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2-Propanol vs Glycerol as Hydrogen Source in Catalytic Activation of Transfer Hydrogenation with (η^6-Benzene)ruthenium(II) Complexes of Unsymmetrical Bidentate Chalcogen Ligands

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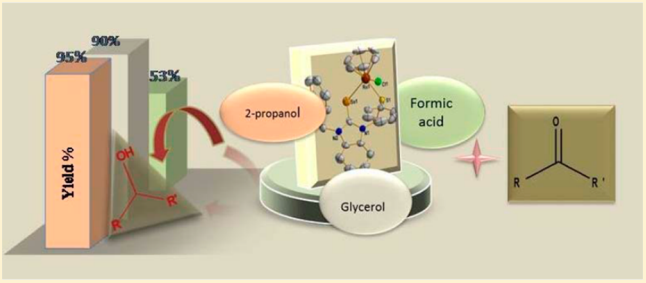
Supporting Information

ABSTRACT: 1*H*-Benzoimidazole on subjection to a sequence of reactions with benzyl bromide, $PhECH_2Cl$ (E = S, Se), and elemental S or Se results in 1-benzyl-3-phenylchalcogenylmethyl-1,3-dihydrobenzoimidazole-2-chalcogenones (**L1**−**L4**), which are unsymmetrical bidentate chalcogen ligands having a unique combination of chalcogenoether and chalcogenone donor sites. Half sandwich complexes, $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L})Cl][PF_6]$ (**1**−**4**), have been synthesized by reactions of $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ with the appropriate **L** at room temperature followed by treatment with NH_4PF_6. **L1**−**L4** and their complexes **1**−**4** have been authenticated with HR-MS and ^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR spectra. The single-crystal structures of **1**−**4** have been determined by X-ray crystallography. Each **L** acts as an unsymmetric (E,E) or (E,E′) bidentate ligand. The Ru atom in **1**−**4** has pseudo-octahedral half-sandwich "piano-stool" geometry. The Ru−S and Ru−Se bond distances (Å) respectively are 2.358(3)/2.3563(18) and 2.4606(11)/2.4737(10) (thio- and selenoether), and 2.4534(17)/2.435(3) and 2.5434(9)/2.5431(10) (thione and selone). Catalytic activation with complexes **1**−**4** has been explored for the transfer hydrogenation (TH) of aldehydes and ketones using various sources of hydrogen. 2-Propanol and glycerol have been compared and found most suitable among the sources screened. The catalytic efficiency of other sources explored, viz. formic, citric, and ascorbic acid, is dependent on the pH of reaction medium and is not promising. A comparative study of 2-propanol and glycerol as hydrogen sources for catalytic activation of TH with **1**−**4** has revealed that with glycerol (for comparable conversion in the same time) more amount of catalyst is needed in comparison to that of 2-propanol. The catalytic process is more efficient with **3** (where Ru is bonded with selone), followed by **1** ≈ **4**, and **2** showing the least activity among all four complexes. The transfer hydrogenation involves an intermediate containing a Ru−H bond and follows a conventional alkoxide intermediate based mechanism. The results of DFT calculations appear to be generally consistent with experimental catalytic efficiencies and bond lengths/angles.



INTRODUCTION

Transfer hydrogenation has an important place among organic transformations. It is used for the reduction of carbonyl compounds to the corresponding alcohols, important (particularly chiral ones) in the pharmaceutical, perfume, and agrochemical industries.[1] Transfer hydrogenation (TH) avoids the use of stoichiometric reducing reagents or hazardous molecular hydrogen,[2] and because of this, it has attracted substantial interest.[3] The TH employs a catalyst and hydrogen source. Several hydrogen sources such as 2-propanol, formic acid, glycerol, and cyclopentanol have been explored[4,5] for this purpose. Similarly, there have been many catalysts screened to activate transfer hydrogenation reactions. Among all the catalysts reported so far, those based on Ru(II), Rh(III), Ir(III), and Ir(I) (TOF 24000) have been the most successful.[6a−o] Other metal catalysts and organocatalysts have also been reported[6p] for transfer hydrogenation, but many of them are slow and the resulting enantioselectivity (in asymmetric TH) is not good. Ruthenium(II) complexes have gotten a good deal of attention in the recent past for catalytic transfer hydrogenation reactions.[7] Noyori and co-workers have studied ruthenium(II) complexes designed with several ligands, BINAP, ethylenediamine, or other 1,2-diamines and PR_3, for catalytic transfer hydrogenation (including asymmetric) and proposed a mechanism involving the N−H group.[8−18] Ruthenium half-sandwich complexes explored for catalytic TH generally have benzene or *p*-cymene.[19] The coligands used to design such complexes include pyridyl/bipyridyl ligands,[20−22] benzimidazoles,[24c] NHCs,[23,24a,b] and triazoles.[25] The promise of metal complexes of organochalcogen ligands has been demonstrated recently in the catalysis of various chemical transformations and as single-source precursors for metal chalcogenide nanoparticles.[26] Half-sandwich ruthenium(II) complexes designed using such ligands catalyze the oxidation of alcohols and transfer hydrogenation of ketones.[27] The promising efficiency of these catalysts has been partially attributed to the strong electron-donating ability of the

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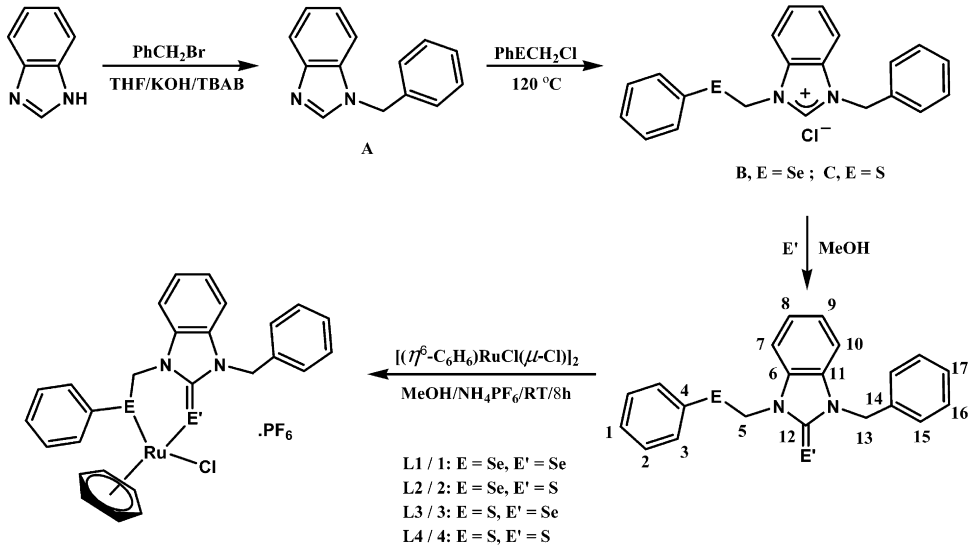
Scheme 1. Synthesis of Ligands L1−L4 and Their Complexes 1−4



chalcogen donor site, particularly in the case of sulfur and selenium. Ligands incorporating both hard (N) and soft donor atoms (S, Se, Te) have been more explored to design half-sandwich ruthenium(II) complexes for TH than have (E,E) ligands (E = S, Se).[28] To the best of our knowledge, half-sandwich complexes of Ru(II) with bidentate ligands having chalcogenoether and chalcogenone donor sites together have not been explored for TH so far. It was therefore thought worthwhile to design 1-benzyl-3-phenylchalcogenylmethyl-1,3-dihydrobenzoimidazole-2-chalcogenone ligands (**L** = **L1−L4**), which are unsymmetric bidentate chalcogen ligands having a unique combination of thione or selone donor site with a thioether or selenoether site. Half-sandwich ruthenium complexes of these ligands have been synthesized and characterized by single-crystal structure studies. A single-crystal structure of a Ru complex of any selone ligand has not been reported to date, and the present report is the first,[29a] whereas one report on the structure of a Ru(II) thione complex is known.[29b] The Ru(II) complexes of **L1−L4** have been explored in detail for transfer hydrogenation of carbonyl compounds using several hydrogen sources. A comparative study of 2-propanol and glycerol has been carried out. DFT calculations have been found to support experimental observations. All of these results are described in this paper.

RESULTS AND DISCUSSION

The syntheses of **L1−L4** and their complexes are summarized in Scheme 1. Ligands **L1−L4** have good solubility in common organic solvents: viz., $CHCl_3$, CH_2Cl_2, CH_3OH, and CH_3CN. In contrast, complexes **1−4** are only moderately soluble in these solvents, except for CH_3CN. They have good solubility in DMSO. The complexes **1−4** and their ligands are insensitive to air and moisture, as they can be stored at room temperature for several months under ambient conditions.

NMR Spectra. The ^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR and mass spectra of **L1−L4** and their complexes **1−4** are given in the Supporting Information. For **B** and **C** (Scheme 1), **L1−L4**, and complexes **1−4** the spectra have been found to be in agreement with their molecular structures (Scheme 1). The structures of **1−4** have been corroborated with their single-crystal structures determined by X-ray diffraction. The signal of the selenoether group at 402.6 ppm in the $^{77}Se\{^1H\}$ NMR spectrum of **L1** is at a slightly lower frequency (2.1 ppm) with respect to that of the selenated precarbene precursor **B** (404.7 ppm), whereas such a signal in the $^{77}Se\{^1H\}$ NMR spectrum of **L2** appears at 396.2 ppm: i.e., at 8.51 ppm lower frequency with respect to that of **B**. The selone signals in the $^{77}Se\{^1H\}$ NMR spectra of **L1** and **L3** appear at 101.8 and 92.5 ppm, respectively. The signals of the selenoether group in the $^{77}Se\{^1H\}$ NMR spectra of **1** and **2** have been found to be shifted to higher frequency (13.4, and 112.0 ppm, respectively), with respect to those of the corresponding free ligand. The shifts probably arise due to coordination of **L1** and **L2** with Ru via Se. In **2** the ligand is (Se,S), whereas in **1** it is (Se,Se). The Se coordinates more strongly than S. Electron transfer to the metal from Se is thus easier in the case of (Se,S) ligand rather than (Se,Se) ligand, as the one Se has to compete with the other in the latter. Thus, a high-frequency shift of large magnitude is more likely to occur in **2**, as observed experimentally. The signal (−11.3 ppm) in $^{77}Se\{^1H\}$ NMR spectrum of **3** due to selone has been found to be shifted to lower frequency by 103.8 ppm with respect to that of free **L3**. In complex **1** a selone peak was not observed. On coordination, the relaxation time of Se increases, which results in a broadening of the signal.[30] The broadening of the signal has been correlated to the coordination of ligands with metal ions.[31] Similar phenomena appear to occur in the present case, which make the selone signal invisible. The invisibility of the selone signal[32] on coordination has been reported earlier as well. The signals for benzimidazolium protons observed at δ 9.85 and 9.91 ppm in the ^1H NMR spectra of **B** and **C**, respectively, are in the range reported for such protons (due to its high acidity) in the case of other imidazolium salts (δ 9.0−12.0).[33,34] In the ^1H NMR spectra of ligands **L1−L4**, there is no benzimidazolium proton signal (at δ 9.85 and 9.91 ppm) due to the formation of thione/selone. The signal of the carbon atom C12 of benzimidazolium has been observed in $^{13}C\{^1H\}$ NMR spectra of **L1−L4** at higher frequency (∼28.2 ppm) with respect to those of free **B** and **C**, due to the formation of thione/selone. The signals of CH_2 (C5 and C13) in $^{13}C\{^1H\}$ NMR spectra of complexes **1−4** have been found to be shifted to higher frequency (∼0.6−2.7 ppm) with respect to those of

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the corresponding free ligand (from **L1**−**L4**). This is due to the coordination of **L1**−**L4** with ruthenium. The signal of C12 in $^{13}C\{^1H\}$ NMR spectra of complexes **1**−**4** has been found to be shifted to lower frequency (~3.4 to 27.2 ppm) with respect to that of the corresponding free ligand. The signals (singlet) of η^6-benzene in ^1H and $^{13}C\{^1H\}$ NMR spectra appear to be shifted to lower frequency with respect to those of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$. This occurs due to substitution of Cl with S and Se, which have relatively lower electronegativities and are stronger donors.

In the mass spectra of ligands **L1**−**L4** peaks appearing at m/z 480.9696, 433.0248, 433.0248, and 385.0793, respectively, may be ascribed to $[\mathbf{L} + Na]^+$ (see the Supporting Information, Figures S5−S8). In the mass spectrum of complex **3** there is a peak at m/z 624.9558, which corresponds to its cation. In the mass spectra of both complexes **1** and **2**, a molecular ion peak or peak of their cation was not observed. However, there is a peak in mass spectra of both complexes at m/z 379.0709, which corresponds to $[C_{21}H_{19}N_2Se]^+$ and appears to be of precursor **B** of ligands.

Crystal Structures. Single crystals of **1**−**4** suitable for X-ray diffraction were grown from 1/3 (v/v) methanol/acetonitrile mixtures and subjected to crystal structure studies.

The crystal data and refinement parameters are given in the Supporting Information (Table S1). The structures (ellipsoids at 30% probability) of the cations of **1**−**4** are shown in Figures 1−4, respectively, with selected bond lengths and angles. H

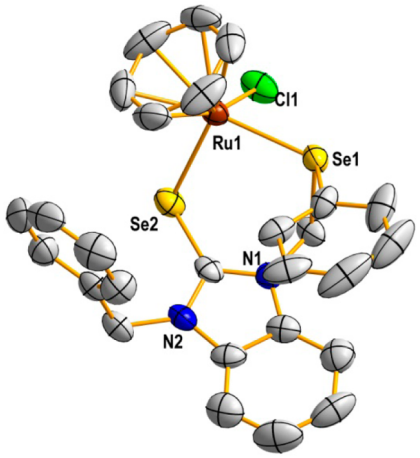

Figure 1. Structure of the cation of **1**. Bond lengths (Å): Ru(1)−Se(1) 2.4606(11), Ru(1)−Se(2) 2.5431(10), Cl(1)−Ru(1) 2.423(2), C(14)−Se(2) 1.876(7), C(6)−Se(1) 1.948(8). Bond angles (deg): Se(1)−Ru(1)−Se(2) 94.62(3), Cl(1)−Ru(1)−Se(2) 85.49(5), Cl(1)−Ru(1)−Se(1) 79.73(6).

atoms and PF_6^- anion are omitted in each figure for clarity. **L1**−**L4** exhibit similar bonding modes in all complexes **1**−**4**. The six-membered chelate ring is formed due to their coordination with ruthenium through chalcogen atoms. In the cation of each of the four complexes there is a pseudo-octahedral half-sandwich "piano stool" type disposition of donor atoms around the Ru center. The centroid of the η^6-benzene ring occupies the center of three octahedral sites, making a triangle. The chalcogen donor atoms of **L1**−**L4** and chlorine complete the coordination sphere. Half-sandwich Ru(II) complexes of ligands containing a seleno- or thioether donor site in conjunction with a selone or thione donor group are not known to us. The present ones complexes probably the

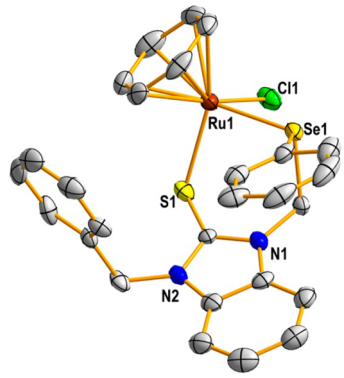

Figure 2. Structure of the cation of **2**. Bond lengths (Å): Ru(1)−Se(1) 2.4737(10), Ru(1)−S(1) 2.4534(17), Cl(1)−Ru(1) 2.4212(17), C(14)−S(1) 1.713(6), C(6)−Se(1) 1.934(7). Bond angles (deg): S(1)−Ru(1)−Se(1) 94.72(5), Cl(1)−Ru(1)−Se(1) 79.42(5), Cl(1)−Ru(1)−S(1) 86.04(6).

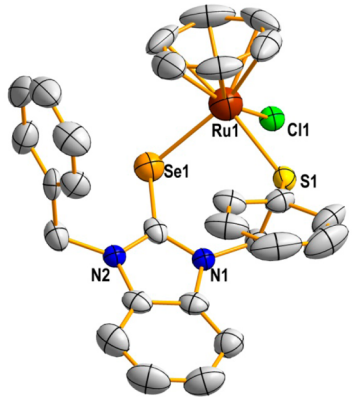

Figure 3. Structure of the cation of **3**. Bond lengths (Å): Ru(1)−S(1) 2.3563(18), Ru(1)−Se(1) 2.5434(9), Ru(1)−Cl(1) 2.4200(19), N(2)−C(14) 1.357(8), Se(1)−C(14) 1.862(7), S(1)−C(6) 1.798(7). Bond angles (deg): S(1)−Ru(1)−Se(1) 93.96(5), Cl(1)−Ru(1)−Se(1) 85.74(5), S(1)−Ru(1) − Cl(1) 80.89(7).

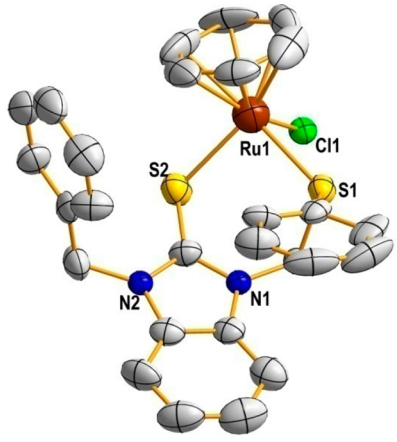

Figure 4. Structure of the cation of **4**. Bond lengths (Å): Ru(1)−S(1) 2.358(3), Ru(1)−S(2) 2.435(3), C(14)−S(2) 1.702(10), C(6)−S(1) 1.777(11). Bond angles (deg): S(1)−Ru(1)−S(2) 93.63(10), S(1)−Ru(1)−Cl(1) 81.08(10), Cl(1)−Ru(1)−S(2) 86.19(11).

first examples. The Ru−S(thione) distances in the cations of **2** and **4** (2.4534(17) and 2.435(3) Å, respectively) are normal.[35,36] The Ru−S(thioether) bond lengths in the cations

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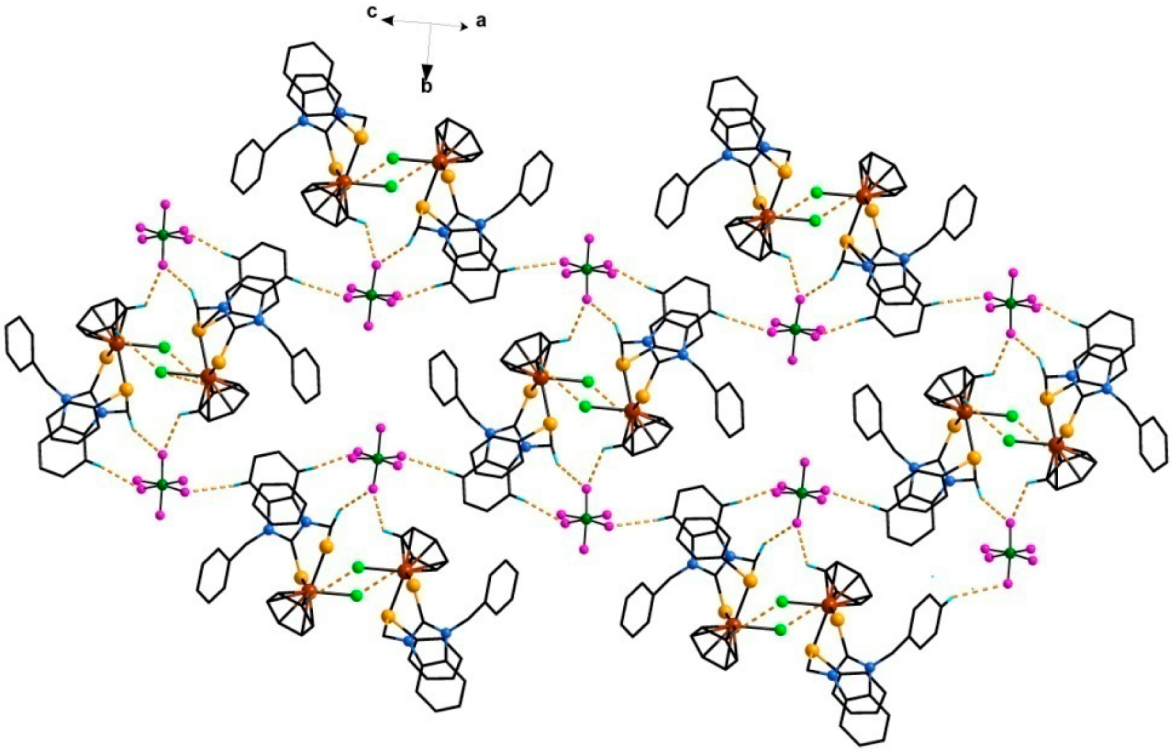

Figure 5. Noncovalent C−H···F interactions in **1**.

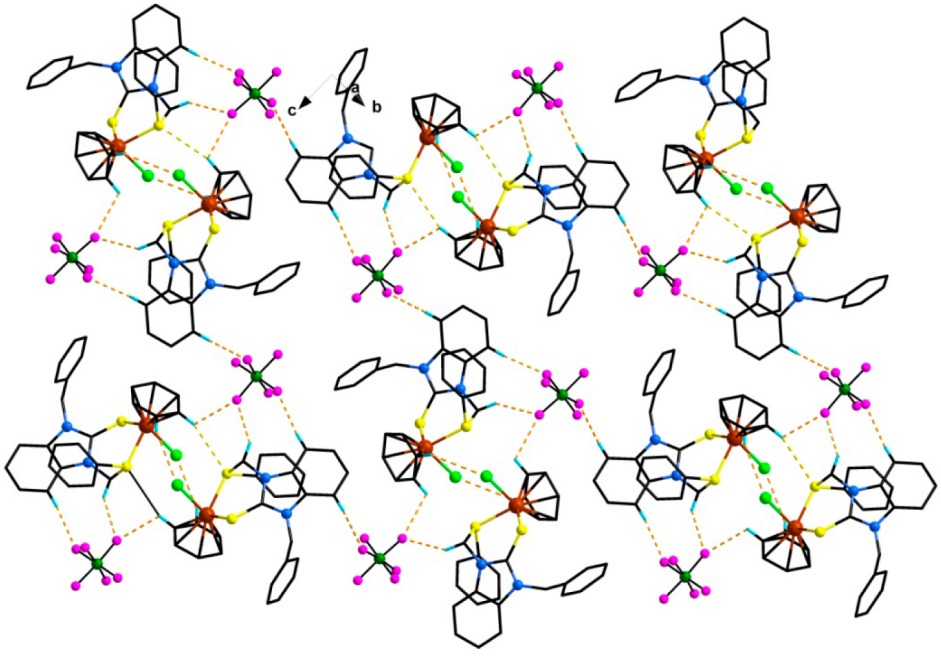

Figure 6. Noncovalent C−H···F interactions in **4**.

of **3** (2.3563(18) Å) and **4** (2.358(3) Å) are in the range (2.3548(15)−2.4156(9) Å) for those of several reported Ru(II) complexes of morpholine- and pyrrolidine-based organosulfur ligands.[27a−c] The Ru−Se(selenoether) bond length in the cation of **1** is 2.4606(11) Å, and that of **2** is 2.4737(10) Å. These values are consistent with the range 2.4756(10)−2.5240(9) Å for similar bond lengths reported for the Ru(II) complexes[27a−c] [RuCl(η^6-*p*-cymene)(*N*-{2-(phenylseleno)-ethyl}pyrrolidine)]$^+$, [RuCl(η^6-C_6H_6)(*N*-[2-(arylseleno)ethyl]-morpholine)]$^+$, and [RuCl(η^6-C_6H_6)(*N*-{2-(phenylseleno)-ethyl}pyrrolidine)]$^+$ and Ru−Se clusters[27d] [Ru_3(μ_3-Se)(μ_3-S)$(CO)_7$(μ-dppm)] and [Ru_3(μ_3-Se)$(CO)_7$(μ_3-CO)(μ-dppm)]. The Ru−Cl bond lengths are in range 2.423(12)−2.420(19) Å and are normal.[27b] The PF_6 anion in complexes **1**−**4** has been found to be involved in C−H···F secondary interactions, resulting in chains, as shown in Figures 5 and 6 for complexes **1** and **4**, respectively. The crystals of **1**−**4** also have C−H···Cl secondary interactions (for details see the Supporting Information, Table S5).

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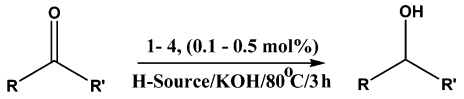
Catalytic Transfer Hydrogenation. A transfer hydrogenation reaction (Scheme 2, in which one organic molecule transfers hydrogen to another) avoids the use of inflammable molecular hydrogen.[2b]

Scheme 2. Transfer Hydrogenation of Carbonyl Compounds



R = Alkyl/Aryl R' = H/Alkyl/Aryl

The catalysis of transfer hydrogenation of aldehydes and ketones at 80 °C has been standardized using benzaldehyde as substrate, **3** (0.5 mol %) as catalyst, and citric acid, ascorbic acid, formic acid, glycerol, or 2-propanol as the source of hydrogen (Table 1). In the presence of citric acid and ascorbic acid the reaction shows negligible conversion (Table 1, entries 1 and 2). However, in the case of formic acid the progress of the reaction is dependent on the pH of the reaction mixture, as at pH 7.0 there is no conversion, whereas at pH 4.0 and 5.0 the conversion to alcohol is around 38%. When the pH is lowered to 3.0, the conversion scales up to 53% (Table 1, entry 3). As the conversions in the presence of glycerol (90%, Table 1, entry 4) and 2-propanol (95%, Table 1, entry 5) were high, they were selected for further studies, particularly the comparative study. In view of the claim of transfer hydrogenation promoted by KOH/NaOH,[37] control reactions of acetophenone (as its hydrogenation is easiest) were carried out under optimum conditions in the absence of catalyst for 3 h in both 2-propanol and glycerol. Approximately 8% conversion to the desired product took place in 2-propanol, whereas in glycerol the product was not detected. In the report of NaOH promoted transfer hydrogenation authors themselves are not fully confident of claim.[37b] In the claim of KOH-promoted transfer hydrogenation two points are important to note. First, for ketones a reaction time of 18−24 h is required, and second, a yield of more than 75% has not been achieved for any aldehyde or ketone.[37a] Thus, the role of the Ru catalyst in the present case is significant. The time profile of both these hydrogen sources is shown in Figure 7. The conversion almost linearly increases up to 2 h, and thereafter the rate is slowed down. Further optimization of the catalytic reaction with these two hydrogen sources has been carried out using **3** as a catalyst with benzaldehyde substrate. The optimum catalyst loading is 0.1 mol % with 2-propanol and 0.5 mol % with glycerol. The KOH was found to be a suitable base at a temperature of 80 °C. To understand the scope of catalytic reactions using Ru complexes **1**−**4** a variety of aldehyde and ketone substrates with varying substituents were studied. With glycerol only **2** and **3** were investigated in detail. The results are given in Tables 2 and 3 for 2-propanol and glycerol, respectively.

Table 1. Screening of Proton Sources for Catalytic Transfer Hydrogenation[a]

entry	H source	conversn, %
1[c]	citric acid	<10
2[c]	ascorbic acid	7
3[c]	formic acid	53
4[b]	glycerol	90
5[b]	2-propanol	95

[a]Reaction conditions: catalyst **3** (0.5 mol %), aldehyde (1 mmol). [b]KOH (2 mL of a 0.2 M solution or 0.4 mmol), bath temperature 80 °C, reaction time 3 h. [c]pH 3.

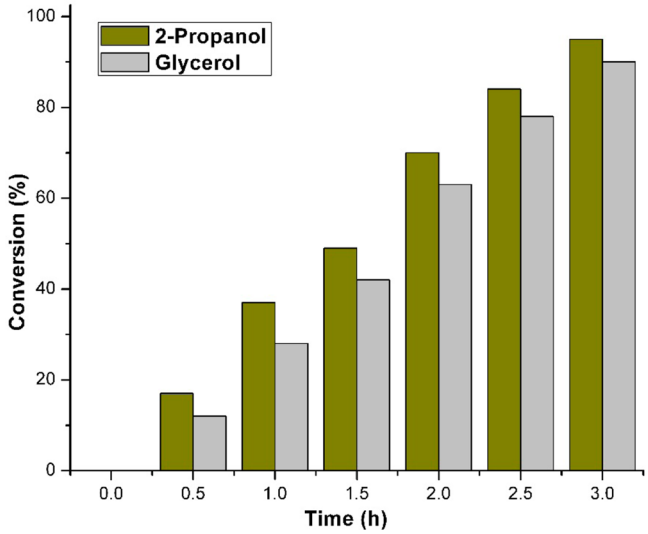


Figure 7. Time profile of the catalytic transfer hydrogenation of benzaldehyde with complex **3** in air. Conditions: catalyst, 0.1 mol % for 2-propanol and 0.5 mol % for glycerol; benzaldehyde, 1.0 mmol; KOH, 0.4 mmol; solvent, 5 mL of glycerol or 2-propanol; temperature, 80 °C. Conversions were monitored with NMR.

Table 2. Catalytic Transfer Hydrogenation in 2-Propanol[a]

		conversn, %			
entry	substrate	1	2	3	4
1	benzaldehyde	93	90	95	93
2	4-methylbenzaldehyde	89	84	90	88
3	4-anisaldehyde	85	82	88	87
4	4-bromobenzaldehyde	88	86	92	89
5	cyclopentanone	91	88	93	90
6	acetophenone	91	90	96	94
7	propiophenone	88	86	90	87
8	4-methylacetophenone	84	82	87	85

[a]Reaction conditions: catalyst, 0.1 mol %; aldehyde/ketone, 1 mmol; KOH, 2 mL of a 0.2 M solution; bath temperature, 80 °C; reaction time, 3 h.

With 2-propanol the conversions (Table 2) have been found to be high in the cases of benzaldehyde (up to 95%, Table 2,

Table 3. Catalytic Transfer Hydrogenation in Glycerol[a]

		conversn, %	
entry	substrate	2	3
1	benzaldehyde	83	90
2	4-anisaldehyde	72	82
3	4-bromobenzaldehyde	81	86
4	cyclopentanone	80	89
5	acetophenone	85	91
6	propiophenone	81	87
7	4-methylacetophenone	74	83

[a]Reaction conditions: catalyst, 0.5 mol %; aldehyde/ketone, 1 mmol; KOH, 0.4 mmol; bath temperature, 80 °C; reaction time, 3 h.

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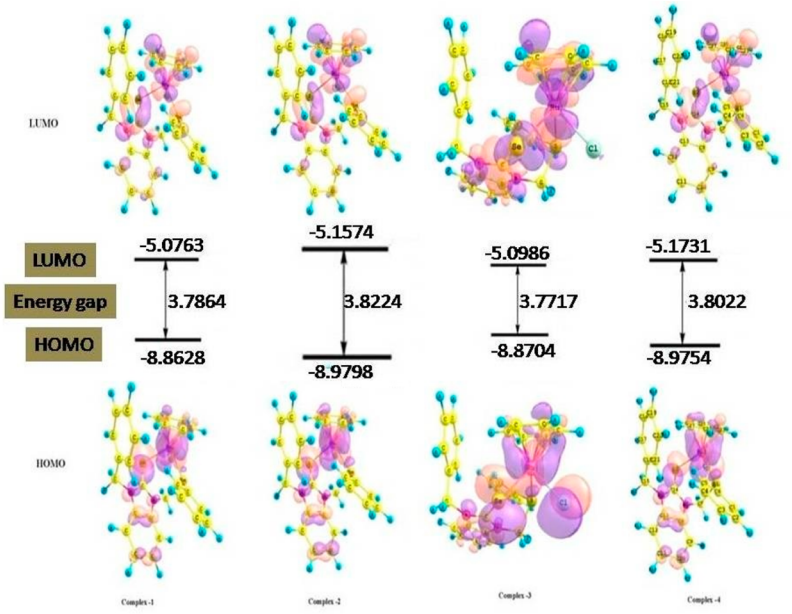

Figure 8. Frontier molecular orbitals of complexes **1**–**4** and their HOMO–LUMO energy gaps.

Table 4. Comparison of Selected Bond Lengths (Å) and Angles (deg) of 1–4 Determined Experimentally and Calculated by DFT

	1		2		3		4	
	bond angle/ length	DFT value	bond angle/ length	DFT value	bond angle/ length	DFT value	bond angle/ length	DFT value
Ru–S/Se(chalcogenoether)	2.4606(11)	2.5625	2.4737(10)	2.564 31	2.3563(18)	2.5094	2.358(3)	2.5061
Ru–Cl	2.4230(2)	2.420 60	2.4212(17)	2.418 45	2.4200(19)	2.4112	2.414(3)	2.4080
Ru–S/Se(chalcogenone)	2.5431(10)	2.630 48	2.4534(17)	2.554 52	2.5434(9)	2.6325	2.435(3)	2.5615
S/Se(chalcogenone)–Ru–S/Se(chalcogenoether)	94.62(3)	93.86	94.72(5)	93.57	93.96(5)	93.26	93.63(10)	92.63
Cl–Ru–S/Se(chalcogenoether)	79.73(6)	77.74	79.42(5)	77.65	80.89(7)	79.105	86.19(11)	79.30
Cl–Ru–S/Se(chalcogenone)	85.49(5)	85.23	86.04(6)	86.04	85.74(5)	85.178	81.08(10)	85.85

entry 1) and acetophenone (up to 96%, Table 2, entry 6) with all of the catalysts **1**–**4**. In case of aliphatic ketones the conversion was up to 93% (Table 2, entry 5 for cyclopentanone). The efficiency of complex **3** is somewhat greater than those of the other three complexes (Table 2).

The comparison of performance of **1**–**4** as catalysts for TH in 2-propanol with the catalysts reported in literature reveals a mixed bag. The catalyst loading required for $[RuCl_2(p\text{-cymene})]_2$[7a] and [Ru(diamine)($\eta^6$-arene)(dimethylimidazole)-(Cl)]$^+$ [7b] is 0.5 mol %, higher than those of the present complexes for good conversion. Further, the reaction time is long, at least 20 h. The complex $[RuBr(OAc)(PPh_3)(p\text{-aNHC})]$[7c] as catalyst is nearly comparable to **1**–**4** and shows almost similar efficiency. The Ru(II) diamide complex[7d] has been used at loading somewhat lower (up to 0.01 mol %) than that for **1**–**4**, and the required reaction time is also short. For the $[RuCl_2(PPh_3)_3]$–ethylenediamine system the optimum catalyst loading is 0.2 mol %.[8] The optimum loadings of complexes of $[RuCl_2(arene)]$ with ImEt–CH_2CH_2OEt for TH have been reported as 0.05–0.5 mol %, which are comparable to those of **1**–**4**.[7e]

The scope of catalytic transfer hydrogenation with glycerol as a hydrogen source and **2** and **3** as catalysts has been explored (Table 3). Aldehydes and ketones were subjected to transfer hydrogenation in glycerol using complexes **2** and **3** (0.5 mol %) as catalysts in the presence of KOH as a base at a temperature of 80 °C (Table 3). The carbonyl compound is reduced to the corresponding alcohol while glycerol is dehydrogenated to dihydroxyacetone (DHA; ^{1}H NMR δ 4.4 and 3.5 ppm) and other products,[38] but all are obtained in low yield and are difficult to separate. The low yield of dihydroxyacetone is not a great concern because glycerol is very cheap and high recovery of this main byproduct is not going to cut the cost of the process very significantly. Using complexes **2** and **3** for catalytic TH, conversions have been found to be high in the cases of benzaldehyde (up to 90%, Table 3, entry 1) and acetophenone (up to 91%, Table 3, entry 5). The complex **3** is somewhat more efficient in comparison to **2** (Table 3). With glycerol as the hydrogen source 1 mol % of the ruthenium species explored for TH, viz. $RuCl_3(TPPS)_3$, $RuCl_3(TPP)_3$, RuCl[(p-cymene)-TsDPEN], and [Ru(η^6-arene)(NHC)CO_3], is needed, which is higher than the required loading of **2** and **3** (0.5 mol %).[7f,g] Further, the reaction time for good conversion is on the order of 24–48 h, whereas with 0.5 mol % of **2** and **3** good conversion occurs in 3 h. The two hydrogen donors glycerol and 2-propanol are efficient for catalytic TH with **1**–**4**; the latter donor is, of course, slightly better.

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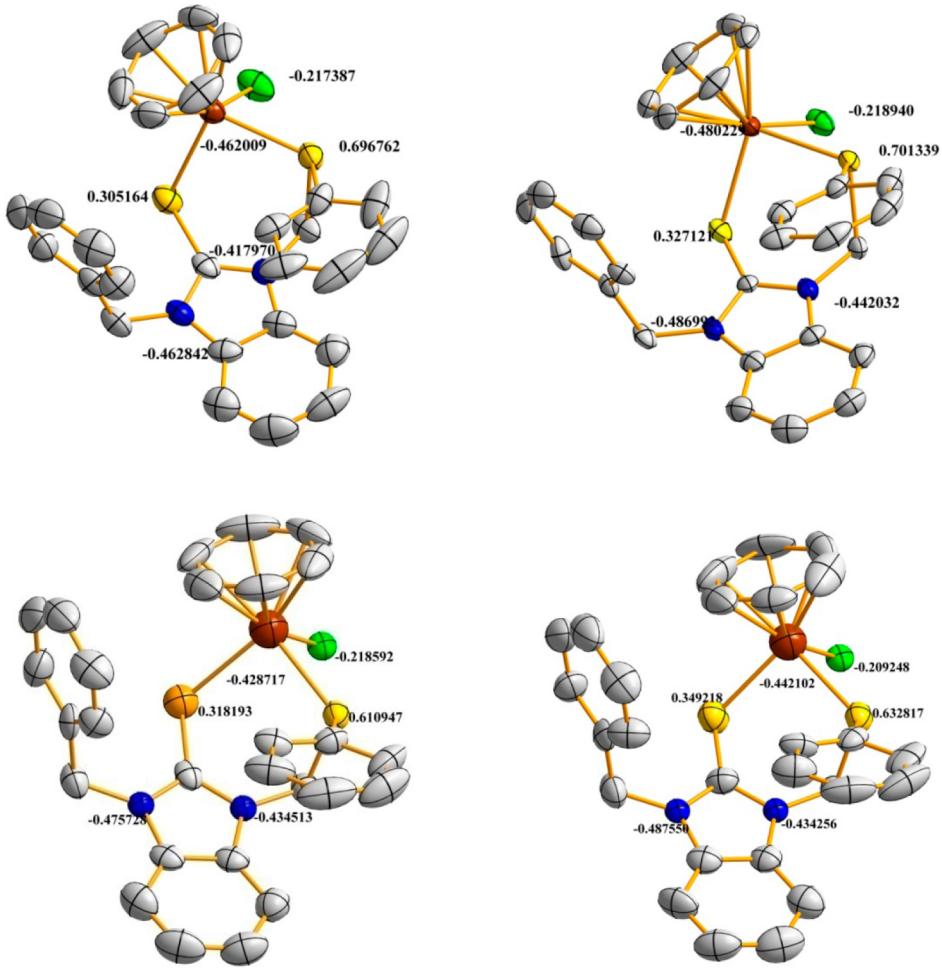

Figure 9. NBO atomic charges of complexes **1**−**4**.

The catalytic TH reactions catalyzed with **3** have been monitored with $^{77}Se\{^{1}H\}$ NMR spectroscopy. The signals in the spectra shift to higher frequency (∼17 ppm). This indicates that probably the Ru−Cl bond is cleaved or weakened very significantly to make a coordination site on metal center available so that formation of an intermediate having a Ru−H bond takes place.[39] In ^{1}H NMR spectra a broad singlet has been noticed around −8.2 to −10.7 ppm during the course of the catalytic reaction. A signal at this position is characteristic of a metal hydride and indicates the formation of a Ru−H bond.[40] Thus, catalytic transfer hydrogenation reactions with the present complexes probably proceed via formation of a metal hydride intermediate, as suggested for the conventional mechanism[41] based on metal alkoxide formation.

DFT Calculations. Density functional theory (DFT) calculations were performed on all complexes **1**−**4**. Their HOMOs (highest occupied molecular orbitals) are positioned primarily over the metal center, chalcogens (S/Se), and Cl with some contribution from the benzimidazole ring (Figure 8). The agreement between the experimentally observed bonding parameters and the calculated values is reasonable[42] for Ru−E(chalcogenoether) (E = S, Se). Ru−Cl, Ru−E′(chalcogenone), and Ru−benzene(centroid) calculated and experimentally found bond lengths may be in general considered consistent with experimental results (Table 4). The calculated and experimental values of bond angles are reasonably close. A correlation to some extent between the HOMO−LUMO energy gap of a complex and its chemical reactivity[43a,b] is expected. This is because the chemical reactivity is related to chemical hardness, defined as the resistance to perturbation in the electron distribution in a molecule.[43b] In terms of frontier orbitals, chemical hardness corresponds to the energy gap between the HOMO and LUMO and is approximated by $\varepsilon_{HOMO} - \varepsilon_{LUMO}$, where ε_{LUMO} and ε_{HOMO} are the LUMO and HOMO energies.[43a,d] The magnitude of HOMO−LUMO energy gaps in **1**−**4** is not unusual: i.e., on the order of 4 eV reported for the complexes of group VIII metal ions with organochalcogen donors.[43c] The large HOMO−LUMO energy gap makes the deformation of the electron cloud difficult, which in turn results in less reactivity.[43d] The HOMO−LUMO energy gap is lower in the case of **1**/**3**(selone analogues) relative to **2**/**4** (thione analogues) (see Figure 8). Thus, the reactivities of complexes of selone ligands are expected to be greater than those of the corresponding thione analogues. This is consistent with the experimentally observed order of catalytic efficiencies of complexes: Se > S (of course only marginal). Natural bond orbital (NBO) analysis of atomic charge for **1**−**4** shows that the charge on the Ru center of the **3** is highest (Figure 9). The presence of high electronic charge on Ru facilitates the formation of ruthenium hydride needed in the case of transfer hydrogenation. Thus, selone-containing species are expected to be more efficient for transfer hydrogenation catalysis, as the nature of Se is soft, which may result in a higher charge on Ru

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in comparison to that for the sulfur analogues. A similar observation is made experimentally.

CONCLUSION

1-Benzyl-3-phenylchalcogenylmethyl-1,3-dihydrobenzoimidazole-2-chalcogenone ligands and their four half-sandwich complexes with (η^6-benzene)Ru^{II} have been synthesized and characterized by NMR and HRMS. The complexes were structurally characterized by single-crystal X-ray diffraction studies. These unsymmetrical bidentate chalcogen ligands having a unique combination of chalcogenoether and chalcogenone donor sites are the first examples of such ligands and have been explored for designing half-sandwich complexes of Ru(II). The disposition of donor atoms around Ru is a pseudo-octahedral "piano-stool" type. These half-sandwich complexes of ruthenium(II) have been explored for the transfer hydrogenation of aldehydes and ketones at a moderate temperature of 80 °C. Of the different hydrogen sources (2-propanol, glycerol, formic acid, citric acid, and ascorbic acid) screened for the catalytic TH reaction, 2-propanol and glycerol were found to be the best. With complexes **2** and **3**, catalytic TH with glycerol is slightly less efficient than that with 2-propanol. Complex **3** shows the highest activity, followed by **1** and **4**, which show almost equal activity; **2** shows the least activity of all. The catalytic transfer hydrogenation with the present complexes probably proceeds via formation of a ruthenium hydride as an intermediate. DFT calculations support the experimental results, both catalytic and structural. Complex **3**, which has the lowest energy gap between the HOMO and LUMO, shows the best catalytic activity among the four complexes.

EXPERIMENTAL SECTION

Physical Measurements. The ^{1}H, ^{13}C{^{1}H}, and ^{77}Se{^{1}H} NMR spectra have been recorded on a NMR spectrometer at 300.13, 75.47, and 57.24 MHz, respectively. The C, H, and N analyses were carried out with a C, H, and N analyzer. X-ray diffraction data on single crystals were collected using Mo Kα (0.71073 Å) radiation at 298(2) K. The software SADABS[44a] was used for absorption correction (if needed) and SHELXTL for space group and structure determination and refinements.[44b,c] Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached in all cases. The least-squares refinement cycles were performed until the model converged. High-resolution mass spectral measurements were performed with electron spray ionization (10 eV, 180 °C source temperature, sodium formate as reference compound) with the sample being taken in CH_3CN. The commercial nitrogen gas was used after passing it successively through traps containing solutions of alkaline anthraquinone, sodium dithionite, alkaline pyrogallol, concentrated H_2SO_4, and KOH pellets. A nitrogen atmosphere, if required, was created using Schlenk techniques. Yields refer to isolated yields of compounds, which have purity ≥95% (established by ^{1}H NMR). All reactions were carried out in glassware dried in an oven, under ambient conditions, except for the syntheses of **L1**−**L4**, which were carried under a nitrogen atmosphere.

DFT Calculations. All DFT calculations were carried out at the Department of Chemistry, Supercomputing Facility for Bioinformatics and Computational Biology, IIT Delhi, with the GAUSSIAN-09 program.[45] The geometries of complexes **1**−**4** were fully optimized by using the M06 hybrid functional. This functional has been shown to give more accurate results for organometallic complexes.[43f] For metal and chalcogen atoms, the LANL2DZ[43g] basis set was used, and for C, H, N, and Cl atoms the 6-31G* basis set was used. Natural bond orbital (NBO) analysis of atomic charges was carried out for all complexes **1**−**4** by using the M06 functional.[43h] All DFT calculations were carried out in the gas phase and at 298.15 K. Geometry optimizations have been done without any symmetry restriction by using X-ray coordinates of the molecule. Frequencies of all complexes have been computed at the same level of theory to confirm that all optimized structures are at true minima, which means they have no imaginary frequencies. The molecular orbital plots have been generated using the Chemcraft program package (http://www.chemcraftprog.com). Cartesian coordinates and associated energies are given in the Supporting Information.

Chemicals and Reagents. The reported methods were used for the synthesis of $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$,[46] chloromethyl phenyl selenide,[47] and 1-benzyl-1*H*-benzoimidazole.[47b] Benzimidazole, benzyl bromide, ruthenium(III) trichloride hydrate, chloromethyl phenyl sulfide, diphenyl diselenide, sodium borohydride, and tetrabutylammonium bromide (TBAB) were procured from Sigma-Aldrich (St. Louis, MO, USA) and used as received. All solvents were dried and distilled before use by standard procedures.[48] The common reagents and chemicals available commercially within India were used.

Synthesis of 3-Benzyl-1-((2-phenylselanyl/2-phenylsulfanyl)methyl)-3*H*-benzoimidazolium Chloride (B/C). **A** (0.417 g, 2.0 mmol) was placed in a Schlenk tube equipped with a magnetic stirrer, and chloromethyl phenyl selenide (0.411 g, 2.0 mmol)/chloromethyl phenyl sulfide (0.318 g, 2.0 mmol) was added. The mixture was heated for 8 h at 120 °C under an N_2 atmosphere and thereafter cooled to room temperature. The white solid that was obtained was washed with dry CH_3CN (2 × 40 mL) and dried in vacuo.

*Data for Compound **B**.* Yield: 0.788 g, 95%. ^{1}H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 5.71 (s, 2H, H13), 6.20 (s, 2H, H5), 7.27−7.23 (m, 4H), 7.42−7.36 (m,6H), 7.65−7.63 (m, 2H), 7.95 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 8.08 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 9.85 (s, 1H, H12). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 142.1 (C12), 134.8 (C3), 134.1 (C4), 131.4 (C6), 130.9 (C11), 130.1 (C2), 129.5 (C15), 129.3(C1), 129.2 (C17), 128.6 (C16), 127.5 (C7), 127.1 (C10), 126.8 (C14), 115.2 (C8), 114.6 (C9), 50.2 (C5), 42.4 (C13). ^{77}Se{^{1}H} NMR (CD_3CN, 25 °C, Me_2Se; δ (ppm)): 404.7.

*Data for Compound **C**.* Yield: 0.682 g, 93%. ^{1}H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 5.73 (S, 2H, H13), 6.14 (S, 2H, H5), 7.37−7.24 (m, 10H), 7.70−7.62 (m, 2H), 7.95 (d, $^3J_{H-H}$ = 8.4 Hz, 1H), 8.08 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 9.91 (s, 1H, H of H12). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 142.3 (C12), 134.1 (C4), 132.8 (C3), 131.4 (C6), 130.8 (C11), 130.2 (C2), 129.5 (C15), 129.3 (C1), 129.2 (C17), 128.5 (C16), 127.5 (C7), 127.3 (C10), 115.1 (C8), 114.6 (C9), 51.1 (C5), 50.2 (C13).

Synthesis of L1−L4. White crystalline compound **B** (2.07 g, 5 mmol) or **C** (1.83 g, 5 mmol) was placed in a 250 mL round-bottom flask fitted with a reflux condenser and treated with dry methanol (75 mL), sulfur (0.176 g, 5.5 mmol)/selenium powder (0.44 g, 5.5 mmol), and anhydrous K_2CO_3 (1.38 g, 10 mmol). The reaction mixture was heated to reflux for 24 h. After completion of the reaction, the solvent was evaporated off under reduced pressure on a rotary evaporator. Dichloromethane (20 mL) and water (20 mL) were added to the residue left. The organic layer was separated and washed thoroughly with water (20 mL). It was dried with anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure to give ligands **L1**−**L4** as white crystalline solids.

*Data for Ligand **L1**.* Yield: 2.03 g, 89%. ^{1}H NMR ($CDCl_3$,25 °C vs Me_4Si): δ (ppm) 5.69 (s, 2H, C13), 5.91 (s, 2H, C5), 7.61−7.64 (m, 2H), 7.38−7.31 (m, 5H), 7.28−7.22 (m, 2H), 7.12−7.05 (m, 3H), 6.85−6.82 (m, 1H), 6.85−6.82 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 167.7 (C12), 136.1 (C3), 135.1 (C4), 132.9 (C6), 132.3 (C11), 129.2 (C2), 128.8 (C15), 128.6 (C1), 123.2 (C17), 127.9 (C16), 127.5 (C7), 123.6 (C10), 123.2 (C14), 110.5 (C8), 110.2 (C9), 50.3 (C5), 43.7 (C13). ^{77}Se{^{1}H} NMR (CD_3CN, 25 °C, Me_2Se): δ (ppm) 402.6, 101.8. HR-MS (CH_3CN): $[C_{21}H_{18}N_2NaSe_2]^+$ m/z 480.9696; calculated value for $[C_{21}H_{18}N_2NaSe_2]^+$ 480.9695 (δ 0.3 ppm).

*Data for Ligand **L2**.* Yield: 1.71 g, 84%. ^{1}H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 5.55 (s, 2H, C13), 5.80 (s, 2H, C5), 7.63−7.60 (m, 2H), 7.36−7.22 (m, 8H), 7.13−7.02 (m, 3H), 6.79−6.77 (m, 1H). ^{13}C{^{1}H}NMR ($CDCl_3$, 25 °C vs Me_4Si): 169.8 (C12), 136.0 (C3),

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135.4 (C4), 131.8 (C6), 131.4 (C2), 131.0 (C11), 128.7 (C15), 128.5 (C1), 128.0 (C17), 127.8 (C16), 127.5 (C7), 123.2 (C10), 122.8 (C14), 109.9 (C8), 109.6 (C9), 48.3 (C5), 41.6 (C13). $^{77}Se\{^1H\}$ NMR (CD_3CN, 25 °C, Me_2Se): δ (ppm) 396.21. HR-MS (CH_3CN): $[C_{21}H_{18}N_2NaSSe]^+$ m/z 433.0248; calculated value for $[C_{21}H_{18}N_2NaSSe]^+$ 433.0244 (δ 0.9 ppm).

Data for Ligand ***L3***. Yield: 1.68 g, 82%. ^1H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 5.66 (s, 2H, C13), 5.90 (s, 2H, C5), 7.49−7.47 (m, 2H), 7.30−7.25 (m, 7H), 7.18−7.03 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 168.1 (C12), 135.0 (C4), 134.2 (C3), 132.7 (C6), 132.1 (C11), 132.1 (C2), 129.0 (C15), 129.0 (C1), 128.5 (C17), 127.8 (C16), 127.3 (C7), 123.5 (C10), 123.2 (C14), 110.6 (C8), 110.1 (C9), 51.9 (C5), 50.1 (C13). $^{77}Se\{^1H\}$ NMR (CD_3CN, 25 °C, Me_2Se): δ (ppm) 92.5. HR-MS (CH_3CN): $[C_{21}H_{18}N_2NaSSe]^+$ m/z 433.0248; calculated value for $[C_{21}H_{18}N_2NaSSe]^+$ 433.0238 (δ 2.5 ppm).

Data for Ligand ***L4***. Yield: 1.45 g, 80%. ^1H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 5.51 (s, 2H, C13), 5.76 (s, 2H, C5), 7.46−7.44 (d, $^3J_{H-H}$ = 7.2 Hz, 2H), 7.28−7.19 (m, 8H), 7.07−7.09 (m, 2H), 7.02−6.99 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_4Si): 170.5 (C12), 134.0 (C3), 132.8 (C4), 132.3 (C6), 131.8 (C11), 131.1 (C2), 129.0 (C15), 128.7 (C1), 128.4 (C17), 127.7 (C16), 127.4 (C7), 123.2 (C10), 122.8 (C14), 110.2 (C8), 109.5 (C9), 49.9 (C5), 48.3 (C13). HR-MS (CH_3CN): $[C_{21}H_{18}N_2NaS_2]^+$ m/z 385.0804; calculated value for $[C_{21}H_{18}N_2NaS_2]^+$ 385.0793 (δ −2.8 ppm).

Syntheses of [(η^6-C_6H_6)Ru(L)Cl][PF_6] (1−4). To a solution of **L1** (0.091 g, 0.2 mmol)/**L2** (0.082 g, 0.2 mmol)/**L3** (0.082 g, 0.2 mmol)/**L4** (0.072 g, 0.2 mmol) made up in CH_3OH (5 mL) was added a solution of $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ (0.050 g, 0.1 mmol) in CH_3OH (5 mL). The mixture was stirred for 8 h at room temperature. The resulting orange solution was filtered, and the volume of the filtrate was reduced (∼7 mL) with a rotary evaporator. It was mixed with solid NH_4PF_6 (0.032 g, 0.2 mmol), and the orange microcrystalline solid resulting instantaneously was filtered, washed with 5 mL of ice-cold CH_3OH, and dried in vacuo. Single crystals of each of the four complexes were obtained from a mixture (1/4) of CH_3OH and CH_3CN.

Data for Complex ***1***. Yield: 0.139 g, 84%. Anal. Calcd for $C_{28}H_{26}ClF_6N_2PRuSe_2$: C, 40.52; H, 3.16; N, 4.27. Found: C, 44.86; H, 3.32; N, 6.57. Mp: 190.0 °C. ^1H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 5.50 (s, 2H, C13), 5.72 (s, 6H, Ru-Ar-H), 5.83 (s, 2H, C5), 8.53 (s, 1H), 7.88−7.78 (m, 2H), 7.73−7.68 (m, 2H), 7.44−7.38 (m, 6H), 7.31−7.26 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 140.5 (C12), 135.6 (C3), 132.3 (C4), 131.5 (C11), 130.8 (C2), 129.9 (C15), 129.7 (C1), 129.3 (C17), 128.5 (C16), 127.5 (C7), 127.3 (C10), 125.9 (C14), 114.3 (C8), 113.9(C9), 84.5 (Ru-Ar-C) 50.9 (C5), 42.4 (C13). $^{77}Se\{^1H\}$ NMR (CD_3CN, 25 °C, Me_2Se): δ (ppm) 416.0. HR-MS (CH_3CN): $[C_{21}H_{19}N_2Se]^+$ m/z 379.0709; calculated value for $[C_{21}H_{19}N_2Se]^+$ 379.0715 (δ −1.60 ppm).

Data for Complex ***2***. Yield: 0.138 g, 88%. Anal. Calcd for $C_{28}H_{26}ClF_6N_2PRuSSe$: C, 42.95; H, 3.35; N, 5.53. Found: C, 41.35; H, 3.94; N, 4.22. Mp: 180 °C. ^1H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 5.72 (s, 2H, C13), 5.79 (6H, Ru-Ar-H), 5.87 (s, 2H, C5), 7.61−7.43 (m, 8H), 7.39−7.21 (m, 5H), 7.01−6.98 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 158.9 (C12), 134.6 (C3), 132.9 (C4), 131.1 (C11), 130.9 (C2), 129.6 (C15), 128.8 (C1), 128.4 (C17), 127.7 (C16), 126.1 (C7), 125.3 (C10), 124.9 (C14), 111.2 (C8), 109.7 (C9), 87.0 (Ru-Ar-C), 49.1 (C5), 44.3 (C13). $^{77}Se\{^1H\}$ NMR (CD_3CN, 25 °C, Me_2Se): δ (ppm) 508.2. HR-MS (CH_3CN): $[C_{21}H_{19}N_2Se]^+$ m/z 379.0709; calculated value for $[C_{21}H_{19}N_2Se]^+$ 379.0708 (δ 3.8 ppm).

Data for Complex ***3***. Yield: 0.127 g, 81%. Anal. Calcd for $C_{28}H_{26}ClF_6N_2PRuSSe$: C, 42.95; H, 3.35; N, 5.53. Found: C, 42.63; H, 2.89; N, 5.32. Mp: 185.0 °C. ^1H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 5.76 (6H, Ru-Ar-H), 5.92 (s, 2H, C13), 5.97 (s, 2H, C5), 7.66−7.63 (m, 3H), 7.54−7.49 (m, 6H), 7.46−7.34 (m, 2H), 7.19 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 152.7 (C12), 134.6 (C3), 133.0 (C4), 132.1(C11), 131.9 (C2), 129.7 (C15), 129.1 (C1), 128.7 (C17), 127.9 (C16), 125.7 (C7), 125.5 (C10), 111.8 (C8), 110.1 (C9), 86.2 (Ru-Ar-C), 53.4 (C5), 50.8 (C13). $^{77}Se\{^1H\}$ NMR (CD_3CN, 25 °C, Me_2Se): δ (ppm) −11.3. HR-MS (CH_3CN): $[C_{27}H_{24}N_2RuSSe]^+$ m/z 624.9558; calculated value for $[C_{27}H_{24}ClN_2RuSSe]^+$ 624.9559 (δ −0.1 ppm).

Data for Complex ***4***. Yield: 0.132 g, 90% Anal. Calcd for $C_{28}H_{26}ClF_6N_2PRuS_2$: C, 45.68; H, 3.56; N, 3.81;. Found: C, 45.51; H, 3.87.; N, 6.64. Mp: 205.0 °C. ^1H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 5.92 (s, 2H, C13), 5.97 (6H, Ru-Ar-H), 6.02 (S, 2H, C5), 7.27−7.16 (m, 8H), 7.38−7.30 (m, 3H), 7.50−7.44 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$,25 °C vs Me_4Si): δ (ppm) 167.1 (C12), 135.6 (C3), 132.2 (C4), 132.0 (C11), 131.7 (C6), 128.8 (C2), 128.5 (C15), 128.3 (C1), 128.2 (C17), 127.3 (C16), 123.6 (C7), 123.2 (C10), 111.2 (C8), 110.5 (C9), 87.6 (Ru-Ar-C), 50.7 (C5), 48.9 (C13).

Catalytic Transfer Hydrogenation Reaction in 2-Propanol. Ketone (1 mmol)/aldehyde (1 mmol), KOH (2 mL of a 0.2 M solution in 2-propanol), and one of the complexes **1**−**4** (0.1 mol %) were heated under reflux (80 °C) in 10 mL of 2-propanol for 3 h. Thereafter 2-propanol was removed with a rotary evaporator and the product that formed was extracted with diethyl ether. The solvent from the extract was evaporated off, resulting in a residue which was analyzed with ^1H NMR spectroscopy.

Catalytic Transfer Hydrogenation Reaction in Glycerol. Ketone (1 mmol)/aldehyde (1 mmol), KOH (0.4 mmol) as a solid, and one of the complexes **1**−**4** (0.5 mol %) were heated under reflux (80 °C) in 10 mL of glycerol for 3 h. Thereafter the product that formed was extracted with diethyl ether. The solvent from the extract was evaporated off, resulting in a residue which was analyzed with ^1H NMR spectroscopy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables, figures, and CIF and xyz files giving crystal data and refinement details, bond lengths and angles, secondary interaction figures and distances, NMR and mass spectra, crystallographic data for **1** (CCDC no. 1002221), **2** (CCDC no. 1002222), **3** (CCDC no. 1002223), and **4** (CCDC no. 1002224), bond lengths, frontier orbitals, and Cartesian coordinates for calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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