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(η^5-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

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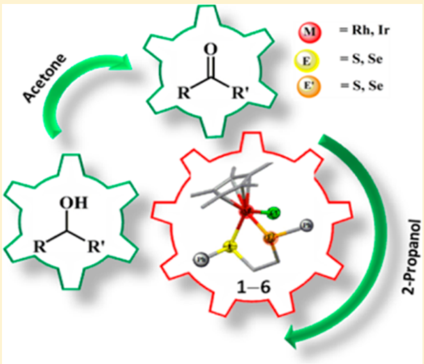
Supporting Information

ABSTRACT: The air- and moisture-insensitive half-sandwich complexes [(η^5-Cp*)Rh(**L**)Cl][PF_6] (**1**−**3**) and [(η^5-Cp*)Ir(**L**)Cl][PF_6] (**4**−**6**) have been prepared by reacting **L** = **L1**−**L3** (1,2-bis(phenylthio)ethane (**L1**), 1-(phenylseleno)-2-(phenylthio)ethane (**L2**) and 1,2-bis(phenylseleno)ethane (**L3**)) with [(η^5-Cp*)RhCl(μ-Cl)]$_2$ and [(η^5-Cp*)IrCl(μ-Cl)]$_2$, respectively, at room temperature followed by treatment with NH_4PF_6. Their HR-MS and ^{1}H, ^{13}C{^{1}H}, and ^{77}Se{^{1}H} NMR spectra have authenticated them. The single-crystal structures of **1**−**6** have been established by X-ray crystallography. Complexes **1**−**6** have been explored for catalytic Oppenauer-type oxidation of alcohols and transfer hydrogenation of ketones with 2-propanol. **3** and **6** were the most efficient in the two catalytic reactions (TON values up to 9.9×10^2 and 9.8×10^3, respectively) and were therefore investigated in detail. **3** is the first example of a Rh(III) species explored for Oppenauer-type oxidation. The catalysis appears to be homogeneous. In transfer hydrogenation it appears that one of the catalytic species is without a Cp* ring. DFT calculations indicate higher reactivity for Rh complexes in comparison to Ir complexes. This order has also been found for the two catalytic reactions experimentally. The calculated bond lengths/angles by DFT are generally consistent with the experimental values.



INTRODUCTION

The diverse applications of chalcogenoethers have been reported in the literature.[1] The transition-metal complexes of mono- and bis(thio-/selenoether) ligands have acquired importance due to their potential applications as models for biological activity,[2a] building blocks for supramolecular framework,[2b] single-source precursors for metal chalcogenide materials,[2c] and catalysts.[2d] The supramolecular chemistry of complexes of chalcogenoethers with all s-, p-, and d-block elements has received much attention.[3] However, bidentate chalcogenoethers explored to design half-sandwich complexes of Rh(III)/Ir(III) suitable for Oppenauer-type oxidation of alcohols and transfer hydrogenation of ketones have not been studied our knowledge. There are few reports known to us in which bis(chalcogenoether) ligands have been reacted with (η^5-Cp*)Rh(III)/Ir(III) to prepare new complexes.[4] The sources of rhodium and iridium for these half-sandwich complexes are the dimers [(η^5-Cp*)RhCl(μ-Cl)]$_2$ and [(η^5-Cp*)IrCl(μ-Cl)]$_2$, respectively, which undergo a rich variety of chemistry via an intermediary chloro bridge cleavage reaction, leading to the formation of a series of interesting neutral and cationic mononuclear complexes.[5]

The Oppenauer-type oxidation of alcohols is interesting, as it does not require a separate oxidant, since non-noxious acetone is used as both an oxidant and a solvent. In the transfer hydrogenation of ketones, 2-propanol is used as the source of hydrogen, which eliminates flammable hydrogen gas.[6] These reactions invariably require catalysts, which therefore have received significant attention.[7] In the transition-metal-catalyzed oxidations of alcohols, oxidizing agents such as *N*-methylmorpholine *N*-oxide (NMO), *tert*-butyl hydroperoxide (*t*BuOOH), sodium oxychloride (NaOCl), sodium periodate ($NaIO_4$), oxygen, and hydrogen peroxide are commonly used.[8] However, the byproducts are not always environmentally friendly. In the Oppenauer-type oxidation of alcohols using acetone as solvent cum oxidant, 2-propanol is a byproduct, which is appealing from both an environmental and an economical point of view. In fact, both acetone and 2-propanol are environmentally friendly[9] and therefore make Oppenauer-type oxidation somewhat green. Some transition-metal complexes have been reported to catalyze Oppenauer-type oxidation.[10] The Ru(II) complexes are efficient catalysts[11] for this purpose, especially bimetallic complexes[11g] with Rh(I), at high temperature and under an inert atmosphere. Some N-heterocyclic carbene (NHC) based (η^5-Cp*)Ir(III) complexes have also been found to be suitable for the Oppenauer-type oxidation of alcohols.[12]

Transfer hydrogenation has emerged as a convenient and versatile method for the reduction of carbonyl compounds;[13] it is an attractive alternative to hydrogenation because it is easy to execute due to the absence of hazardous hydrogen gas and

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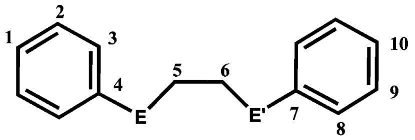
pressure vessels to handle it.[6] Transfer hydrogenation of ketones has been catalyzed by a number of ruthenium species, including half-sandwich complexes.[14] However, Rh and Ir complexes, particularly half-sandwich types containing organochalcogen ligands, have scarcely been explored.[15] Herein, we report the synthesis and single-crystal structural aspects of complexes **1**−**6** of (η^5-Cp*)Rh(III)/Ir(III) with bis(thio-/selenoether) ligands (**L1**−**L3**; Chart 1). Their applications in catalyzing the Oppenauer-type oxidation of alcohols with acetone and transfer hydrogenation of ketones with 2-PrOH have been explored. Reactions of half-sandwich complexes of both Rh(III) and Ir(III) with the Se,Se ligand **L3** have been found to show the highest catalytic efficiency among the present six complexes. All of these results are given in the present paper. Density functional theory (DFT) calculations have been carried out and support the experimental results (both catalysis and structural aspects). It appears that a Rh/Ir species without a Cp* ring also contributes to catalysis of transfer hydrogenation.

Chart 1

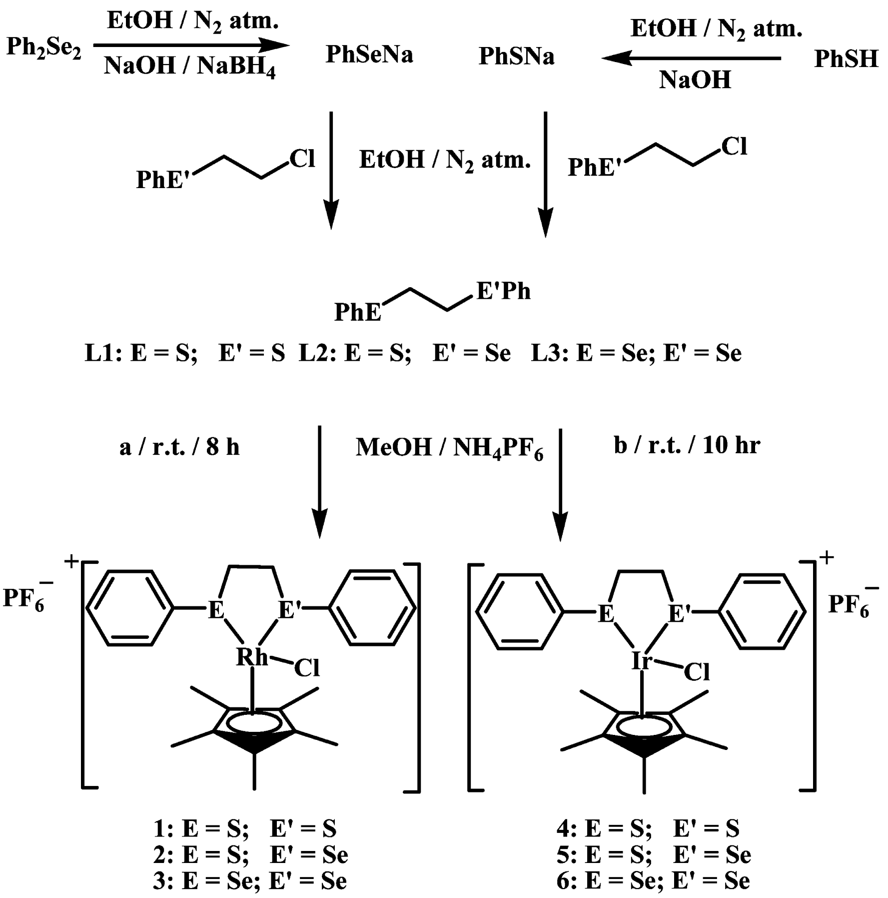


L1: E = S, E' = S L2: E = S, E' = Se L3: E = Se, E' = Se

■ RESULTS AND DISCUSSION

The syntheses of **L1**−**L3** and their complexes are summarized in Scheme 1. Complexes **1**−**6** all appear to be formed by chloro bridge cleavages of [(η^5-Cp*)RhCl(μ-Cl)]$_2$/[(η^5-Cp*)IrCl(μ-Cl)]$_2$ followed by reaction with bis(thio-/selenoether) ligands **L1**−**L3** at room temperature, facilitated due to chloride extraction with NH_4PF_6. The ligand **L2** has been synthesized for the first time. The procedures used for the synthesis of **L1** and **L3** are simpler than those used earlier[2,16] and give a relatively higher yield, ~95%. Ligands **L1**−**L3** have good solubility in the common organic solvents $CHCl_3$, CH_2Cl_2, CH_3OH, and CH_3CN. Complexes **1**−**6** are moderately soluble in solvents such as $CHCl_3$, CH_2Cl_2, and CH_3OH but have good solubility in CH_3CN. The pale yellow liquids **L1**−**L3** are stable under ambient conditions and can be stored at room temperature for several months. The solutions of complexes **1**−**6** made in CH_3CN are also stable for several months under ambient conditions. The elemental analyses and multinuclear NMR, IR, and mass spectral data of **1**−**6** are consistent with single-crystal structures deduced from X-ray diffraction and given below.

Scheme 1. Synthesis of Ligands L1−L3 and Complexes 1−6



a = [(η^5-Cp*)RhCl(μ-Cl)]$_2$; b = [(η^5-Cp*)IrCl(μ-Cl)]$_2$.

Crystal Structures. Crystals of **1**−**6** of suitable quality for X-ray diffraction were obtained by vapor diffusion of diethyl ether into concentrated solutions of these complexes made in a methanol/acetonitrile mixture (1/4 v/v). The crystallographic and refinement data for **1**−**6** are summarized in the Supporting Information (Tables S1 and S2). The crystal system for both the complexes **1** and **4** is orthorhombic. The presence of pseudosymmetry in the structure suggests the higher symmetry space group *Pbca*, but attempts to refine the structure in this space group resulted in unacceptably high *R* and R_w values. Thus, the structures were solved in space group $Pn2_1a$. Consequently, a "B" level pseudosymmetry error appears in their CIFs. Such an observation is not uncommon in the case of an orthorhombic system and was also reported earlier.[17] **L1**−**L3** exhibit identical bonding modes in all of the complexes **1**−**6**: i.e., a five-membered ring is formed on their coordination with both the metal centers. The molecular structure diagrams of the cations of **1**−**6** are given in Figures 1−6, respectively, with selected bond lengths and angles. The H atoms and PF_6^- anions have been omitted for clarity, and ellipsoids are given at the 30% probability level (carbon atoms are in stick forms). In their cations there is a pseudo-octahedral half-sandwich "piano-stool" disposition of donor atoms around Rh/Ir. The centroid of the η^5-Cp* ring occupies nearly the center of a triangular face of an octahedron. A chelate ring with the metal center is formed through chalcogen atoms, and a chlorine atom completes the coordination sphere. This results in an overall three-legged piano-stool conformation.

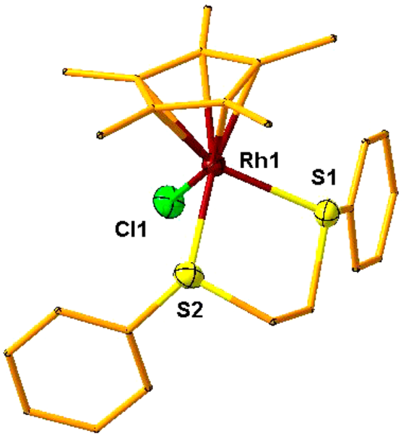


Figure 1. Structure of the cation of **1**. Bond lengths (Å): Rh(1)−S(1) 2.380(2), Rh(1)−S(2) 2.386(2), Rh(1)−Cl(1) 2.3702(14), Rh−C 2.140(6)−2.203(7). Bond angles (deg): S(1)−Rh(1)−S(2) 86.52(5), S(1)−Rh(1)−Cl(1) 90.35(7), S(2)−Rh(1)−C1(1) 93.71(7).

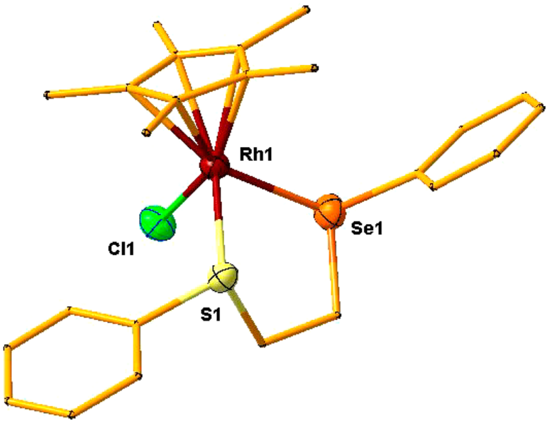


Figure 2. Structure of the cation of **2**. Bond lengths (Å): Rh(1)−Se(1) 2.5037(10), Rh(1)−S(1) 2.3692(19), Rh(1)−Cl(1) 2.4090(19), Rh−C 2.144(8)−2.136(9). Bond angles (deg): S(1)−Rh(1)−Se(1) 84.47(6), S(1)−Rh(1)−Cl(1) 94.15(7), Se(1)−Rh(1)−C1(1) 81.02(6).

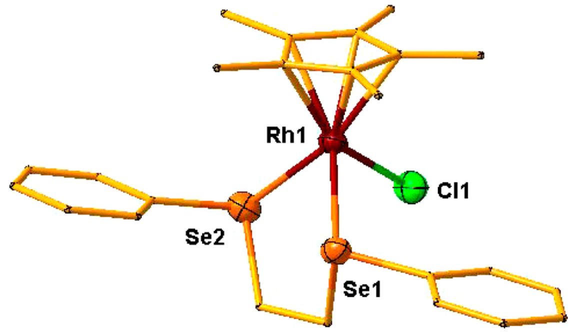


Figure 3. Structure of the cation of **3**. Bond lengths (Å): Rh(1)−Se(1) 2.4579(13), Rh(1)−Se(2) 2.4864(12), Rh(1)−Cl(1) 2.408(2), Rh−C 2.148(9)−2.189(9). Bond angles (deg): Se(1)−Rh(1)−Se(2) 84.25(4), Se(1)−Rh(1)−Cl(1) 94.25(8), Se(2)−Rh(1)−C1(1) 80.98(6).

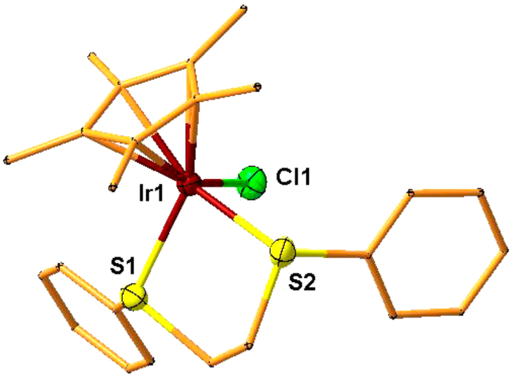


Figure 4. Structure of the cation of **4**. Bond lengths (Å): Ir(1)−S(1) 2.3559(18), Ir(1)−S(2) 2.3422(18), Ir(1)−Cl(1) 2.3712(9), Ir−C 2.183(7)−2.191(6). Bond angles (deg): S(1)−Ir(1)−S(2) 86.83(4), S(1)−Ir(1)−Cl(1) 89.89(7), S(2)−Ir(1)−C1(1) 92.71(7).

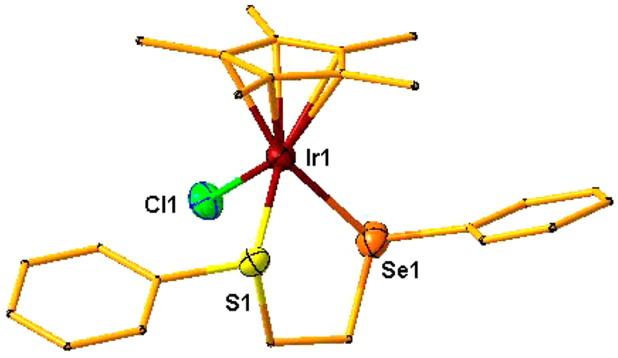


Figure 5. Structure of the cation of **5** .Bond lengths (Å): Ir(1)−Se(1) 2.4892(9), Ir(1)−S(1) 2.3553(17), Ir(1)−Cl(1) 2.4101(18), Ir−C 2.144(9)−2.185(10). Bond angles (deg): S(1)− Ir(1)−Se(1) 84.97(5), S(1)−Ir(1)−Cl(1) 93.26(7), Se(1)−Ir(1)−C1(1) 80.19(6).

The Rh−S bond distances in **1** (2.380(2) and 2.386(2) Å) and **2** (2.3692(19) Å) are of the same order and are consistent with the values reported for $[(\eta^5\text{-Cp*})\text{RhCl}(1,1'\text{-}(1,2\text{-}$

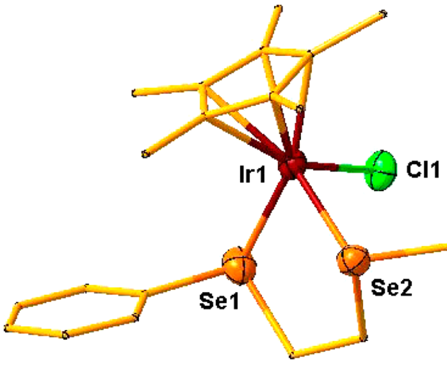


Figure 6. Structure of the cation of **6**. Bond lengths (Å): Ir(1)−Se(1) 2.4863(8), Ir(1)−Se(1) 2.4455(8), Cl(1)−Ir(1) 2.4059(16), Ir−C 2.187(8)−2.186(7). Bond angles (deg): Se(1)−Ir(1)−Se(2) 85.77(3), Se(1)− Ir(1)−Cl(1) 80.12(5), Se(2)−Ir(1)−C1(1) 92.86(5).

ethanediyl)bis(3-methylimidazole-2-thione)]Cl (2.3967(11) Å)[18] and [(η^5-Cp*)RhCl{2-(phenylthiomethyl)pyridine}]PF_6 (2.383(2) Å).[15] The Rh−Se bond lengths of **2** (2.5037(10) Å) and **3** (2.4579(13) and 2.4864(12) Å) are shorter than that of [η^5-Cp*RhCl{η^2-$(SePPh_2)_2N$}]BF_4 (2.5266(8) Å)[19] but consistent with the value 2.487(1) Å reported for a half-sandwich complex of Rh(III) with 2-(phenylselenomethyl)-pyridine.[15] The Rh−C(Cp* centroid) distances (1.794−1.809 Å) of complexes **1**−**3** are normal.[20]

The Ir−S bond distances for **4** (2.3559(18) and 2.3422(18) Å) and **5** (2.3553(17) Å) are similar and fall in the range 2.318(1)−2.3872(10) Å, in which Ir−S bond lengths of [η^5-Cp*Ir(CO)(μ-STol)Pt(STol)(PPh_3)],[21] [η^5-Cp*Ir(η^2-ppy-S-*p*-tol)(H_2O)][OTf]$_2$,[22] [η^5-Cp*Ir(4,6-di-*tert*-butyl-(2-methylthiophenylimino)-*o*-benzoquinone]$(PF_6)\cdot CH_2Cl_2$[23] and [η^5-Cp*Ir-(*n*BuPPh$_2$)({7-(S)PPh$_2$}-8-S-7,8-$C_2B_9H_{10}$)][24] have been reported. The Ir−Se distances in **5** (2.4892(9) Å) and **6** (2.4863(8) and 2.4455(8) Å) are somewhat longer than the values reported for [η^5-Cp*Ir{$Se_2C_2(CO_2Me)_2$}] (2.3494(7) and 2.3520(7) Å).[25] The Ir−Se bond lengths of [η^5-Cp*IrCl(μ-SeCOC$_6H_5$)(κ^2-SeCOC$_6H_4$−)Ir(η^5-Cp*)] (2.445(2)−2.495(1) Å)[26] and [η^5-Cp*Ir(μ^3-Se)$_2${PtTol(PPh_3)}$_2$] (2.416(1)−2.422(1) Å)[21] are consistent with those of **5** and **6**. The Ir−η^5-Cp*(centroid) distances in **4**−**6** (1.814−1.820 Å) are consistent with the reported values for complexes [(η^5-Cp*)Ir(phpy)Cl] (1.863 Å).[27] The PF_6^- anion has been found to be involved in C−H···F secondary interactions in each of the complexes **1**−**6**, resulting in chains and sometimes a helical pattern (Figure 7). The secondary interactions and H···F distances for other complexes are given in the Supporting Information (Figures S1−S6 and Table S5).

Spectral Data. The signals in $^{77}Se\{^1H\}$ NMR spectra of **2**, **3** and **5**, **6** appear shifted to a higher frequency by ~65 ppm (Supporting Information, Figures S13−S18) in comparison to these of free **L2** and **L3**, due to their coordination with Rh/Ir through Se. Two signals observed in the $^{77}Se\{^1H\}$ NMR spectra of **3** and **6** are due to diastereomers. In the ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**−**6** signals of protons and carbon atoms generally appear at higher frequencies relative to those of free ligands which coordinate with Rh and Ir in a bidentate mode. The magnitude of shift to higher frequency is large for $(E)CH_2CH_2(E')$ (E = E′ = S, Se; E/E′ = S/Se): up to 10.1 ppm in $^{13}C\{^1H)$ NMR and, for protons attached to them, up to 0.82 ppm. In the ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**−**3** the signals of the η^5-Cp* group (two singlets in ^1H NMR) were found shifted to lower frequency (maximum shifts ~0.3 and 2.1 ppm, respectively) with respect to those of [(η^5-Cp*)RhCl(μ-Cl)]$_2$. The substitution of Cl with less electronegative S and Se appears to be the reason for it. Similar shifting of Cp* signals of

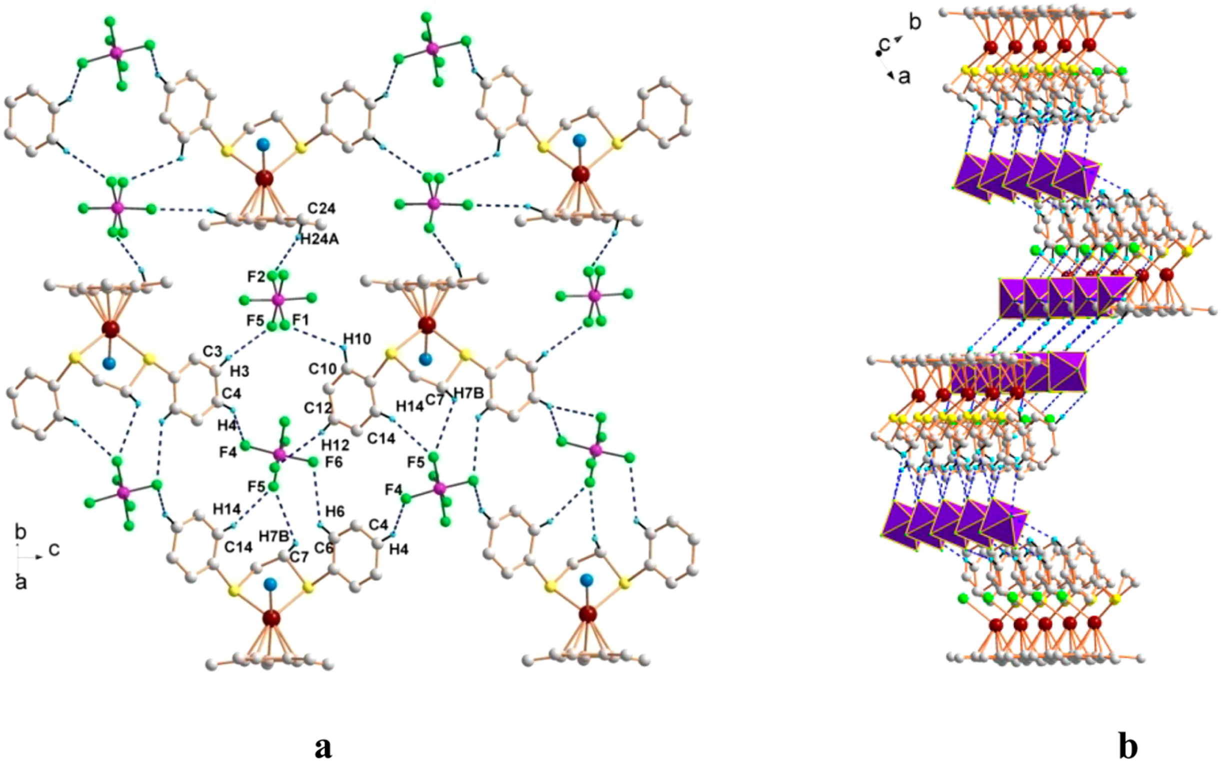


Figure 7. (a) Noncovalent C−H···F interactions in **1**. (b) Helical chain formed in the crystal of **1** by noncovalent interactions.

4–**6** with respect to those of $[(\eta^5\text{-Cp*})\text{IrCl}(\mu\text{-Cl})]_2$ were observed in their ^{1}H and ^{13}C{^{1}H} NMR spectra.

HRMS spectra of complexes **1**–**6** indicate that chloride in all of them is considerably labile, and consequently a molecular ion peak is not observed in any case. The peak of the species $[\text{M} - \text{Cl}]^+$ has been observed in the spectra of all complexes **1**–**6** (Supporting Information, Figures S7–S12). In some spectra the peak of the fragment $[(\eta^5\text{-Cp*})\text{MCl}]^+$ (M = Rh, Ir) has also been observed.

Scheme 2. Transfer Hydrogenation of Ketones

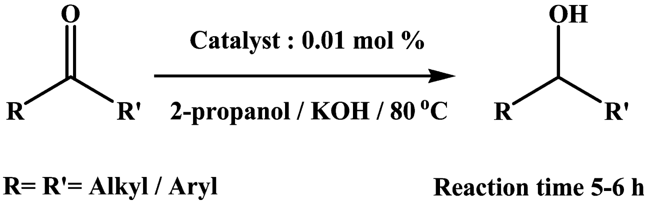


Table 2. Effect of Catalyst Loading on TON and TOF for Transfer Hydrogenation of Acetophenone Catalyzed by 3 and 6[a]

entry	amt of catalyst (mol %)	time (h)	conversion (%)[b]	TON	TOF (h^{-1})
1[c]	5	0.50	99	19.8	40
2[d]	5	0.50	92	18.4	37
3[d]	5	0.75	99	19.8	26
4[c]	1	1.5	96	96	64
5[d]	1	1.5	85	85	57
6[d]	1	2	95	95	48
7[c]	0.1	3	98	980	327
8[d]	0.1	3	88	880	293
9[d]	0.1	4	98	980	245
10[c]	0.01	5	98	9800	1960
10[d]	0.01	5	90	9000	1800
11[d]	0.01	6	98	9800	1634
12[c]	0.001	10	95	95000	9500
13[d]	0.001	10	85	85000	8500
14[d]	0.001	15	94	94000	6267

[a] Conditions: 1 mmol of acetophenone, 10 mol % of KOH, 15 mL of 2-propanol, 80 °C, in air. [b] Determined by NMR. [c] Rh complex **3**. [d] Ir complex **6**.

Catalytic Studies. *Transfer Hydrogenation of Ketones.* Transfer hydrogenation of ketones (Scheme 2) using 2-propanol as the hydrogen donor catalyzed with present complexes **1**–**6** (0.01 mol %) (5 h with **1**–**3** and 6 h with **4**–**6**) at the moderate temperature of 80 °C has been explored. The reduction of ketones to the corresponding alcohols occurs in the presence of KOH, which was reported earlier to be the best inorganic base for such reactions.[28] The most efficient conversions (up to 98%) were found in the case of acetophenone with all of the complex catalysts, while in the case of aliphatic ketones the conversions were up to 93%. The complexes of the Se,Se ligand were found to be somewhat more efficient as catalysts than the corresponding S,S/S,Se analogues, as for the substrate cyclopropanone TON values were found to be 8000, 8500, 9300, 8000, 8400, and 9000, respectively, for complexes **1**–**6**. Thus, detailed investigations were carried out for complexes **3** and **6**. The percent conversions and TONs are given in Table 1. Using 5 mol % of catalyst **3**, 99% conversion may be achieved in 30 min (Table 2). The conversions do not significantly improve when the reaction time is increased from 5–6 to 10 h with 0.01 mol % loading of catalyst. In comparison to the amounts of most other Rh and Ir species reported for transfer hydrogenation (TH), the mole percent loading required in the case of **3** and **6** is only one tenth or lower.[29] When the transfer hydrogenation reactions catalyzed with **3** and **6** are monitored with ^{77}Se{^{1}H} NMR spectroscopy, it is observed that the signals in the spectra shift to higher frequency (20–25 ppm), indicating that probably the M–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 M–H bond can take place.[30] The transfer hydrogenation reactions catalyzed with **3** and **6** were also monitored with ^{1}H NMR spectra. After 1 h a broad singlet was noticed around δ −9.8 and −13.1 ppm, respectively. These signals are characteristic of hydrides and indicate the formation

Table 1. Catalytic Applications of Complexes 3 and 6

transfer hydrogenation of ketones[a]			Oppenauer-type oxidation of alcohols[c]		
	TON (conversion (%))[b]			TON (conversion (%))[b]	
substrate	3	6	substrate	3	6
cyclopentanone	9300 (93)	9000 (90)	cyclopentanol	900 (90)	880 (88)
cyclohexanone	9200 (92)	9200 (92)	cyclohexanol	910 (961)	900 (90)
acetophenone	9800 (98)	9800 (98)	benzyl alcohol	920 (92)	920 (92)
propiophenone	9600 (96)	9600 (96)	4-methoxybenzyl alcohol	980 (98)	980 (98)
benzophenone	9600 (96)	9600 (96)	4-methylbenzyl alcohol	900 (90)	880 (88)
4-methylacetophenone	9400 (94)	9400 (94)	4-chlorobenzyl alcohol	820 (82)	800 (80)
4-chloroacetophenone	9600 (96)	9500 (95)	1-phenylethanol	980 (98)	950 (95)
2-octanone	8600 (86)	8500(85)	benzhydrol	900 (96)	900 (90)
2-pentanone	8800 (88)	8800 (88)	1-phenylpropanol	910 (91)	920 (92)
			1-(4-methylphenyl)ethanol	920 (92)	940 (94)
			1-(4-chlorophenyl)ethanol	850 (85)	800 (80)
			2-octanol	900 (90)	910 (91)
			2-pentanol	990 (99)	990 (99)

[a] Conditions: 1 mmol of substrate (ketone), 10 mol % of KOH, catalyst 0.01 mol %, 15 mL of 2-propanol, 80 °C, time 5 h for **3** and 6 h for **6**, in air. [b] Conversion determined by NMR. [c] Conditions: 1 mmol of substrate (alcohol), 15 mL of acetone (0.1% water), catalyst 0.1 mol %, 1.5 mmol of K_2CO_3, 80 °C, time 5 h for **3** and 7 h for **6**, in air.

of a M−H bond.[12] Thus, catalytic reactions with the present complexes probably proceed via formation of a metal hydride complex intermediate. In ^{1}H NMR spectra recorded while transfer hydrogen is progressing in the presence of any of **1**−**6** a small signal appears around 1.91 ppm, which is possibly due to free Cp*, as it is not observed in the ^{1}H NMR spectrum of any of these complexes. This indicates that probably a species generated with the loss of Cp* (most likely as $[(Solv)_nML]^{3+}$) is also present during catalysis.[31] In the case of transfer hydrogenation catalyzed with the Ru(II)−arene system the loss of arene and participation of ringless species in catalysis has been recently proposed.[32] It is possible that a similar thing is happening in the present case, as some role of $[(Solv)_nML]^{3+}$ in catalysis cannot be ruled out. However, the formation of its dimer and its role in catalysis is ruled out, as the TOF increases with lower amounts of catalyst.

The catalytic efficiency varies with chalcogen donor sites in the ligand. It varies in the order Se,Se > Se,S > S,S when the other coligands are the same and may be tailored by a stronger electron-donating tendency of Se toward the metal center, thus promoting the formation of hydride with it. The formation of an M−H-containing intermediate and the absence of NH group (essential for the Noyori mechanism[6]) in the ligand system suggest that transfer hydrogenation by **1**−**6** is catalyzed by a conventional mechanism:[13] i.e., via alkoxide formation. The Rh(III) species appear to be better catalysts than those of Ir(III) (Table 2), as in the case of Ir complexes for conversions comparable with those of Rh analogues with the same catalyst loading, the reaction time needed is somewhat longer.

Oppenauer-Type Oxidation of Alcohols. The Oppenauer-type oxidation of alcohols in the presence of **1**−**6** (0.1 mol %) (Scheme 3) using acetone as an oxidant at 80 °C in the presence of K_2CO_3 has been studied. Maximum conversions were reached in 5 h with catalysts **1**−**3** and in 7 h with catalysts **4**−**6** (Scheme 3). As for transfer hydrogenation, the catalytic efficiency follows the order Se,Se > Se,S > S,S when the other coligands are the same. For example, TON values for oxidation of 1-phenylethanol are 840, 900, 980, 750, 800, and 880, respectively, for **1**−**6**. Thus, detailed investigations were carried out with **3** and **6**. The percent conversions and TON values have been summarized in Table 1. A conversion of 99% is obtained in 15 min if a catalyst loading of 5 mol % is used (Table 3). The representative catalytic reactions in the presence of **3** and **6** have been monitored by ^{77}Se{^{1}H} and ^{1}H NMR. The signals in ^{77}Se{^{1}H} NMR spectra have been found to be shifted to higher frequency (21−28 ppm) in the course of the reaction. In ^{1}H NMR spectra new signals at δ −9.1 and −12.5 ppm have been found to appear in the course of catalysis with **3** and **6**, respectively. These signals may be ascribed to the formation of metal hydride species.[12] Therefore, the oxidation of alcohols appears to be catalyzed by **1**−**6** via the pathway suggested in Scheme 4. The greater catalytic efficiency of **3** and **6** relative to other complexes may be tailored by a stronger electron-donating tendency of Se toward the metal center, thus promoting the formation of hydride with it. Similarly, Rh(III) species are somewhat better catalysts than Ir(III) species. This has been corroborated by the fact that more time is needed in the case of Ir complexes to get conversions comparable to those of Rh species (Table 3).

Scheme 3. Oppenauer-Type Oxidation of Alcohols

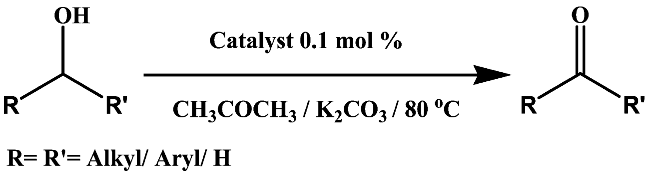
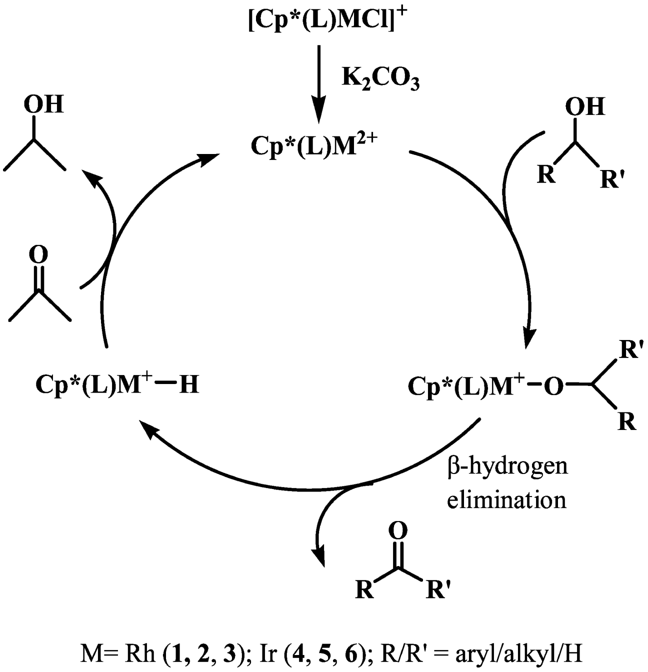


Table 3. Effect of Catalyst Loading on TON and TOF for Oxidation of 1-Phenylethanol Catalyzed by 3 and 6[a]

entry	amt of catalyst (mol %)	time (h)	conversion (%)[b]	TON	TOF (h^{-1})
1[c]	5	0.25	99	19.8	79
2[d]	5	0.25	88	17.6	70
3[d]	5	0.50	98	19.6	39
4[c]	1	1	99	99	99
5[d]	1	1	85	85	85
6[d]	1	1.5	96	96	64
7[c]	0.1	5	98	980	327
8[d]	0.1	5	88	880	293
9[d]	0.1	7	95	950	238
10[c]	0.01	10	92	9200	920
10[d]	0.01	10	76	7600	760
11[d]	0.01	12	88	8800	733
12[c]	0.001	30	95	9500	317
13[d]	0.001	30	85	8500	283
14[d]	0.001	35	94	9400	269

[a] Conditions: 1 mmol of 1-phenylethanol, 15 mL of acetone (0.1% water), 1.5 equiv of K_2CO_3, 80 °C, in air. [b] Determined by NMR. [c] Rh complex **3**. [d] Ir complex **6**.

Scheme 4. Proposed Mechanism of Oppenauer-Type Oxidation of Alcohols



3 is the first example of an Rh(III) species explored for Oppenauer-type oxidation. In comparison to other Ir and Ru species the required mole percent loading of **6** (for an almost similar reaction time) is lower or comparable.[11,12]

Homogeneous vs Heterogeneous Transfer Hydrogenation Catalysis. It has been reported that transfer hydrogenation in glycerol catalyzed with iridium complexes under microwave conditions results in the formation of Ir NPs which have a negative effect on the catalytic process.[33] It is possible that such metal NPs are formed with the present complexes also and make some contribution to catalysis. Thus, it is important to understand whether the present transfer hydrogenation catalysis is homogeneous or heterogeneous, and a mercury poisoning test[34] has been executed for this purpose. The mercury poisoning test with acetophenone in 2-propanol using catalysts **3** and **6** showed no significant inhibition of conversion to products (Table 4). Thus, the present catalysis appears to be homogeneous in nature. The PPh_3 poisoning test has also been used.[35] In the presence of 5 equiv of PPh_3 the reaction occurs with only a 6% decrease in percent conversion (Table 5). This supports the homogeneous nature of catalysis, as inferred from the Hg test. There was also no visible sign of formation of NPs.

Table 4. Mercury Test for Catalytic Transfer Hydrogenation[a]

entry	catalyst/Hg	time (h)	conversion (%)[b]
1[c]	1/0	3	98
2[d]	1/0	3	88
3[c]	1/400	3	90
4[d]	1/400	3	82

[a]Conditions: 1 mmol of acetophenone, 10 mol % of KOH, 15 mL of 2-propanol, catalyst 0.1 mol %, 80 °C, in air. [b]Determined by NMR. [c]Rh complex **3**. [d]Ir complex **6**.

Table 5. PPh_3 Poisoning Test for Catalytic Transfer Hydrogenation[a]

entry	catalyst/PPh_3	time (h)	conversion (%)[b]
1[c]	1/0	3	98
2[d]	1/0	3	88
3[c]	1/5	3	92
4[d]	1/5	3	85

[a]Conditions: 1 mmol of acetophenone, 10 mol % of KOH, 15 mL of 2-propanol, catalyst 0.1 mol %, 80 °C, in air. [b]Determined by NMR. [c]Rh complex **3**. [d]Ir complex **6**.

DFT Calculations. Density functional theory (DFT) calculations (see the Experimental Section for details) were performed on all six complexes **1**–**6**. The HOMOs (highest occupied molecular orbitals) of all complexes are essentially similar and are positioned primarily over the Rh or Ir and the Cp* ring, with some contribution of S or Se and Cl donor atoms. The d orbitals of Rh(III)/Ir(III) interacting with π orbitals of the η^5-Cp* ring and the p orbital of chlorine and chalcogen atoms constitute these HOMOs (see the Supporting Information Figures S19 and S20). The calculated bond lengths/angles are given in Table 6. The agreement between the experimentally observed bonding parameters and the calculated values is better for M–Cl and M–Cp*(centroid). The difference between calculated and observed M–E (E = S, Se) bond distances in some cases is ~0.03 Å. The calculated and experimentally found bond angles are generally close (Table 6), except in a few cases: e.g., S1–Rh–S2 and S1–Ir–S2.

The HOMO/LUMO energies of a complex may be correlated to some extent to its chemical reactivity.[36] The LUMO has a higher energy than the HOMO in **1**–**6** and also varies more with the complex. Therefore, it may be involved more intimately in the catalytic process (probably in an associative manner) and may cause reactivity differences. The HOMO–LUMO energy gaps of Rh complexes are smaller than those of Ir complexes (see Table 7), and their variation is contributed more by the LUMO, which suggests that this energy gap may be correlated to catalytic activity: that is, a small gap in Rh complexes relative to Ir analogues may result in higher reactivity for the former. As the LUMO is antibonding between Cp* and metal, an increase of its electron density may be responsible for dissociation of Cp*. The DFT calculations have placed more negative natural bond orbital atomic charge on Rh (see Figures S20 and S21 (Supporting Information) and Table 7), which may facilitate hydride formation. The M–H formation is generally considered as the rate-determining step, and therefore charge may be a controlling influence. This observation is consistent with the higher activity of Rh species in comparison to Ir species.

CONCLUSION

The half-sandwich "piano-stool" complexes $[(\eta^5\text{-Cp*})\text{Rh}(\mathbf{L})\text{Cl}][\text{PF}_6]$ and $[(\eta^5\text{-Cp*})\text{Ir}(\mathbf{L})\text{Cl}][\text{PF}_6]$ (**1**–**6**) of bis(thio-/selenoether) ligands (**L** = **L1**–**L3**) have been synthesized and characterized by multinuclear NMR, HR-MS, and X-ray crystallography . The complexes are the first examples of half-sandwich complexes of rhodium(III)/iridium(III) with S,S, S,Se, and Se,Se ligands explored for the transfer hydrogenation of ketones and Oppenauer-type oxidation of alcohols. They show promising TON values (transfer hydrogenation reactions of ketones of up to 9.8×10^3, oxidation of alcohols of up to 9.9×10^2). Further, **3** is the first example of a Rh(III) species explored for Oppenauer-type oxidation. Their air and moisture stability is an additional advantage. The catalytic efficiencies follow the orders Rh > Ir and Se,Se > Se,S > S,S. The higher catalytic efficiency of Rh species appears to be consistent with DFT calculations.

EXPERIMENTAL SECTION

Physical Measurements. IR spectra in the range 4000–400 cm^{-1} were recorded on a Nicolet Protége 460 FT–IR spectrometer as KBr pellets. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 Series II C, H, and N analyzer. High-resolution mass spectral measurements were performed with electron spray ionization (10 eV, 180 °C source temperature, sodium formate as reference compound) on a Bruker MIcroTOF-Q II instrument, the sample being taken in CH_3CN. The ^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, and 57.24 MHz, respectively. The chemical shifts are given in ppm relative to known standards. Yields refer to isolated yields of compounds which have purity ≥95% (established by ^1H NMR). All reactions have been carried out in glassware dried in an oven, under ambient conditions, except for the synthesis of **L1**–**L3**. A nitrogen atmosphere, if required, was created using Schlenk techniques. 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. For single-crystal structures the data were collected on a Bruker AXS SMART Apex CCD diffractometer using Mo Kα (0.71073 Å) radiation at 298(2) K. The software SADABS[37] was used for absorption correction (if needed) and SHELXTL for space group, structure determination, and refinements.[38] 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.

Chemical and Reagents. Diphenyl diselenide, thiophenol, $NaBH_4$, chloroethanol, and ammonium hexafluorophosphate procured

Table 6. Comparison of Selected Bond Lengths (Å) and Angles (deg) of 1−6 Determined Experimentally and Calculated by DFT

1			2			3		
	bond angle/ length	optimized value		bond angle/ length	optimized value		bond angle/ length	optimized value
Rh−S(1)	2.380(2)	2.558	Rh−Se(1)	2.5037(10)	2.585	Rh−Se(1)	2.4579(13)	2.564
Rh−Cl(1)	2.3702(14)	2.425	Rh−Cl(1)	2.4090(19)	2.440	Rh−Cl(1)	2.408(2)	2.442
Rh−S(2)	2.3702(14)	2.524	Rh−S(1)	2.3692(19)	2.515	Rh−Se(2)	2.4864(12)	2.587
Rh−C[a]	1.809(0)	1.807	Rh−C[a]	1.806(1)	1.821	Rh−C[a]	1.794(3)	1.827
S1−Rh−S2	86.52(5)	78.54	Se1−Rh−S1	84.47(6)	83.24	Se1−Rh−Se2	84.25(4)	83.58
S1−Rh−Cl	90.35(7)	93.78	Se1−Rh−Cl	81.02(6)	79.81	Se1−Rh−Cl	94.25(8)	93.36
Cl−Rh−S2	93.71(7)	92.03	Cl−Rh−S1	94.15(7)	92.40	Cl−Rh−Se2	80.98(6)	80.72
4			5			6		
	bond angle/ length	optimized value		bond angle/ length	optimized value		bond angle/ length	optimized value
Ir−S(1)	2.3559(18)	2.524	Ir−Se(1)	2.4892(9)	2.595	Ir−Se(1)	2.4863(8)	2.591
Ir−Cl(1)	2.3712(9)	2.426	Ir−Cl(1)	2.4101(18)	2.449	Ir−Cl(1)	2.4059(16)	2.451
Ir−S(2)	2.3422(18)	2.562	Ir−S(1)	2.3553(17)	2.514	Ir−Se(2)	2.4455(8)	2.568
Ir−C[a]	1.818(0)	1.797	Ir−C[a]	1.814(0)	1.807	Ir−C[a]	1.820(1)	1.814
S1−Ir−S2	86.83(4)	79.15	Se1−Ir−S1	84.97(5)	81.93	Se1−Ir−Se2	85.77(3)	83.32
S1−Ir−Cl	89.89(7)	91.60	Se1−Ir−Cl	80.19(6)	80.20	Se1−Ir−Cl	80.12(5)	79.84
Cl−Ir−S2	92.71(7)	89.58	Cl−Ir−S1	93.26(7)	90.98	Cl−Ir−Se2	92.86(5)	92.07

[a] C = centroid of Cp*.

Table 7. HOMO−LUMO Energy Gap of 1−6 and Natural Bond Orbital (NBO) Analysis of Atomic Charge

		NBO atomic charge			
complex	energy gap (eV)	metal	chalcogen E	chalcogen E′	Cl
1	3.7552	−0.197	+0.437	+0.463	−0.401
2	3.8254	−0.288	+0.457	+0.795	−0.394
3	3.7644	−0.376	+0.738	+0.798	−0.398
4	4.4333	−0.114	+0.478	+0.469	−0.380
5	4.4632	−0.220	+0.478	+0.810	−0.380
6	4.4148	−0.324	+0.816	+0.757	−0.377

from Sigma−Aldrich (USA) were used as received. (2-Chloroethylthio)benzene,[39] (2-chloroethylseleno)benzene,[40] $[(\eta^5\text{-Cp*})\text{RhCl}(\mu\text{-Cl})]_2$,[41] and $[(\eta^5\text{-Cp*})\text{IrCl}(\mu\text{-Cl})]_2$[42] were prepared according to literature methods. All of the solvents were dried and distilled before use by standard procedures.[43] Common reagents and chemicals available locally were used.

DFT Calculations. All DFT calculations were carried out at the Department of Chemistry, Supercomputing Facility for Bioinformatics and Computational Biology, IIT Delhi, with the GAUSSIAN-09 program,[44] with an immediate objective of understanding the present complexes. The geometry of complexes **1**−**6** was optimized at the M06[45] level using a LANL2DZ[46] basis set for metal and chalcogen atoms and 6-31G* basis sets for C, H, and Cl. Natural bond orbital (NBO) analysis of atomic charges was carried out for all compounds **1**−**6** by using the M06 functional.[45] All calculations were carried out in the gas phase and at 298.15 K. Geometry optimizations were carried out without any symmetry restriction with X-ray coordinates of the molecule. Harmonic force constants were computed at the optimized geometries to characterize the stationary points as minima. The molecular orbital plots were made using the Chemcraft program package (http://www.chemcraftprog.com). Cartesian coordinates and associated energies are given in the Supporting Information (Table S6).

Synthesis of Ligands L1 and L2. Sodium hydroxide (0.224 g, 6 mmol) dissolved in 5 cm^3 of water was added dropwise to thiophenol (0.5 mL, ~5 mmol) taken up in 50 cm^3 of dry ethanol and refluxed for 0.5 h under an N_2 atmosphere. (2-Chloroethylthio)benzene/(2-chloroethylseleno)benzene (5 mmol) dissolved in 20 cm^3 of ethanol was added dropwise, and the refluxing of the mixture was continued further for 3 h. After it was cooled to room temperature, the mixture was poured into 100 cm^3 of distilled water, neutralized with dilute sodium hydrochloride, and extracted with 100 cm^3 of chloroform. The extract was washed with water (3 × 50 cm^3) and dried over anhydrous sodium sulfate. Its solvent was evaporated off under reduced pressure on a rotary evaporator, resulting in **L1**/**L2** as a pale yellow oil.

Ligand L1. Yield: 1.15 g, ~95%. ^{1}H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 3.08 (s, 4H, H_5, H_6), 7.22−7.30 (m, 6H, H_{1-2}, H_{9-10}), 7.49−7.65 (m, 4H, H_3, H_8). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 33.4 (C_5, C_6), 126.0 (C_1, C_{10}), 127.9 (C_4, C_7), 129.1 (C_2, C_9), 132.9 (C_3, C_8). IR (KBr, cm^{-1}): 3038 (m; $\nu_{C-H(aromatic)}$), 2952 (s; $\nu_{C-H(aliphatic)}$), 1490 (m; $\nu_{C=C(aromatic)}$), 764 (m; $\nu_{C-H(aromatic)}$).

Ligand L2. Yield: 1.30 g, 91%. ^{1}H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 3.01−3.08 (m, 2H, H_6), 3.12−3.19 (m, 2H, H_5), 7.16−7.26 (m, 6H, H_{1-2}, H_{9-10}), 7.44−7.61 (m, 4H, H_3, H_8). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 26.5 (C_6), 34.2 (C_5), 126.5 (C_1), 127.3 (C_{10}), 129.0 (C_2), 129.2 (C_9), 130.0 (C_2), 131.6 (C_7), 133.2 (C_8), 135.1 (C_7). ^{77}Se{^{1}H}NMR (CD_3CN, 25 °C vs Me_2Se): δ (ppm) 321.73. IR (KBr, cm^{-1}): 3076 (m; $\nu_{C-H(aromatic)}$), 2992 (s; $\nu_{C-H(aliphatic)}$), 1483 (m; $\nu_{C=C(aromatic)}$), 775 (m; $\nu_{C-H(aromatic)}$).

Synthesis of L3. Diphenyl diselenide (0.6245, 2.0 mmol) dissolved in 30 cm^3 of ethanol was treated with a solution (made in 5% NaOH) of $NaBH_4$ (0.149 g, 4.0 mmol; added dropwise) under an N_2 atmosphere until it become colorless due to the formation of PhSeNa. (2-Chloroethylseleno)benzene (0.878 g, 4.0 mmol) dissolved in 5 cm^3 of ethanol was added to the colorless solution with constant stirring. The reaction mixture was stirred further for 3−4 h and poured into 100 cm^3 of ice-cold distilled water and extracted with $CHCl_3$ (5 × 40 cm^3). The extract was washed with water (3 × 50 cm^3) and dried over anhydrous sodium sulfate. Its solvent was evaporated off under reduced pressure on a rotary evaporator, resulting in **L3** as a pale yellow oil. Yield: 1.25 g, 92%. ^{1}H NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 3.16 (s, 4H, H_5, H_6), 7.26−7.28 (m, 4H, H_2, H_9), 7.44−7.45 (m, 4H, H_3, H_8), 7.62−7.65 (m, 2H, H_1, H_{10}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_4Si): δ (ppm) 27.2 (C_5, C_6), 127.2 (C_1, C_{10}), 127.7 (C_4, C_7), 129.2 (C_2, C_9), 133.1 (C_3, C_8). ^{77}Se{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_2Se): δ (ppm) 339.9. IR (KBr, cm^{-1}): 3067 (m; $\nu_{C-H(aromatic)}$), 2982 (s; $\nu_{C-H(aliphatic)}$), 1485 (m; $\nu_{C=C(aromatic)}$), 753 (m; $\nu_{C-H(aromatic)}$).

Synthesis of Complexes 1−3. The solid $[(\eta^5\text{-Cp*})\text{RhCl}(\mu\text{-Cl})]_2$ (0.05 g, 0.1 mmol) and appropriate ligand **L1**−**L3** (0.2 mmol) dissolved in CH_3OH (15 cm^3) were mixed, and 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 cm^3) with a rotary evaporator. It was mixed with solid NH_4PF_6 (0.032 g, 0.2 mmol), and the resulting orange microcrystalline solid was filtered, washed with 10 cm^3 of ice-cold CH_3OH, and dried in vacuo. Single crystals of **1**−**3** were obtained by diffusion of diethyl ether into their solutions (1 cm^3) made in a mixture (1/4) of CH_3OH and CH_3CN.

Complex 1. Yield: 0.106 g, ~85%. Anal. Calcd for $C_{24}H_{29}ClRhS_2[PF_6]$: C, 43.35; H, 4.40. Found: C, 43.59; H, 4.19. Mp: 260 °C. ^{1}H NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 1.57 (s, 15H, H of Me(Cp)), 3.43−3.68 (m, 4H, H_6, H_5), 7.33−7.58 (m, 6H, H_{1-2}, H_{9-10}), 7.73 (m, 4H, H_3, H_8). ^{13}C{^{1}H} NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 8.4 (C of Me(Cp*)), 39.9 (C_5, C_6), 96.3 (C of Cp*), 129.3 (C_1, C_{10}), 131.3 (C_4, C_7), 131.8 (C_2, C_9), 133.4 (C_3, C_8). HR-MS (m/z, CH_3CN)" $[M]^+$ 519.0449, calculated value for $C_{24}H_{29}ClRhS_2$ 519.0450 (δ −0.3 ppm). IR (KBr, cm^{-1}): 3142 (m; $\nu_{C-H(aromatic)}$), 2920 (s; $\nu_{C-H(aliphatic)}$), 1578 (m; $\nu_{C=C(aromatic)}$), 839 (s; ν_{P-F}),749 (m; $\nu_{C-H(aromatic)}$).

Complex 2. Yield: 0.112 g, ~80%. Anal. Calcd for $C_{24}H_{29}ClRhSeS[PF_6]$: C, 40.49; H, 4.11. Found: C, 40.65; H, 4.08. Mp: 242 °C. ^{1}H NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 1.49 (s, 15H, H of Me(Cp*)), 3.26−3.65 (m, 2H, H_5), 3.68−4.01 (m, 2H, H_6), 7.46−7.69 (m, 8H, H_{2-3}, H_{8-9}), 8.05−8.07 (m, 2H, H_1, H_{10}). ^{13}C{^{1}H} NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 8.41 (C of Me(Cp*), 33.0 (C_5), 39.1 (C_6), 100.9 (C of Cp*), 129.5 (C_1), 130.0 (C_{10}), 130.9 (C_2), 131.6 (C_9), 131.8 (C_3), 132.0 (C_7), 132.5 (C_8), 132.6 (C_4) . ^{77}Se{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_2Se): δ (ppm) 389.8. HR-MS (m/z, CH_3CN): $[M]^+$ 566.9897; calculated value for $C_{24}H_{29}RhSSe$ 566.9891 (δ −1.0 ppm). IR (KBr, cm^{-1}): 3158 (m; $\nu_{C-H(aromatic)}$), 2991 (s; $\nu_{C-H(aliphatic)}$), 1586 (m; $\nu_{C=C(aromatic)}$), 844 (s; ν_{P-F}), 745 (m; $\nu_{C-H(aromatic)}$).

Complex 3. Yield: 0.128 g, ~85%. Anal. Calcd for $C_{24}H_{29}ClRhSe_2[PF_6]_2$: C, 37.99; H, 3.85. Found: C, 37.50; H, 3.92. Mp: 240 °C. ^{1}H NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 1.54 (s, 15H, H of Me(Cp*)), 3.31−3.63 (m, 2H, H_5), 3.65−3.89 (m, 2H, H_6), 7.45−7.67 (m, 8H, H_{2-3}, H_{8-9}), 7.85−7.88 (m, 2H, H_1, H_{10}). ^{13}C{^{1}H}NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 8.7 (C of Me(Cp*)), 33.0 (C_5), 36.1 (C_6), 100.1 (C of Cp*), 126.5 (C_1), 129.8 (C_{10}), 130.3 (C_4), 130.9 (C_7), 131.4 (C_2), 131.5 (C_9), 132.6 (C_3), 133.6 (C_8). ^{77}Se{^{1}H} NMR (CD_3CN, 25 °C vs Me_2Se): δ (ppm) 403.8 (Se_1), 413.8 (Se_2). HR-MS (m/z, CH_3CN): $[M]^+$ 614.9337; calculated value for $C_{24}H_{29}ClRhSe_2$ 614.9337 (δ 0.1 ppm). IR (KBr, cm^{-1}): 3150 (m; $\nu_{C-H(aromatic)}$), 2972 (s; $\nu_{C-H(aliphatic)}$), 1574 (m; $\nu_{C=C(aromatic)}$), 849 (s; ν_{P-F}), 743 (m; $\nu_{C-H(aromatic)}$).

Synthesis of Complexes 4−6. The solid $[(\eta^5\text{-}Cp^*)IrCl(\mu\text{-}Cl)]_2$ (0.05 g, 0.1 mmol) and appropriate ligand **L1**−**L3** (0.2 mmol) dissolved in CH_3OH (15 cm^3) were mixed, and the mixture was stirred for 10 h at room temperature. The resulting yellow solution was filtered. After workup as described for **1**−**3**, single crystals of **4**−**6** were obtained by diffusion of diethyl ether into their solution (1 cm^3) made in a mixture (1/4) of CH_3OH and CH_3CN.

Complex 4. Yield: 0.124 g, ~82%. Anal. Calcd for $C_{24}H_{29}ClIrS_2[PF_6]$: C, 38.22; H, 3.88. Found: C, 38.37; H, 3.57. Mp: 282 °C. ^{1}H NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 1.79 (s, 15H, H of Me(Cp*)), 3.39−3.78 (m, 4H, H_6, H_5), 7.33−7.50 (m, 6H, H_{1-2}, H_{9-10}), 7.61−7.73 (m, 4H, H_3, H_8). ^{13}C{^{1}H} NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 7.9 (C of Me(Cp*)), 38.4 (C_5, C_6), 95.1 (C of Cp*), 129.2 (C_1, C_{10}), 130.0 (C_4, C_7), 130.4 (C_2, C_9), 133.0 (C_3, C_8). HR-MS (m/z, CH_3CN): $[M]^+$ 609.1021; calculated value for $C_{24}H_{29}ClIrS_2$ 609.1013 (δ −1.4 ppm). IR (KBr, cm^{-1}): 3192 (m; $\nu_{C-H(aromatic)}$), 2922 (s; $\nu_{C-H(aliphatic)}$), 1578 (m; $\nu_{C=C(aromatic)}$), 838 (s; ν_{P-F}), 749 (m; $\nu_{C-H(aromatic)}$).

Complex 5. Yield: 0.135 g, ~85%. Anal. Calcd for $C_{24}H_{29}ClIrSeS[PF_6]$: C, 35.98; H, 3.65. Found: C, 35.64; H, 3.92. Mp: 270 °C. ^{1}H NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 1.48 (s, 15H, H of Me(Cp*)), 3.28−3.57 (m, 2H, H_5), 3.69−3.75 (m, 2H, H_6), 7.47−7.65 (m, 8H, H_{2-3}, H_{8-9}), 7.96−7.98 (m, 2H, H_1, H_{10}). ^{13}C{^{1}H} NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 8.20 (C of Me(Cp*), 34.4 (C_5), 39.7 (C_6), 94.4 (C of Cp*), 128.0 (C_1), 129.4 (C_{10}), 129.8 (C_2), 130.0 (C_9), 130.2 (C_3), 131.6 (C_7), 132.4 (C_8), 132.9 (C_4). ^{77}Se{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_2Se): δ (ppm) 357.52. HR-MS (m/z, CH_3CN): $[M]^+$ 657.0483; calculated value for $C_{24}H_{29}ClIrSSe$ 657.0457 (δ −4.0 ppm). IR (KBr, cm^{-1}): 3175 (m; $\nu_{C-H\ (aromatic)}$), 2922 (s; $\nu_{C-H(aliphatic)}$), 1576 (m; $\nu_{C=C(aromatic)}$), 841 (s; ν_{P-F}), 749(m; $\nu_{C-H(aromatic)}$).

Complex 6. Yield: 0.145 g, ~85%. Anal. Calcd for $C_{24}H_{29}ClIrSe_2[PF_6]_2$: C, 33.99; H, 3.45. Found: C, 33.80; H, 3.69. Mp: 265 °C. ^{1}H NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 1.43 (s, 15H, H of Me(Cp*)), 3.25−3.58 (m, 2H, H_5), 3.61−3.76 (m, 2H, H_6), 7.21−7.27 (m, 4H, H_2, H_9), 7.32−7.4. (m, 4H, H_3, H_8), 7.44−7.47 (m, 2H, H_1, H_{10}). ^{13}C{^{1}H}NMR (CD_3CN, 25 °C vs Me_4Si): δ (ppm) 8.3 (C of Me(Cp*), 32.3 (C_5), 37.2 (C_6), 94.4 (C of Cp*), 129.4 (C_1), 129.6 (C_{10}), 130.2 (C_4), 130.5 (C_7), 131.4 (C_2), 131.7 (C_9), 131.8 (C_3), 133.6 (C_8). ^{77}Se{^{1}H} NMR (CD_3CN, 25 °C vs Me_2Se): δ (ppm) 397.2 (Se_1), 405.0 (Se_2). HR-MS (m/z, CH_3CN): $[M]^+$ 704.9928; calculated value for $C_{22}H_{29}ClIrSe_2$ 704.9904 (δ −3.3 ppm). IR (KBr, cm^{-1}): 3154 (m; $\nu_{C-H(aromatic)}$), 2993 (s; $\nu_{C-H(aliphatic)}$), 1576 (m; $\nu_{C=C(aromatic)}$), 840 (s; ν_{P-F}), 746 (m; $\nu_{C-H(aromatic)}$).

Procedure for Catalytic Oppenauer-Type Oxidation of Alcohols. The appropriate complex **1**−**6** (0.1 mol %) dissolved in 15 cm^3 of acetone (containing ~0.1% water) was mixed with the alcohol substrate (1 mmol) and K_2CO_3 (1.5 mmol). The mixture was refluxed at 80 °C for 5 h (**1**−**3**) or 7 h (**4**−**6**). The reaction was followed by ^{1}H NMR spectroscopy. On completion of the reaction the reaction mixture was cooled to room temperature and the solvent was evaporated off using a rotary evaporator. The residue having an oxidized product was extracted with 20 cm^3 of petroleum ether (40−60 °C). The solvent from the petroleum ether extract was evaporated off, and the oxidized product present in the residue was analyzed by its ^{1}H NMR spectrum. The products were authenticated by comparing their NMR spectra with those of standard samples.

Procedure for Catalytic Transfer Hydrogenation of Ketones. A solution of a ketone (1 mmol) made in 2-propanol (15 cm^3), KOH (10 mol %), and the appropriate complex from **1**−**6** (0.01 mol % dissolved in CH_3CN) was mixed and heated at 80 °C for 5 h in the case of **3** and 6 h in the case of **6**. The reaction was followed by ^{1}H NMR spectroscopy. After completion of the reaction, the reaction mixture was cooled to room temperature. The solvent was removed on a rotary evaporator, and the resulting semisolid was extracted with diethyl ether (3 × 20 cm^3). The extract was passed through a short column (~8 cm^3 in length) of silica gel. The column was washed with ~50 cm^3 of diethyl ether. All the eluates from the column were mixed, and the solvent from the mixture was evaporated off on a rotary evaporator. The resulting residue was subjected to ^{1}H NMR. The final conversions are reported as an average of two runs of each catalytic reaction.

Hg Poisoning Test. An excess of Hg (Hg/(Rh,Ir) 400/1) was placed in the reaction flask. Thereafter the transfer hydrogenation reaction of acetophenone (1.0 mmol) with 2-propanol (15 mL) using **3** or **6** (0.1 mol %) as catalyst was carried out in the flask under optimum conditions. A conversion of ~90% was observed after 3 h of reaction.

PPh_3 Poisoning Test. To the transfer hydrogenation reaction mixture of acetophenone with 2-propanol (15 mL) was added PPh_3 (0.5 mol %) under the optimum conditions after addition of catalyst **3** or **6** (0.1 mol %). After 3 h of reaction ~92% of the product was obtained.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving crystal and refinement data, bond lengths and angles, secondary interaction distances, structures, NMR and mass spectra, crystallographic data (CCDC nos. 926183, 926184, 926185, 926186, 926187, and 926188, respectively, for **1**−**6**), and HOMO−LUMO energy gaps and partial charges. 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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