Trans. 44(44) (2015) 19141-19152.

[60] K. Yamaguchi, M. Matsushita, N. Mizuno, Efficient Hydration of Nitriles to Amides in Water, Catalyzed by Ruthenium Hydroxide Supported on Alumina, Angew. Chem. Int. Ed. 43(12) (2004) 1576-1580.

[61] E. Choi, C. Lee, Y. Na, S. Chang, [RuCl2(p-cymene)]2 on Carbon: An Efficient, Selective, Reusable, and Environmentally Versatile Heterogeneous Catalyst, Org. Lett. 4(14) (2002) 2369-2371.

[62] S.H. Yang, S. Chang, Highly Efficient and Catalytic Conversion of Aldoximes to Nitriles, Org. Lett. 3(26) (2001) 4209-4211.

[63] N.A. Owston, A.J. Parker, J.M.J. Williams, Highly Efficient Ruthenium-Catalyzed Oxime to Amide Rearrangement, Org. Lett. 9(18) (2007) 3599-3601.

[64] R. García-Álvarez, A.E. Díaz-Álvarez, J. Borge, P. Crochet, V. Cadierno, Ruthenium-Catalyzed Rearrangement of Aldoximes to Primary Amides in Water, Organometallics 31(17) (2012) 6482-6490.

[65] G. Sheldrick, SADABS v. 2.10, Bruker AXS Inc., Madison, Wisconsin, USA (2003).

[66] B.S.Furniss, A.J. Hannaford, P.W.G. Smith, A.R.Tatchell, Vogel's Textbook of Practical Organic Chemistry, 5th ed., ELBS, Longman Group U K Ltd1989.

[67] M. A. Ali, T. Punniyamurthy, Palladium Catalyzed One-Pot Conversion of Aldehydes to Amides, *Adv. Synth. Catal.*, 352, (2010) 288-292.

[68] N. A. Owston, A. J. Parker, J. M. J. Williams, Iridium Catalysed Conversion of Alcohols into amides via Oximes, *Org. Lett.*, *9*, (2007) 73-75.

[69] T. Xu, H. Alper, Palladium Catalyzed Amino-Carbonylation of Aryl Iodides using Aqueous Ammonia, *Tetrahedron Lett.*, *54*, (2013) 5496-5499.

[70] G. F. Rebeca, C. Pascale, C. Victorio, M. M. Isabel, L. Ramón, Phosphinous Acid□Assisted Hydration of Nitriles: Understanding the Controversial Reactivity of Osmium and Ruthenium Catalysts, *Chem. Eur. J.*, *23*, (2017) 15210-15221.

[71] Q. Xinxin, A. Han-Jun, C. Chuang-Xu, P. Jin-Bao, Y. Jun, W. Xiao-Feng, A Convenient Palladium□Catalyzed Aminocarbonylation of Aryl Iodides to Primary Amides under Gas□Free Conditionsm and Ruthenium Catalysts, *Eur. J. Org. Chem.*, *2017*, (2017) 7222-7225.

[72] M. Rezaei, K. Amani, K. Darvishi, One–pot green catalytic synthesis of primary amides in aqueous medium by CuII–immobilized silica–based magnetic retrievable nanocatalyst,*Catal. Commun.*, *91*, (2017) 38-42.

Highlights

- Synthesis and characterization of three novel Ru(II) half-sandwich complexes of pyrazolated chalcogenoether ligands.
- Catalytic potential of the complexes for one-pot conversion of aldehyde to amide.
- Due to the stronger σ-donor properties of selenium, the Ru complex of Se ligand was found to be more efficient as compare to the sulphur and tellurium analogues.