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Half-Sandwich Rhodium/Iridium(III) Complexes Designed with Cp* and 1,2-Bis(phenylchalcogenomethyl)benzene as Catalysts for Transfer Hydrogenation in Glycerol

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Supporting Information

ABSTRACT: The reactions of 1,2-bis(phenylthiomethyl)benzene(**L1**) and 1,2-bis(phenylselenomethyl)benzene(**L2**) with $[(\eta^5\text{-Cp*})\text{MCl}(\mu\text{-Cl})]_2$ (M = Rh or Ir) at room temperature, followed by treatment with NH_4PF_6 have resulted in air and moisture insensitive half-sandwich complexes of composition $[(\eta^5\text{-Cp*})\text{M}(\mathbf{L})\text{Cl}][PF_6]$ (Rh, **1**−**2**; Ir, **3**−**4**; **L** = **L1** or **L2**). Their HR-MS, ^{1}H, ^{13}C{^{1}H}, and ^{77}Se{^{1}H} NMR spectra were found to be characteristic. The single crystal structures of **1**−**4** have been established by X-ray crystallography. The complexes **1**−**4** have been found efficient for catalytic transfer hydrogenation (TH) of aldehydes and ketones in glycerol, which acts as a solvent and hydrogen source. Complexes **1**−**2** are the first examples of Rh species explored for TH in glycerol. The catalysis appears to be homogeneous. The complexes of the (Se, Se) ligand are marginally efficient than the corresponding complexes of the (S, S) ligand. The reactivity of Rh complexes in comparison to those of Ir also appears to be somewhat more. The results of DFT calculations appear to be generally consistent with experimental catalytic efficiencies and bond lengths/angles.

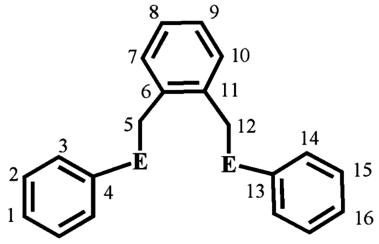
INTRODUCTION

The combination of an efficient catalyst and a nontoxic solvent like glycerol is attractive. Further, edible and biodegradable glycerol[1] is attractive due to its low cost, ready availability,[2] and renewability,[3] being the main byproduct in oleochemical production. Several processes of the conversion of biomass to chemicals and fuels occur via glycerol.[4] Nonhazardous glycerol is also a good solvent as it dissolves inorganic salts, acids, bases, enzymes, transition-metal complexes, and organic compounds (poorly miscible in water). Thus, in glycerol a variety of transformations is feasible. Hydrophobic solvents such as ethers and hydrocarbons being immiscible with glycerol may be used to remove products from it by simple extraction. The high boiling point (290 °C) makes it a suitable solvent for reactions to be carried out at a high temperature (not possible with the 2-propanol known for its use in transfer hydrogenation (TH)). Distillation is a feasible technique for the separation of the products of reactions carried out in glycerol, which being a nonflammable solvent does not require special handling or storage.[5]

TH is a convenient and versatile method for the reduction of carbonyl groups of ketones and aldehydes.[7] 2-Propanol has been widely used as a source of hydrogen in TH. It eliminates inflammable hydrogen gas and the need for pressure vessels.[8] Use of glycerol as a hydrogen source is successful for TH reactions[6] but has received less attention. In TH reactions, glycerol is dehydrogenated to several products including dihydroxyacetone.[9] However, low yield of dihydroxyacetone is not a big concern as glycerol is very cheap, and low recovery of this main byproduct is not going to cut the cost very significantly. TH of organic carbonyl compounds requires a catalyst. Several ruthenium species including half-sandwich ones have been reported to catalyze TH reactions in glycerol,[9] However, rhodium/iridium complexes are much less explored for TH reactions, particularly in glycerol.[10]

In view of our current research interest in the designing of transition metal catalysts for reactions such as C−C coupling, oxidation of alcohol, and TH[11] using organochalcogen ligands, it was thought worthwhile to synthesize complexes of 1,2-bis(phenylchalcogenomethyl)benzene (**L1**−**L2**, Chart 1) with η^5-Cp*Rh(III)/Ir(III) and explore them as TH catalysts in

Chart 1



L1: E = S L2: E = Se

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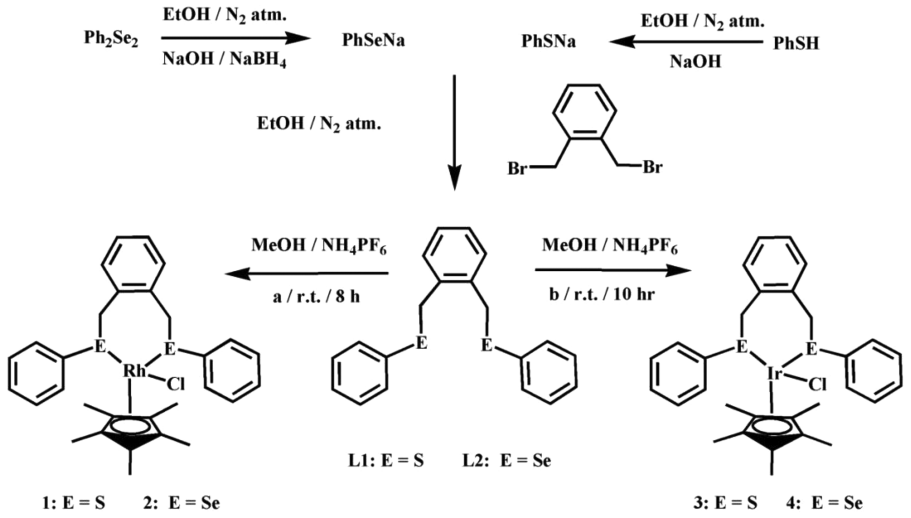
Scheme 1. Synthesis of Ligands L1−L2 and Complexes 1−4



a = $[(\eta^5\text{-Cp*})RhCl(\mu\text{-Cl})]_2$; b = $[(\eta^5\text{-Cp*})IrCl(\mu\text{-Cl})]_2$

glycerol (solvent and hydrogen source). To our knowledge, there is no use of glycerol as a hydrogen source in TH catalyzed with Rh/Ir(III) complexes of organochalcogen ligands. The present Rh complexes (**1**−**2**) are the first examples of Rh species explored for TH in glycerol. Herein we present the results of such investigations. Complexes **1**−**4** have been characterized with X-ray diffraction. The catalytic efficiencies of the present half-sandwich complexes of Rh/Ir(III) with **L1** and **L2** have been found promising. The results of density functional theory (DFT) calculations have also been included in this article and have been found to be consistent with several experimental results.

RESULTS AND DISCUSSION

The syntheses of **L1**−**L2** and their complexes (**1**−**4**) have been summarized in Scheme 1. The present procedures for the preparation of **L1** and **L2** are easier than the reported ones[12] and give higher yields (up to 95%). In $CHCl_3$, CH_2Cl_2, CH_3OH, and CH_3CN, the solubility of **L1**−**L2** is good. Complexes **1**−**4** are moderately soluble in $CHCl_3$, CH_2Cl_2, and CH_3OH, but in CH_3CN, their solubility is good. The air and moisture insensitive pale yellow liquids **L1**−**L2** can be stored at room temperature under ambient conditions for several months. The solutions of complexes **1**−**4** made in CH_3CN are also stable for several months under ambient conditions. The results of elemental analyses of complexes **1**−**4** are consistent with the single crystal structures (determined with X-ray diffraction) given below.

Crystal Structures. Half-sandwich complexes of rhodium(III) (**1**−**2**) and iridium(III) (**3**−**4**) appear to be formed by chloro bridge cleavage of $[(\eta^5\text{-Cp*})RhCl(\mu\text{-Cl})]_2$/$[(\eta^5\text{-Cp*})IrCl(\mu\text{-Cl})]_2$ followed by reaction with 1,2-bis(phenylthio/selenomethyl) benzene (**L1**/**L2**) at room temperature, which is facilitated by chloride extraction with NH_4PF_6. The single crystals of complexes **1**−**4** of quality suitable for X-ray diffraction were grown by diffusion of diethyl ether into concentrated solutions of the complexes made in 1:4 (v/v) methanol−acetonitrile mixtures. The crystallographic and refinement data for **1**−**4** are summarized in Supporting Information (Tables S1 and S2). The ligands **L1** and **L2** are bonded to metal ions in a bidentate mode in all complexes **1**−**4**, resulting in a seven membered chelate ring with both of them. The molecular structure diagrams of cations of **1**−**4** are given in Figures 1 to 4 with selected bond lengths and angles.

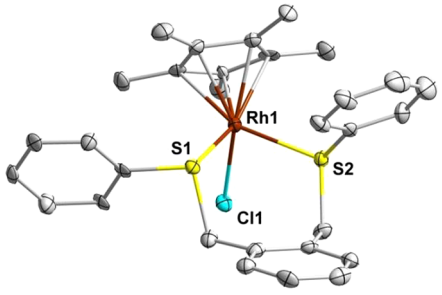


Figure 1. Structure of the cation of **1** with ellipsoids at the 50% probability level. Bond lengths (Å): Rh(1)−S(1), 2.3861(12); Rh(1)−S(2), 2.3948(14); Cl(1)−Rh(1), 2.4084(11); and Rh−C, 2.179(5)−2.188(5). Bond angles (deg): S(1)−Rh(1)−S(2), 93.41(5); S(1)−Rh(1)−Cl(1), 92.15(4); and S(2)−Rh(1)−C1(1), 86.84(4).

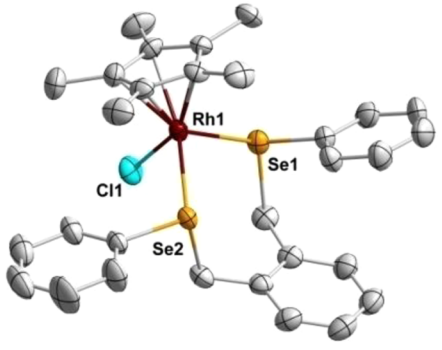


Figure 2. Structure of the cation of **2** with ellipsoids at the 30% probability level. Bond lengths (Å): Rh(1)−Se(1), 2.4874(11); Rh(1)−Se(2), 2.488(11); Cl(1)−Rh(1), 2.4039(16); Rh−C, and 2.173(5)−2.188(5). Bond angles (deg): Se(1)−Rh(1)−Se(1), 96.64(2); Se(1)−Rh(1)−Cl(1), 83.32(5); and Se(2)−Rh(1)−C1(1), 93.39(5).

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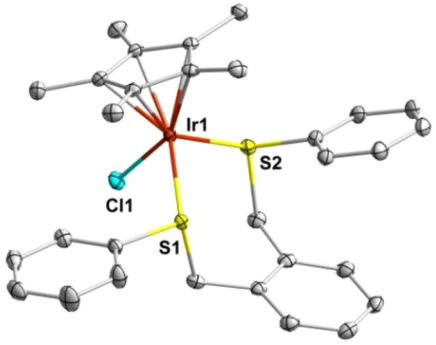

Figure 3. Structure of the cation of **3** with ellipsoids at the 30% probability level. Bond lengths (Å): Ir(1)−S(1), 2.3640(7); Ir(1)−S(2), 2.3694(8); Cl(1)−Ir(1), 2.4173(7); and Ir−C, 2.186(3)−2.202(3). Bond angles (deg): S(1)−Ir(1)−S(2), 96.23(2); S(1)−Ir(1)−Cl(1), 91.84(3); and S(2)−Ir(1)−C1(1), 83.82(3).

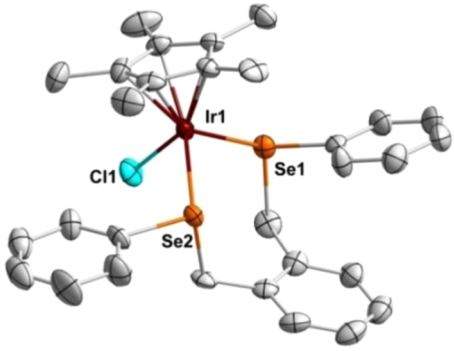

Figure 4. Structure of the cation of **4** with ellipsoids at the 30% probability level. Bond lengths (Å): Ir(1)−Se(1), 2.4922(13); Ir(1)−Se(2), 2.4547(12); Cl(1)−Ir(1), 2.417(2); and Ir−C 2.170(9)−2.218(9). Bond angles (deg): Se(1)−Ir(1)−Se(2), 96.55(4); Se(1)−Ir(1)−Cl(1), 83.52(8); and Se(2)−Ir(1)−C1(1), 93.23(7).

The H atoms and PF_6^- are omitted for clarity. The rhodium and iridium complexes have almost similar molecular structure. 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.

The Rh−S bond distances in **1** [2.3861(12) and 2.3948(14) Å] are normal, as their values for complexes [η^5-Cp*RhCl(1,1′-(1,2-ethanediyl)bis(3-methylimidazole-2-thione)]Cl [2.3967(11) Å][13] and [η^5-Cp*RhCl{2-(phenylthiomethyl)-pyridine}]PF_6 [2.383(2) Å][14] are of the same order. The Rh−Se bond lengths of the cation of **2** [2.4874(11) and 2.488(11) Å] are somewhat shorter than that of complex [η^5-Cp*RhCl{η^2-$(SePPh_2)_2N$}] [2.5266(8) Å][15] but similar to the values reported for the half-sandwich complex of Rh(III) with the 2-(phenylselenomethyl)pyridine ligand [2.487(1) Å].[14] The Rh−C (Cp* centroid) distances of complexes **1** and **2** [1.806(3) and 1.810(5) Å, respectively] are normal.[16] The Ir−S bond distances of **3** [2.3640(7) and 2.3694(8) Å] are within the range [2.318(1)−2.3872(10) Å] in which such bond lengths of [η^5-Cp*Ir-(CO)(μ-STol)Pt(STol)(PPh_3)],[17] [η^5-Cp*Ir(η^2-ppy-S-*p*-tol)(H_2O)][OTf]$_2$,[18] [η^5-Cp*Ir(4,6-di-*t*-butyl-(2-methylthiophenylimino)-*o*-benzoquinone]-[PF_6].CH_2Cl_2,[19] [η^5-Cp*Ir(*n*BuPPh$_2$)({7-(S)PPh$_2$}-8-S-7,8-$C_2B_9H_{10}$)],[20] and [η^5-Cp*IrCl{2-(phenylthiomethyl)-pyridine}]PF_6[14] have been reported. The Ir−Se bond distances in **4** [2.4922(13) and 2.4547(12) Å] are consistent with the values reported for [η^5-Cp*IrCl{2-(phenylselenomethyl)-pyridine}]PF_6 [2.4531(10) Å],[14] [η^5-Cp*IrCl(μ-$SeCOC_6H_5$)-(κ^2-$SeCOC_6H_4$−)Ir(η^5-Cp*)] [2.445(2)− 2.495(1) Å],[22] and [η^5-Cp*Ir(μ^3-Se)$_2${PtTol(PPh_3)}$_2$] [2.416(1)−2.422(1) Å][17] but longer than the values reported for [η^5-Cp*Ir-{$Se_2C_2(CO_2Me)_2$}] [2.3494(7) and 2.3520(7) Å].[21] The Ir−η^5-Cp*(centroid) distances (Å) in **3** [1.814(1)] and **4** [1.812(8)] are normal and consistent with the values reported for complex [(η^5-Cp*)Ir(phpy)Cl] [1.863 Å].[23] The PF_6^- has been found to be involved in C−H···F secondary interactions in all complexes **1**−**4**, resulting in chains. In Figures 5 and 6, they are shown for complexes **1** and **2**. For the other two complexes, noncovalent interactions are given in Supporting Information (see Table S5 for C−H···F distances and Figures S1 and S2).

Spectral Data. The NMR spectral data of complexes **1**−**4** are consistent with their single-crystal structures. Two signals observed in the $^{77}Se\{^1H\}$ NMR spectrum (Supporting Information, Figures S3−S5) of each of the two complexes **2**

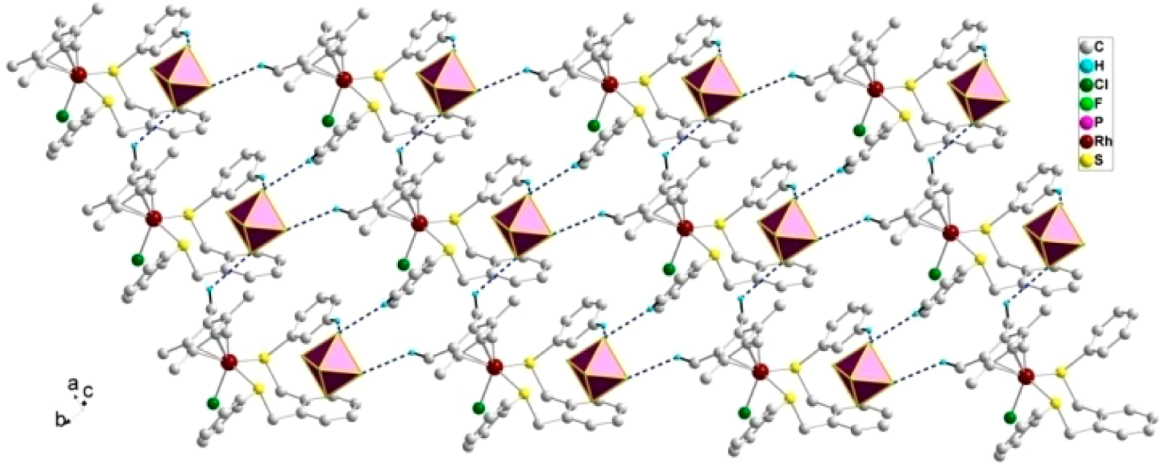

Figure 5. Three dimensional packing framework viewing noncovalent C−H···F interactions in the crystal lattice contain PF_6 in a polyhedral form of complex **1**.

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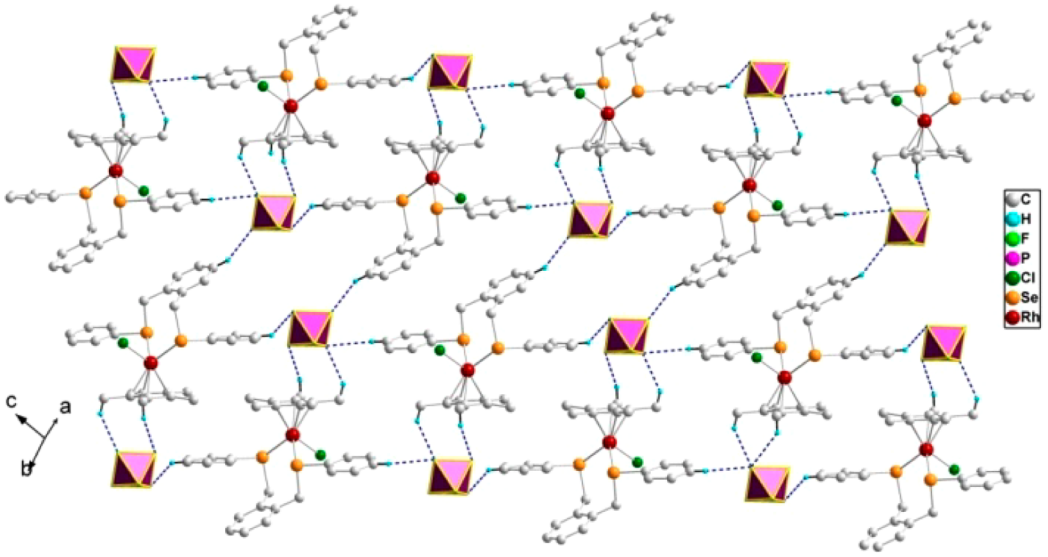


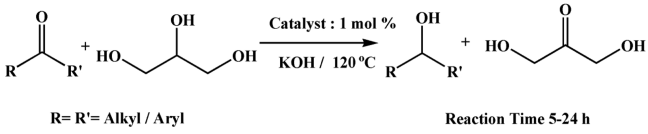
Figure 6. Three dimensional packing framework viewing noncovalent C−H···F interactions in the crystal lattice contain PF_6 in a polyhedral form of complex **2**.

and **4** may be assigned to diastereomers. One signal in the $^{77}Se\{^1H\}$ spectrum of **2** is shifted to a higher frequency (up to ~9.0 ppm) in comparison to those of free **L2**. It is probably due to the coordination of **L2** with the Rh center through Se. However, in the case of complex **4** the signals in the $^{77}Se\{^1H\}$ NMR spectrum have been observed shifted to a lower frequency by ~20 ppm with respect to that of free **L2**. In ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**−**4**, 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 shifts to higher frequencies for fragment $PhCH_2(E)$ (E = S or Se) [up to 8.5 ppm for carbon atoms in $^{13}C\{^1H\}$ NMR spectra and 1.25 ppm for protons attached to them in ^1H NMR] imply that the coordination of ligands **L1** and **L2** with Rh/Ir through S/Se appears to exist in solution. The signals due to the η^5-pentamethylcyclopentadienyl group ^1H(singlet) and $^{13}C\{^1H\}$ NMR spectra of complexes **1**−**4** were found shifted to a lower frequency (maximum shift ~0.25 and 2.5 ppm respectively) with respect to those of $[(\eta^5\text{-Cp*})RhCl\text{-}(\mu\text{-Cl})]_2/[(\eta^5\text{-Cp*})IrCl(\mu\text{-Cl})]_2$. This may be due to the substitution of Cl with S and Se, which have relatively lower electronegativity.

HR-MS spectra of structurally similar complexes **1**−**4** indicate that PF_6^- is considerably labile and that consequently the molecular ion peak in the mass spectra is not observed. Instead, the peak of cationic fragment species M^+ has been observed in the spectra of all complexes, **1**−**4**. In all mass spectra, the peaks of fragment $[(\eta^5\text{-Cp*})RhCl]^+$ or $[(\eta^5\text{-Cp*})IrCl]^+$ and ligands have also been observed (see Supporting Information Figures S6−S9).

Transfer Hydrogenation of Carbonyl Compounds. The TH of aldehydes and ketones in glycerol (also a hydrogen donor) catalyzed with complexes **1**−**4** (1 mol %) in the presence of KOH has been studied at a temperature of 120 °C (Scheme 2). The carbonyl compound and product both were monitored with ^1H NMR. The carbonyl compound is reduced to the corresponding alcohol, while glycerol is dehydrogenated to dihydroxyacetone (DHA; ^1H NMR: δ 4.4 and 3.5 ppm) and other products[6a] but all in low yield and difficult to separate. The low yield of dihydroxyacetone is not a big concern because

Scheme 2. Transfer Hydrogenation of Carbonyls with Glycerol



glycerol is very cheap, and high recovery of this main byproduct is not going to cut the cost of processes very significantly. The conversion (yield up to 98%) has been found fastest in the case of benzaldehyde with all of the present complex catalysts. The time profile is shown in Figure 7, and conversion/yield almost

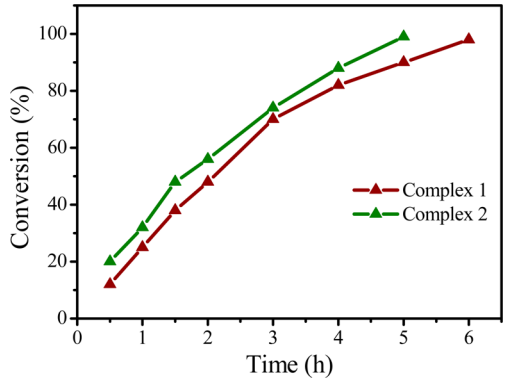


Figure 7. Time profile of catalytic TH of benzaldehyde using complex **1** and **2**. Conditions: 1 mol % of catalyst, 1.0 mmol of benzaldehyde, KOH (1.5 mmol), and 5 mL of glycerol at 120 °C, in air.

linearly increases up to 3 h, and thereafter the rate slows down. The values of percent yields (1−10% lower than conversions) are given in Table 1 and appear promising. The complexes (**2** and **4**) of Se ligand **L2** are more efficient as catalysts relative to the corresponding S analogues (**1** and **3**). To our knowledge, no other example of a rhodium complex used as the catalyst for TH with glycerol exists for comparison. Iridium complexes, including half-sandwich ones known for this purpose[10] have been used in much larger amounts (2.5 mol %) than **2** and **4** (1

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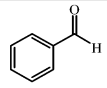
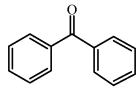
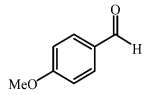
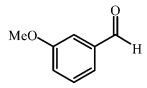
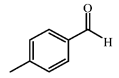
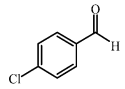
Table 1. Transfer Hydrogenation of Carbonyl Compounds[a]

Entry	Substrate	Catalyst	Time(h)	Yield[b](%)
1		1	6	92
		2	5	98
		3	10	90
		4	8	95
2		1	20	85
		2	20	90
		3	24	80
		4	24	80
3		1	24	60
		2	24	70
		3	24	55
		4	24	60
4		1	15	88
		2	15	92
		3	16	82
		4	16	85
5		1	15	90
		2	8	98
		3	15	86
		4	10	90
6		1	15	95
		2	12	90
		3	15	85
		4	16	90
7		1	15	85
		2	13	90
		3	15	85
		4	15	92

[a]Conditions: 2 mmol substrate, 3.0 mmol KOH, 8 mL of glycerol, and 1 mol % catalyst at 120 °C, in air. [b]Isolated yield.

mol %). As only few substrates used in the present work are common with these reports, the scope of comparison is somewhat narrow, making any generalization difficult. For comparable conversions, the reaction times with **2** and **4** are shorter than those reported with some N-heterocyclic carbene based Ir complexes[10a] but longer in comparison to values reported for a few other Ir complexes.[10b] In comparison to Ru species[6c,9] viz. Ru(*p*-cymene)Cl_2, $RuCl_2(TPPS)_3$ (TPPS: tris(3-sulfophenyl)phosphine trisodium salt), and [Ru(η^6-arene)-(NHC)CO_3] reported for the catalysis of TH in glycerol (in the presence of KOH/NaOH), the present Rh and Ir complexes are more efficient as yields are better in a shorter time frame for benzaldehyde and relative to some Ru species, the required catalyst loading is also low. On monitoring the TH reactions catalyzed with **2** and **4** with $^{77}Se\{^1H\}$ NMR spectroscopy, it is observed that the signals in the spectra shift to higher frequency (21−28 ppm), indicating that probably the M−Cl bond is cleaved or weakened very significantly to make a coordination site on the metal center available so that formation of an intermediate having a M−H bond finally can takes place.[24] The TH reactions catalyzed with **2** and **4** were also monitored with ^1H NMR spectra. After 1 h, a broad singlet was noticed around δ −11.7 and −12.4 ppm, respectively. These signals are characteristic of hydride and indicate the formation of an M−H bond.[25] Thus, catalytic reactions with the present complexes probably proceed via the formation of a metal−hydride complex intermediate.

The catalytic efficiency varies in the order (Se, Se) > (S, S) when other coligands are the same. The stronger electron-donating tendency of Se than S toward the metal center probably promotes the formation of hydride, resulting in higher efficiency in the case of the Se ligand. In TH catalyzed with **1**−**4**, the formation of the M−H-containing intermediate and the absence of the NH group in the ligand system together suggest that a conventional mechanism via alkoxide formation[26] is most plausible. The Rh(III) species appears to be a better catalyst than Ir(III) (Table 1) because in the case of Ir complexes for conversions comparable with those of Rh analogues with same catalyst loading, the reaction time needed is somewhat more. This observation is supported by DFT calculations.

Homogeneous vs Heterogeneous Transfer Hydrogenation Catalysis. Formation of Ir NPs has been reported in TH in glycerol catalyzed with iridium complexes under microwave conditions. Such NPs have been found to show a negative effect on the catalytic process.[10a] Thus, to understand the possibility of heterogeneous contribution to the catalytic process, i.e., whether the present TH catalysts are homogeneous or heterogeneous, a mercury poisoning test[27] has been executed. With the benzaldehyde substrate in glycerol using catalysts **2** and **4**, the mercury poisoning test has been found negative, i.e., there is no significant inhibition of product formation (Table 2). Thus, the present catalysis appears to be

Table 2. Mercury Test for Catalytic Transfer Hydrogenation[a]

entry	catalyst/Hg	time (h)	conversion[b]
1[c]	1/0	5	99
2[d]	1/0	6	98
3[c]	1/400	5	92
4[d]	1/400	6	88

[a]Conditions: 1 mmol benzaldehyde, 1.5 mmol KOH, 5 mL of glycerol, and 1 mol % catalyst at 120 °C, in air. [b]Determined by ^1H NMR. [c]Rh complex **2**. [d]Ir complex **4**.

homogeneous. The PPh_3 poisoning test has also been used.[28] In the presence of 5 equiv of PPh_3, the reaction occurs with only a 5% decrease in percent conversion (Table 3). The homogeneous nature of catalysis is supported as inferred on the basis of the Hg test.

Table 3. PPh_3 Poisoning Test for Catalytic Transfer Hydrogenation[a]

entry	catalyst/PPh_3	time (h)	conversion[b]
1[c]	1/0	5	99
2[d]	1/0	6	98
3[c]	1/5	5	94
4[d]	1/5	6	93

[a]Conditions: 1 mmol benzaldehyde, 1.5 mmol KOH, 5 mL of glycerol, and 1 mol % catalyst at 120 °C in air. [b]Determined by ^1H NMR. [c]Rh complex **2**. [d]Ir complex **4**.

DFT Calculations. DFT calculations (see Experimental Section for details) were performed on all four complexes **1**−**4**. An analysis of lowest energy configurations and frontier orbitals leads to qualitative insight of these complexes. The HOMOs (highest occupied molecular orbitals) of all complexes are essentially similar and positioned primarily over the Rh or Ir and Cp* ring. The S or Se and Cl donor atoms have only small

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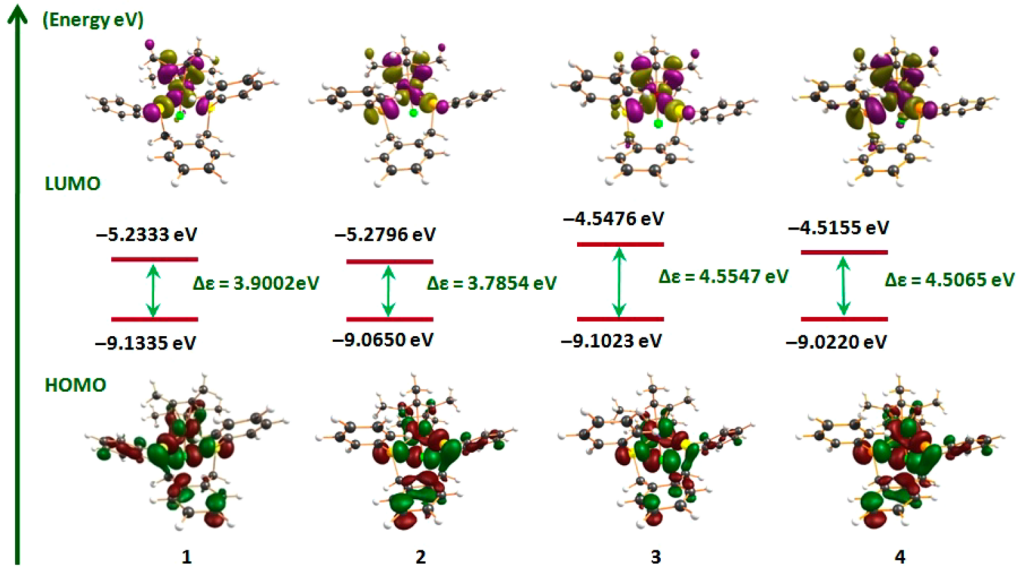


Figure 8. Frontier molecular orbitals of complexes **1**−**4** and their HOMO−LUMO energy gap.

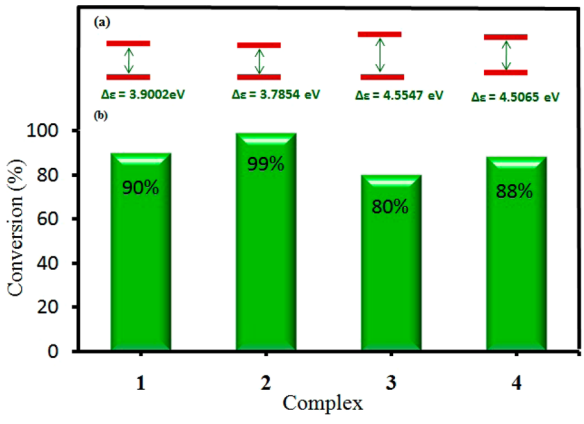
Table 4. Comparison of Selected Bond Lengths (Å) and Angles (deg) of 1−4 Determined Experimentally and Calculated by DFT[a]

	1		2		3		4	
	bond angle/length	DFT value	bond angle/length	DFT value	bond angle/length	DFT value	bondangle/length	DFT value
M−E(1)	2.3861(12)	2.541	2.4874(11)	2.591	2.3640(7)	2.542	2.4922(13)	2.599
M−Cl(1)	2.4084(11)	2.429	2.4039(16)	2.445	2.4173(7)	2.445	2.417(2)	2.454
M−E(2)	2.3948(14)	2.543	2.4887(11)	2.598	2.3694(8)	2.538	2.4547(12)	2.598
M−C[a]	1.806(3)	1.820	1.810(5)	1.836	1.814(1)	1.808	1.812(8)	1.822
E1−M−E2	93.41(5)	93.07	96.64(2)	96.18	96.23(2)	93.43	96.55(4)	95.88
E1−M−Cl	92.15(4)	90.23	83.32(5)	82.36	91.84(3)	90.14	83.52(8)	81.62
Cl−M−E2	86.84(4)	84.35	93.39(5)	92.07	83.82(3)	82.43	93.23(7)	90.76

[a]M = rhodium or iridium, E = sulfer or selenium, C[a] = centroid of Cp*).

share of these HOMOs. The d-orbitals of Rh(III)/Ir(III) interacting with the π orbitals of the η^5-Cp* ring and the p-orbital of chlorine and chalcogen atoms constitute these HOMOs (see Figure 8 for complexes **1**−**4**). The detailed calculated bond length/angle parameters are given in Table 4). The agreement between the experimentally observed bonding parameters and those calculated by DFT is better for M−Cl and M−Cp* (centroid). The difference between calculated and observed M−E (E = S or Se) bond distances is of the order of 0.1 Å. The calculated and experimentally found bond angles are also reasonably close (Table 4) except in a few cases, e.g., S1−Ir−S2, where the difference is of the order 2°. The HOMO−LUMO (lowest unoccupied molecular orbital) energy gap of a complex may influence its chemical reactivity.[29] This energy gap changes between Rh and Ir species mainly due to the variation in the energy of LUMO. The HOMO−LUMO energy gaps between **1** and **3**, and **2** and **4** sufficiently differ (Figure 8 and Supporting Information, Table S4) indicating the higher reactivity of Rh complexes than those of Ir. The HOMO−LUMO energy gap for complexes of the (Se, Se) ligand is somewhat lower than those of the corresponding complexes of (S, S) analogues (see Figure 8 and Chart 2). This may be the cause of the somewhat higher reactivity of complexes of the (Se, Se) ligand than those of its (S, S) analogue. This is consistent with the observed catalytic efficiency of complexes **1**−**4** (Table 1 and Chart 2). The natural bond orbital atomic charge (see Table S4 and Figure S10 in Supporting Information) on metal is more negative in the case of Rh bonded to the Se ligand. This may promote the M−H bond and appears to be consistent with the experimental catalytic efficiency orders, Rh > Ir and (Se, Se) > (S, S).

Chart 2. (a) HOMO-LUMO Energy Gaps of 1−4 and (b) Conversions (%) in 5 h for Transfer Hydrogenation of Benzaldehyde Catalyzed with 1−4 (1 mol %) with Glycerol



CONCLUSIONS

Half-sandwich piano-stool complexes [(η^5-Cp*)Rh(**L**)Cl][PF_6] and [(η^5-Cp*)Ir(**L**)Cl][PF_6] (**1**−**4**) of 1,2 bis(phenylthio/

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selenomethyl) benzene ligands (**L** = **L1**−**L2**) have been synthesized and characterized by multinuclei 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), and (Se, Se) ligands explored for TH of carbonyl compounds using glycerol as a solvent and hydrogen donor. The 1 mol % of present Ir species required for efficient catalysis is lower than the value 2.5 mol % reported to be optimum in case of Ir complexes known earlier for this purpose. The **1**−**2** are the first examples of Rh species explored for TH in glycerol. The yields were promising. The air and moisture stability of **1**−**4** is an additional advantage. The catalytic efficiencies follow the orders Rh > Ir and (Se, Se) > (S, S), which are corroborated by DFT studies. There is no NP formation in the catalytic process which appears to be homogeneous. The formation of the M−H bond in the absence of the NH group suggests a conventional mechanism via alkoxide formation for TH.

EXPERIMENTAL SECTION

Physical Measurements. The ^{1}H, ^{13}C{^{1}H}, and ^{77}Se{^{1}H} NMR spectra were recorded on a 300 MHz 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 a purity ≥95% [established by ^{1}H NMR]. IR spectra in the range 4000−400 cm^{-1} were recorded on a FT−IR spectrometer as KBr pellets. The C, H, and N analyses were carried out with a C, H, and N analyzer. For single crystal structures, the data were collected on a CCD diffractometer using Mo Kα (0.71073 Å) radiation at 298(2) K. The software SADABS[30] was used for absorption correction (if needed) and SHELXTL for space group, structure determination, and refinements.[31] 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. High resolution mass spectral measurements were performed with electron spray ionization (10 eV, 180 °C source temperature, and sodium formate as reference compound) taking samples in CH_3CN. All reactions have been carried out in glassware dried in an oven, under ambient conditions except for the synthesis of **L1** and **L2**. The commercial nitrogen gas has been used after passing it successively through traps containing solutions of alkaline anthraquinone, sodium dithionite, alkaline pyrogallol, concentrated H_2SO_4, and KOH pellets. Nitrogen atmosphere if required was created using Schlenk techniques.

Chemical and Reagents. Diphenyldiselenide, thiophenol, $NaBH_4$, 1,2-bis(bromomethyl)benzene, and ammonium hexafluorophosphate procured from Sigma−Aldrich (USA) were used as received. The $[(\eta^5\text{-Cp}^*)\text{RhCl}(\mu\text{-Cl})]_2$[32] and $[(\eta^5\text{-Cp}^*)\text{IrCl}(\mu\text{-Cl})]_2$[33] were prepared according to literature methods. All of the solvents were dried and distilled before use by standard procedures.[34] The common reagents and chemicals available locally were used.

DFT Calculations. All DFT calculations were carried out at the Department of Chemistry, Supercomputing Facility for Bioinformatics and Computational Biology, IIT Delhi, with the Gaussian-09 program[35] with an immediate objective of identifying the reactivity order in the present series of compounds. The geometry of complexes **1** to **4** was optimized at the M06[36] level using a LANL2DZ[37] 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 has been done for all compounds **1** to **4** by using the M06 functional.[36] All calculations have been carried out in 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).

Synthesis of L1. 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 in 50 cm^3 of dry ethanol and refluxed for 0.5 h under N_2 atmosphere. 1,2-Bis(bromomethyl)benzene (2.5 mmol) dissolved in 5 cm^3 of ethanol was added dropwise and the refluxing of the mixture continued further for 1 h. After cooling to room temperature, the mixture was poured into 100 cm^3 of distilled water, neutralized with dilute sodium hydroxide, 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** as a pale yellow oil.

L1: yield 0.76 g, ∼95%. ^{1}H NMR ($CDCl_3$, 25 °C vs Me_4Si) δ (ppm): 4.21 (s, 4H, H_5, H_{12}), 7.11−7.18 (m, 4H, H_{7-10}), 7.19−7.25 (m, 6H, H_{1-2}, H_{15-16}), 7.26−7.30 (m, 4H, H_3, H_{14}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_4Si) δ (ppm): 36.7 (C_5, C_{12}), 126.6 (C_1, C_{16}), 127.7(C_3, C_{14}), 128.9 (C_2, C_{15}), 130.4 (C_7, C_{10}), 130.6 (C_8, C_9), 135.6 (C_4, C_{13}), 136.3 (C_6, C_{11}). IR (KBr, cm^{-1}): 3020 (m; $\nu_{\text{C−H (aromatic)}}$), 2940 (s; $\nu_{\text{C−H (aliphatic)}}$), 1475 (m; $\nu_{\text{C=C (aromatic)}}$), 750 (m; $\nu_{\text{C−H(aromatic)}}$).

Synthesis of L2. Diphenyldiselenide (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 N_2 atmosphere until it became colorless due to the formation of PhSeNa. 1,2-Bis(bromomethyl)benzene (2.0 mmol) dissolved in 5 cm^3 of ethanol was added to the colorless solution with constant stirring. The reaction mixture was stirred further for 2−3 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 **L2** as a pale yellow oil. Yield: 0.75 g, ∼90%. ^{1}H NMR ($CDCl_3$, 25 °C vs Me_4Si) δ (ppm): 4.18 (s, 4H, H_5, H_{12}), 7.02−7.09 (m, 4H, H_{7-10}), 7.18−7.27 (m, 6H, H_{1-2}, H_{15-16}), 7.41−7.44 (m, 4H, H_3, H_{14}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_4Si) δ (ppm): 29.7 (C_5, C_{12}), 127.4 (C_1, C_{16}), 129.0 (C_2, C_{15}), 130.5 (C_7, C_{10}), 130.6 (C_8, C_9), 131.6 (C_4, C_{13}), 133.8 (C_3, C_{14}), 136.5 (C_6, C_{11}). ^{77}Se{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_2Se) δ (ppm): 358.8, IR (KBr, cm^{-1}): 3060 (m; $\nu_{\text{C−H (aromatic)}}$), 2934 (s; $\nu_{\text{C−H (aliphatic)}}$), 1479 (m; $\nu_{\text{C=C (aromatic)}}$), 736 (m; $\nu_{\text{C−H (aromatic)}}$).

Synthesis of Complexes 1−2. The solid $[(\eta^5\text{-Cp}^*)\text{RhCl}(\mu\text{-Cl})]_2$ (0.05 g, 0.1 mmol) and ligand **L1**/**L2** (0.2 mmol) dissolved in CH_3OH (15 cm^3) were mixed together and the mixture 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 colored microcrystalline solid was filtered, washed with ice-cold 10 cm^3 of CH_3OH, and dried *in vacuo*. Single crystals of **1**and **2** were obtained by the diffusion of diethyl ether into their solutions (4 cm^3) made in a mixture (1:4) of CH_3OH and CH_3CN.

Compound **1**: yield 0.126 g, ∼85%. Anal Calcd for $C_{30}H_{33}ClRhS_2\cdot[PF_6]$: C, 48.62; H, 4.49; found, C, 48.59; H, 4.48. Mp 260 °C. ^{1}H NMR (CD_3CN, 25 °C vs Me_4Si) δ (ppm): 1.49 (s, 15H, H of Me(Cp)), 4.29−4.35 (m, 4H, H_5, H_{12}), 7.06−7.21 (m, 4H, H_{7-10}), 7.35−7.56 (m, 6H, H_{1-2}, H_{15-16}), 7.58−7.76 (m, 4H, H_3, H_{14}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_4Si) δ (ppm): 8.14 (C of Me(Cp*), 44.6 (C_5, C_{12}), 101.3 (C of Cp*), 127.4 (C_1, C_{16}), 128.6(C_3, C_{14}), 129.2 (C_2, C_{15}), 130.1 (C_7, C_{10}), 131.3 (C_8, C_9), 132.2 (C_4, C_{13}), 133.8 (C_6, C_{11}). HR-MS (CH_3CN) $[M]^+(m/z)$ = 595.0776; calulated value for $C_{30}H_{33}ClRhS_2$ = 595.0762 (δ: −2.5 ppm). IR (KBr, cm^{-1}): 3054 (m; $\nu_{\text{C−H (aromatic)}}$), 2972 (s; $\nu_{\text{C−H (aliphatic)}}$), 1442 (m; $\nu_{\text{C=C (aromatic)}}$), 831 (s; $\nu_{\text{P−F}}$), 764 (m; $\nu_{\text{C−H(aromatic)}}$).

Compound **2**: yield 0.150 g, ∼90%. Anal Calcd for $C_{30}H_{33}ClRhSe_2\cdot[PF_6]$: C, 43.16; H, 3.98; found, C, 43.65; H, 3.92. Mp 242 °C. ^{1}H NMR ($CDCl_3$, 25 °C vs Me_4Si) δ (ppm): 1.38 (s, 15H, H of Me(Cp)), 4.25−5.23 (m, 4H, H_5, H_{12}), 7.20−7.30 (m, 4H, H_{7-10}), 7.52−7.61 (m, 6H, H_{1-2}, H_{15-16}), 8.21−8.26 (m, 4H, H_3, H_{14}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_4Si) δ (ppm): 8.03 (C of Me(Cp*), 38.2 (C_5, C_{12}), 100.9 (C of Cp*), 129.5 (C_1, C_{16}), 129.7 (C_2, C_{15}), 129.9 (C_7, C_{10}), 131.4 (C_8, C_9), 132.1 (C_4, C_{13}), 133.7 (C_3, C_{14}), 135.3 (C_6, C_{11}). ^{77}Se{^{1}H} NMR ($CDCl_3$, 25 °C vs Me_2Se) δ (ppm): 294.7 (Se1), 367.3 (Se2) HR-MS (CH_3CN) $[M]^+$ (m/z) = 690.9632; calulated value for $C_{30}H_{33}ClRhSe_2$ = 960.9652 (δ: 2.9 ppm).

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IR (KBr, cm^{-1}): 3063 (m; $\nu_{C-H\ (aromatic)}$), 2979 (s; $\nu_{C-H\ (aliphatic)}$), 1443 (m; $\nu_{C=C\ (aromatic)}$), 829 (s; ν_{P-F}), 774 (m; $\nu_{C-H(aromatic)}$).

Synthesis of Complexes 3−4. The solid $[(\eta^5\text{-Cp}^*)IrCl(\mu\text{-Cl})]_2$ (0.05 g, 0.1 mmol) was mixed with a ligand out of **L1**−**L2** (0.2 mmol) dissolved in CH_3OH (15 cm^3) and the mixture stirred for 10 h at room temperature. The resulting yellow solution was filtered. After a work up as described for **1**−**2**, single crystals of **3**−**4** were obtained by the diffusion of diethyl ether into their solution (4 cm^3) made in a mixture (1:4) of CH_3OH and CH_3CN.

Compound **3**: yield 0.136 g, ∼82%. Anal Calcd for $C_{30}H_{33}ClIrS_2\cdot[PF_6]$: C, 43.39; H, 4.01; found, C, 43.53; H, 4.14. Mp 260 °C. ^1H NMR (CD_3CN, 25 °C vs Me_4Si) δ (ppm): 1.39 (s, 15H, H of Me(Cp)), 4.31−4.38 (m, 4H, H_5, H_{12}), 7.15−7.28 (m, 4H, H_{7-10}), 7.31−7.57 (m, 6H, H_{1-2}, H_{15-16}), 7.91−8.21 (m, 4H, H_3, H_{14}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_4Si) δ (ppm): 8.09 (C of Me(Cp*), 35.8 (C_5, C_{12}), 95.0 (C of Cp*), 129.0 (C_1, C_{16}), 129.8 (C_3, C_{14}), 131.7 (C_2, C_{15}), 132.3 (C_7, C_{10}), 133.6 (C_8, C_9), 134.1 (C_4, C_{13}), 135.8 (C_6, C_{11}). HR-MS (CH_3CN) $[M]^+(m/z)$ = 685.1331; calulated value for $C_{30}H_{33}ClIrS_2$ = 685.1326 (δ: −0.6 ppm). IR (KBr, cm^{-1}): 3092 (m; $\nu_{C-H\ (aromatic)}$), 2957 (s; $\nu_{C-H\ (aliphatic)}$), 1444 (m; $\nu_{C=C\ (aromatic)}$), 831 (s; ν_{P-F}), 747 (m; $\nu_{C-H\ (aromatic)}$).

Compound **4**: yield 0.157 g, ∼85%. Anal Calcd for $C_{30}H_{33}ClIrSe_2\cdot[PF_6]$: C, 38.99; H, 3.60; found, C, 38.79; H, 3.82. Mp 242 °C. ^1H NMR ($CDCl_3$, 25 °C vs Me_4Si) δ (ppm): 1.30 (s, 15H, H of Me(Cp)), 4.40−5.43 (m, 4H, H_5, H_{12}), 7.17−7.31 (m, 4H, H_{7-10}), 7.45−7.63 (m, 6H, H_{1-2}, H_{15-16}), 8.16−8.18 (m, 4H, H_3, H_{14}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_4Si) δ (ppm): 8.37 (C of Me(Cp*), 36.2 (C_5, C_{12}), 93.9 (C of Cp*), 129.3 (C_1, C_{16}), 129.9 (C_2, C_{15}), 131.0 (C_7, C_{10}), 131.9 (C_8, C_9), 132.2 (C_4, C_{13}), 133.3 (C_3, C_{14}), 135.1 (C_6, C_{11}). $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_2Se) δ (ppm): 257.7 (Se1), 339.0 (Se2) HR-MS (CH_3CN) $[M]^+$ (m/z) = 781.0215; calulated value for $C_{30}H_{33}ClIrSe_2$ = 781.0219 (δ: 0.5 ppm). IR (KBr, cm^{-1}): 3075 (m; $\nu_{C-H\ (aromatic)}$), 2942 (s; $\nu_{C-H\ (aliphatic)}$), 1443 (m; $\nu_{C=C\ (aromatic)}$), 830 (s; ν_{P-F}), 739(m; $\nu_{C-H\ (aromatic)}$).

Procedure for the Catalytic Transfer Hydrogenation of Carbonyl Compounds. A capped round-bottomed flask containing a stirrer bar was charged with the solution of a substrate (2 mmol) made in glycerol (8 cm^3), KOH (3.0 mmol), and a complex from **1** to **4** (1 mol %). The mixture was heated at 120 °C for an appropriate time as given in Table 1. After completion of the reaction, the reaction mixture was cooled to room temperature and mixed with water (20 cm^3). The mixture was extracted with diethyl ether (3 × 20 cm^3), and the solvent from the extract was removed on a rotary evaporator resulting in a semisolid. It was mixed with silica gel and the mixture filled in a short column (∼8 cm^3 in length). The column was washed with ∼50 cm^3 of diethyl ether. All of the eluates from the column were mixed, and solvent from the mixture was evaporated off on a rotary evaporator to isolate the product as liquid or solid. The yields of these isolated products were calculated and reported in Table 1. The ^1H NMR authenticating these products are reported in Supporting Information (Figures S11−S17).

Hg Poisoning Test. An excess of Hg (Hg/Rh/Ir: 400:1) was taken in a reaction flask. The TH reaction of benzaldehyde (1.0 mmol) with glycerol (5 mL) using **2** or **4** (1 mol %) as catalyst was carried out in the flask under optimum conditions. An ∼92% conversion (with ^1H NMR) was observed after 5−6 h of reaction.

PPh_3 Poisoning Test. To the TH reaction of benzaldehyde with glycerol (5 mL), PPh_3 (5 mol %) was added under optimum conditions after the addition of catalyst **2** or **4** (1 mol %). After 5−6 h of reaction, the conversion was found to be ∼94%.

■ ASSOCIATED CONTENT

Supporting Information

Crystal data and refinement parameters, bond lengths and angles, HOMO−LUMO energy gap and partial charges, distances of noncovalent interactions, noncovalent interactions, NMR and mass spectra, and CIF (CCDC numbers: 971499, 971500, 971501, and 971502 (for **1** to **4**, respectively). 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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