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Transfer Hydrogenation (pH Independent) of Ketones and Aldehydes in Water with Glycerol: Ru, Rh, and Ir Catalysts with a COOH Group near the Metal on a (Phenylthio)methyl-2-pyridine Scaffold

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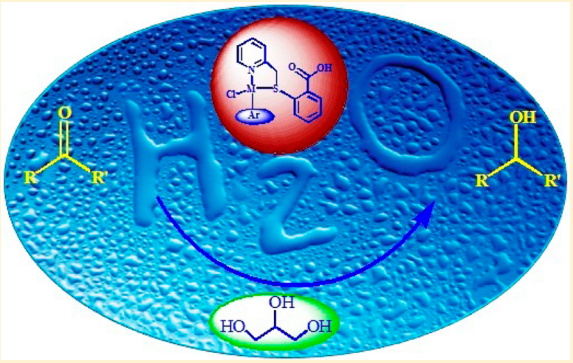
Supporting Information

ABSTRACT: The reactions of 2-(pyridine-2-ylmethylsulfanyl)-benzoic acid (**L**) with $[(\eta^5\text{-Cp*}/\eta^6\text{-benzene})\text{MCl}(\mu\text{-Cl})]_2$, (benzene, M = Ru; Cp*, M = Rh, Ir) at room temperature followed by treatment with NH_4PF_6 result in a new class of water-soluble half-sandwich complexes $[(\eta^5\text{Cp*}/\eta^6\text{-benzene})\text{M}(\mathbf{L})\text{Cl}][PF_6]$ (**1**−**3**, respectively, for M = Ru, Rh, Ir). Their characteristic HR-MS and ^{1}H and ^{13}C{^{1}H} NMR spectra have been found. The single-crystal structures of **1**−**3** have been established with X-ray crystallography. The Ru−S, Rh−S, and Ir−S bond lengths are 2.4079(6), 2.3989(10), and 2.3637(14) Å, respectively. Complexes **1**−**3** have been found to be efficient for catalytic transfer hydrogenation (TH) of carbonyl compounds in water with glycerol as a hydrogen donor. Glycerol has been explored for TH in water for the first time. The efficiency in water of other hydrogen sources, viz. HCOOH, citric acid, ascorbic acid, and 2-propanol, is less and/or is pH dependent. Catalysis with glycerol as a hydrogen source is pH independent and appears to be homogeneous. Higher reactivity for the Rh complex in comparison to the Ru and Ir species has been observed. DFT calculations are generally consistent with the experimental values of bond lengths and angles and catalytic reactivity order.



INTRODUCTION

Efficient catalytic protocols, eco-friendly solvents, and minimum amounts of waste are considered important for chemical processes. Thus, the use of water instead of organic solvents has an important place in current research.[1] Water as a solvent has a number of advantages over organic solvents. It is inexpensive, easily available, nontoxic, and safe to handle. Therefore, its use may result in significant gains in environmental, economic, and safety terms. Many catalytic reactions in the aqueous phase, including transfer hydrogenation, are known.[2−5] Transfer hydrogenation, a versatile process for the reduction of carbonyl compounds,[6] viz. ketones and aldehydes, generally uses 2-propanol as the source of hydrogen and eliminates inflammable hydrogen gas and required pressure vessels to handle it.[7] Ruthenium, rhodium, and iridium species, including half-sandwich complexes,[4,5,8] catalyze transfer hydrogenation (TH) of the carbonyl compounds. The number of ruthenium species used for this purpose is larger than those of rhodium and iridium. Some of these catalysts have enabled efficient transfer hydrogenation in water.[4,5] For catalysis in water the catalyst has to be preferably water soluble. For the design of water-soluble organometallic complexes, the ligands surrounding the metal should be hydrophilic in nature. Joó and Bényei[9] have reported the use of $[RuCl_2(TPPMS)_2]$ (TPPMS = 4-(diphenylphosphino)benzenesulfonic acid) for transfer hydrogenation in aqueous medium. Sasson and Blum[10] have employed the water-insoluble catalyst $[RuCl_2(PPh_3)_3]$ and the phase-transfer agent TPPMS for the biphasic reduction of aldehydes with aqueous sodium formate. Ogo and co-workers have developed the water-soluble complexes $[Ir(\eta^5\text{-Cp*})(H_2O)_3]^{2+}$ and $[Ru(\eta^6\text{-}C_6Me_6)(H_2O)_3]^{2+}$ for reducing aldehydes and ketones in water.[11] The complexes of the 1,3,5-triaza-7-phosphaadamantane (PTA) ligand with Ru(II) have been employed in biphasic TH[12] carried out in aqueous medium. The complexes of bipyridine (bpy) and its derivatives have been found suitable for TH in aqueous medium. Some examples are $[Ir(\eta^5\text{-Cp*})(bpy)(H_2O)]^{2+}$,[13] $[Ru(\eta^6\text{-}C_6Me_6)(bpy)(H_2O)]^{2+}$,[11b] $[Ru(\eta^6\text{-arene})(dhbp)Cl]^{+}$,[14] (dhbp = 6,6′-dihydroxy-2,2′-bipyridyl), and $[Ru(\eta^6\text{-arene})(dmobpy)Cl]^{+}$[15] (dmobpy = 4,4′-dimethoxy-2,2′-bipyridine). Complexes of Ru(II), Rh(III), and Ir(III) with the tosylated diamine ligands TsDPEN (*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine) and Ts-CYDN (*N*-(*p*-toluenesulfonyl)-1,2-cyclohexanediamine) have been designed and employed for TH (including asymmetric TH) in water.[4b,16] Carreira and co-workers have explored $(\eta^5\text{-Cp*})Ir^{III}$ complexes with fluorinated Ts-DPEN ligands for catalysis of TH in water[17] to understand the effect of fluorine on catalysis. A HCOONa/HCOOH mixture has been used as the hydrogen donor in most of the reported catalytic

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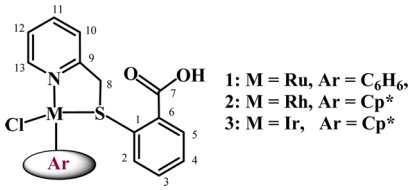
THs in water. Catalysis with this hydrogen donor is pH dependent and many times an excess (up to 10 mmol) is required. However, there has been no report using glycerol as the hydrogen donor for TH in water to our knowledge. There are some recent reports on using glycerol as a solvent and hydrogen source in TH carried out in organic solvents.[18−20]

Platinum group metal complexes of organochalcogen ligands are promising catalysts for several organic reactions, including the transfer hydrogenation of carbonyl compounds.[21] Apart from efficiency, these catalysts are attractive due to their insensitivity to air and moisture, solubility in various organic solvents, and stability in solution. In view of the efficiency of half-sandwich complexes of Ru(II), Rh(III), and Ir(III) with organochalcogen ligands for TH[21] and the fact that glycerol has been unexplored for it in water, we herein report a new class of stable and water-soluble half-sandwich complexes of Ru(II), Rh(III), and Ir(III) with 2-(pyridin-2-ylmethylsulfanyl)benzoic acid (**1**−**3**, respectively; Chart 1), which catalyze TH in aqueous medium using glycerol as a hydrogen source. The catalysis is not only efficient but pH independent. The synthesis and single-crystal structural aspects of these complexes **1**−**3** have also been reported in this paper. Density functional theory (DFT) calculations have been carried out and are consistent with experimental relative catalytic efficiencies and structural features. These results have also been made part of the present paper.

Chart 1



RESULTS AND DISCUSSION

The syntheses of **L** and its complexes are outlined in Scheme 1. The procedure used for the synthesis of ligand **L** has been reported earlier.[22] The half-sandwich ruthenium(II) (**1**), rhodium(III) (**2**), and iridium(III) (**3**) complexes appear to be formed by chloro bridge cleavages of $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$, $[(\eta^5\text{-}Cp^*)RhCl(\mu\text{-}Cl)]_2$, and $[(\eta^5\text{-}Cp^*)IrCl(\mu\text{-}Cl)]_2$, respectively, followed by reaction with 2-(pyridin-2-ylmethylsulfanyl)benzoic acid (**L**) at room temperature, facilitated by chloride extraction with NH_4PF_6. Complexes **1**−**3** are moderately soluble in $CHCl_3$, CH_2Cl_2, and CH_3OH, but in CH_3CN their solubility is good. In the presence of KOH the three complexes are soluble in water. They appear to be stable to air and moisture and can be stored at room temperature for several months under ambient conditions (as evidenced by their ^1H NMR spectra). The elemental analyses and multinuclear NMR, IR, and mass spectral data of **1**−**3** are consistent with their structures on the basis of single-crystal X-ray diffraction (Scheme 1).

Crystal Structures. Crystals of **1**−**3** of quality suitable for X-ray diffraction were obtained by diffusion of diethyl ether into concentrated solutions of the complexes made up in a methanol/acetonitrile mixture (1/4 v/v). The crystallographic and refinement data for **1**−**3** are summarized in the Supporting Information (Table S1). The ligand exhibits an identical bonding mode in all complexes **1**−**3**: i.e., a five-membered ring is formed on its coordination with the metal center via the pyridyl nitrogen and sulfur. The molecular structure diagrams of cations of **1**−**3** are shown in Figures 1−3, respectively, with selected bond lengths and angles. The ellipsoids are shown at the 30% probability level, and PF_6^- and H atoms are omitted for clarity. In cations of all the complexes there is a pseudo-

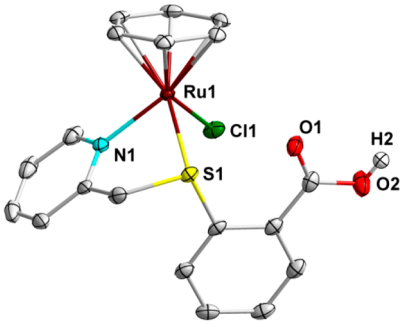


Figure 1. Molecular structure of the cation of **1**. Bond lengths (Å): Ru(1)−S(1) 2.4079(6), Ru(1)−N(1) 2.103(2), Cl(1)−Ru(1) 2.3842(6), Ru−C 2.198(2)−2.221(2). Bond angles (deg): S(1)−Ru(1)−N(1) 80.16(6), S(1)−Ru(1)−Cl(1) 91.95(2), N(1)−Ru(1)−C1(1) 86.67(6), O(1)−C(7)−O(2) 122.9(2).

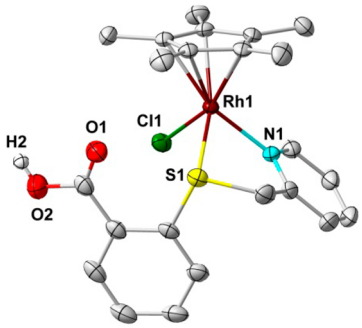
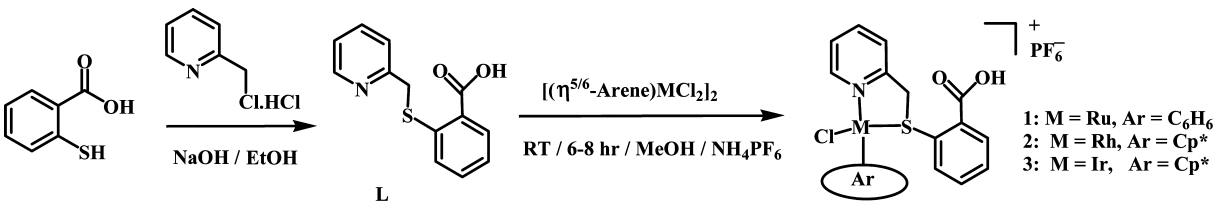


Figure 2. Molecular structure of the cation of **2**. Bond lengths (Å): Rh(1)−S(1) 2.3989 (10), Rh(1)−N(1) 2.107(3), Cl(1)−Rh(1) 2.3724(10), Rh−C 2.155(3)−2.170(4). Bond angles (deg): S(1)−Rh(1)−N(1) 81.37(9), S(1)−Rh(1)−Cl(1) 94.53(4), N(1)−Rh(1)−C1(1) 87.05(9), O(1)−C(7)−O(2) 121.8(4).

Scheme 1. Synthesis of Ligand L and Complexes 1−3



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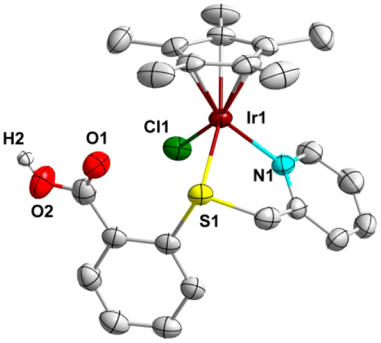

Figure 3. Molecular structure of the cation of **3**. Bond lengths (Å): Ir(1)−S(1) 2.3637 (14), Ir(1)−N(1) 2.099(4), Cl(1)−Ir(1) 2.3791(15), Ir−C 2.145(6)−2.194(5). Bond angles (deg): S(1)−Ir(1)−N(1) 81.78(14), S(1)−Ir(1)−Cl(1) 93.44(5), N(1)−Ir(1)−C1(1) 85.33(13), O(1)−C(7)−O(2) 122.9(7).

octahedral half-sandwich "piano-stool" disposition of donor atoms around Ru, Rh, or Ir. The centroid of the η^6-C_6H_6/η^5-Cp* ring occupies nearly the center of a triangular face of an octahedron. The sulfur, nitrogen, and chlorine atoms along with η^6-C_6H_6/η^5-Cp* complete the coordination sphere of Ru/Rh/Ir. The Ru−S bond length of **1** (2.4079(6) Å) is within the range (2.3548(15)−2.4156(9) Å) in which such a bond length of several species has been reported.[21a−d,23b] The Ru−C(C_6H_6 centroid) distance of complex **1** (1.688(1) Å) is consistent with the values 1.685(1)−1.687(1) Å reported earlier.[23b] The Rh−S bond distance in **2** (2.3989(10) Å) is consistent with the values reported for the complexes [η^5-Cp*RhCl{2-(phenylthiomethyl)pyridine}]PF_6 (2.383(2) Å)[23a] and [η^5-Cp*RhCl(1,1′-(1,2-ethanediyl)bis(3-methylimidazole-2-thione))]Cl (2.3967(11) Å).[24] The Rh−C(Cp* centroid) distance of complex **2** (1.785(0) Å) is somewhat shorter than the reported values (1.794−1.809 Å).[23] The Ir−S bond distance of **3** (2.3637(14) Å) falls in the range (2.318(1)−2.3872(10) Å) in which Ir−S bond lengths of [η^5-Cp*IrCl{2-(phenylthiomethyl)pyridine}]PF_6[23a] and [η^5-Cp*Ir(CO)(μ-STol)Pt(STol)(PPh_3)][25] have been reported. The Ir−C(Cp* centroid) distance in **3** (1.805(1) Å) is consistent with the value reported for the complex [(η^5-Cp*)Ir(phpy)Cl] (1.863 Å).[26] Significant hydrogen bonding occurs in the crystal structures of complexes **1**−**3**. Their carboxylic groups are involved in intramolecular (O of COOH and H of Cp* or C_6H_6) as well as intermolecular hydrogen bonding (see Figure 4 for **1**). Another important noncovalent interaction is C−O···S (2.648(2) Å; sum of van der Waals radii 3.32 Å) (Figure 4 for **1**). The anion PF_6^- has been found to be involved in O−H···F and C−H···F secondary interactions in all of the complexes **1**−**3**, resulting in a three-dimensional packing framework. In Figure 5 this is shown for complex **1**. The significant secondary interactions for the other two complexes are detailed in Supporting Information (Figures S1 and S2 and Table S3).

Spectral Data. NMR spectral data of ligand **L** and its complexes **1**−**3** were found to be characteristic and consistent in the case of **1**−**3** with their single-crystal structures. In ^{1}H and ^{13}C{^{1}H} NMR spectra of **1**−**3** signals of protons and carbon atoms generally appear at higher frequencies relative to those of the free ligand, which coordinates with Ru, Rh, and Ir in a bidentate mode. The magnitude of the shift to higher frequency is large for $PyCH_2(S)$ (up to 8.03 ppm) in ^{13}C{^{1}H} NMR spectra and for protons attached to its carbon atoms (up to 0.65 ppm) in ^{1}H NMR spectra. These observations imply that there is a coordination of ligand **L** through S/N with the metal centers. In ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** signals (singlet) of η^6-benzene have been found shifted to lower frequency (up to 0.3 and 4.4 ppm, respectively) with respect to those of [η^6-(C_6H_6)$RuCl_2$]$_2$. In ^{1}H and ^{13}C{^{1}H} NMR spectra of complex **2**, the signals of the η^5-pentamethylcyclopentadienyl group (singlet in ^{1}H NMR) were found at lower frequency (maximum shifts ∼0.12 and 2.9 ppm, respectively) with respect to those of [(η^5-Cp*)RhCl(μ-Cl)]$_2$. This may be due to substitution of Cl with S and N, which have relatively lower electronegativity. Similar observations regarding shifting of signals with respect to those of [(η^5-Cp*)IrCl(μ-Cl)]$_2$ were made in ^{1}H and ^{13}C{^{1}H} NMR spectra of **3**.

HR-MS spectra of structurally analogous complexes **1**−**3** indicate that PF_6^- is considerably labile and consequently a molecular ion peak in mass spectra is not observed. The peak of fragment the [M − (H + Cl)]$^+$ has been observed in the spectrum of complex **2**, whereas the species [M]$^+$ has been found in the spectra of complexes **1** and **3** (M = cation of **1**−**3**). The peaks of the fragments [(η^6-C_6H_6)RuCl]$^+$, [(η^5-Cp*)-RhCl]$^+$, and [(η^5-Cp*)IrCl]$^+$ have also been observed in the mass spectra of **1**−**3**, respectively.

Catalytic Transfer Hydrogenation of Carbonyl Compounds. The activity of complexes **1**−**3** (0.5−1.0 mol %) for catalytic transfer hydrogenation (TH) of carbonyl compounds in water was explored using formic acid (sodium formate as base), citric acid, ascorbic acid, and glycerol (using KOH as a base with all three) as hydrogen sources (Table 1). The amount of HCOOONa/HCOOH required for TH was large, and the catalytic conversion was pH dependent. The TH in aqueous

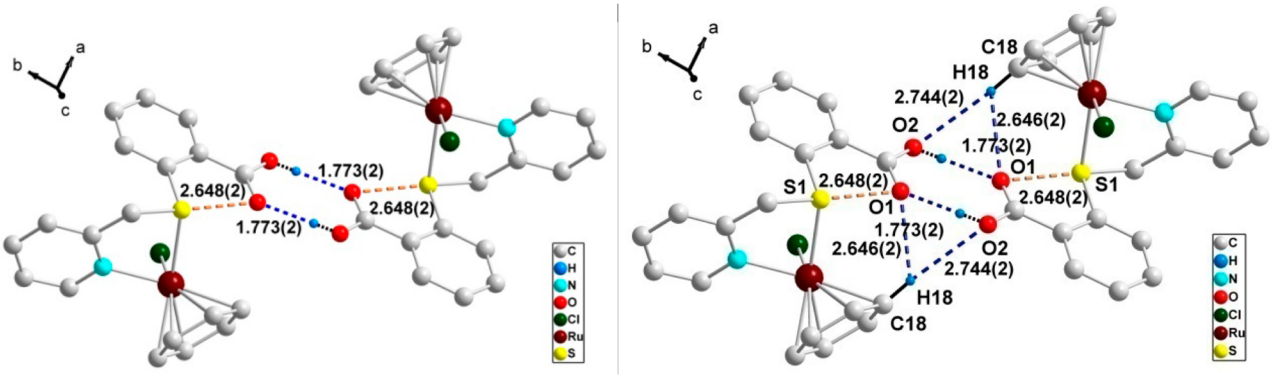

Figure 4. Noncovalent O−H···O and C−O···S interactions in **1**.

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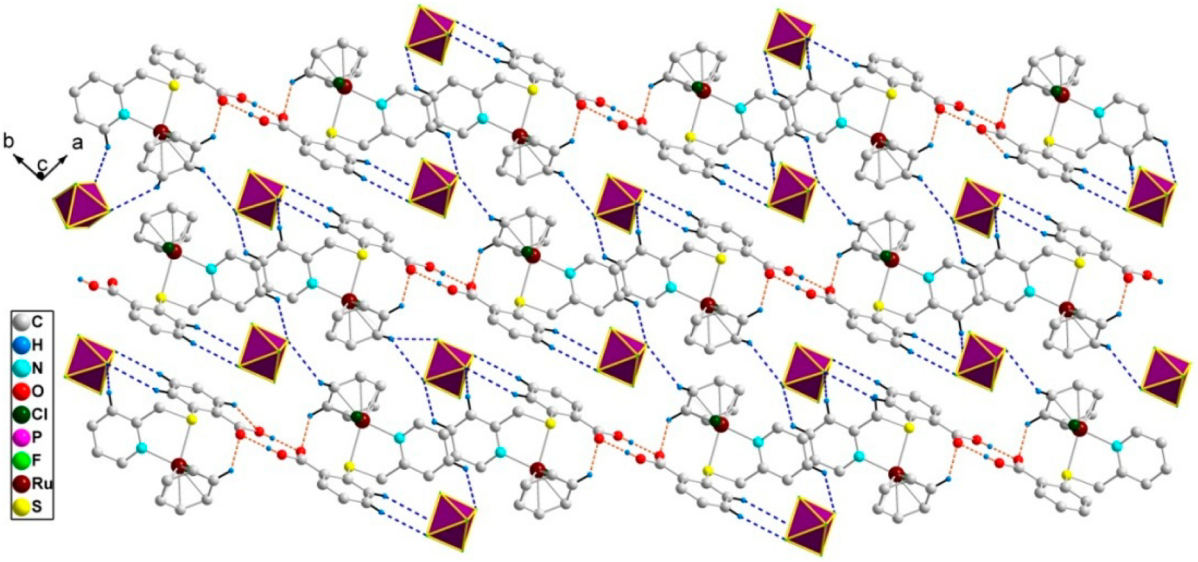
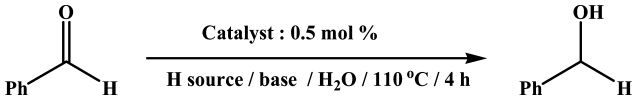


Figure 5. Three-dimensional packing framework showing noncovalent C−H···F and O−H···O interactions in the crystal of **1**. PF_6 is in the polyhedral form.

Table 1. Optimization of Reaction Conditions of Transfer Hydrogenation[a]

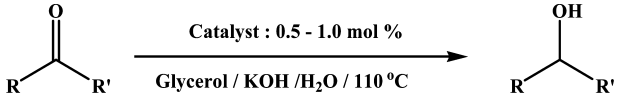


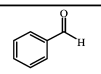
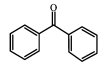
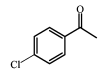
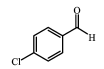
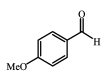
entry	omplex	base/amt (mmol)	H source/amt (mmol)	pH	conversion[b] (%)
1	**1**	HCOONa/10	formic acid/5	2.5	92
2	**2**	HCOONa/10	formic acid/5	2.5	98
3	**3**	HCOONa/10	formic acid/5	2.5	88
4	**2**	HCOONa/1	formic acid/1	2.5	70
5	**2**	HCOONa/5	formic acid/5	2.5	98
6	**2**	HCOONa/5	formic acid/5	5.5	70
7	**2**	HCOONa/5	formic acid/5	10	62
8	**2**	KOH/1	citric acid/2	5	36
9	**2**	KOH/1	citric acid/2	2.5	42
10	**2**	KOH/1	ascorbic acid/2	5	20
11	**2**	KOH/1	ascorbic acid/2	2.5	30
12	**2**	KOH/0.1	2-propanol/5		64
13	**2**	KOH/1	glycerol/1	2.5	99
14	**2**	KOH/1	glycerol/1	10	98
15	**2**	KOH/1	glycerol/1		99
16	**2**	KOH/5	glycerol/5		99

[a]Conditions: 1 mmol of benzaldehyde, catalyst **1**−**3** 0.5 mol %, 5 mL of water, temperature 110 °C. [b]Conversion determined with NMR.

medium was the most efficient and pH independent with glycerol as a hydrogen source at 110 °C. Thus, TH in water with glycerol has been studied in detail. The carbonyl compounds were reduced to the corresponding alcohols, while glycerol was dehydrogenated to give dihydroxyacetone (DHA: ^{1}H NMR δ 4.4 and 3.5 ppm) and other products.[18] As a model reaction, the reduction of benzaldehyde in water using glycerol was studied. The reaction conditions were optimized (Table 1). KOH (1 mmol) was found most suitable as a base. Thereafter, complexes **1**−**3** for promoting aqueous transfer hydrogenation reactions of several ketones and aldehydes having other functional groups as substituents were studied under optimum reaction conditions. The percent conversions are given in Table 2. The most efficient conversion (up to 99%) for all of the catalysts was found in the case of benzaldehyde.

Table 2. Transfer Hydrogenation of Carbonyl Compounds[a]



Entry	Substrate	Catalyst	Mol %	Time(h)	Conversion[b] (%)
1		**1**	0.5	5	98
		2	0.5	4	99
		3	0.5	6	95
2		**1**	1.0	20	85
		2	1.0	18	90
		3	1.0	22	85
3		**1**	1.0	20	90
		2	1.0	20	98
		3	1.0	24	88
4		**1**	1.0	15	86
		2	1.0	12	92
		3	1.0	16	80
5		**1**	1.0	15	80
		2	1.0	12	90
		3	1.0	15	82
6		**1**	0.5	10	95
		2	0.5	8	95
		3	0.5	12	90
7		**1**	0.5	12	75
		2	0.5	10	80
		3	0.5	15	80
8		**1**	0.5	12	90
		2	0.5	10	95
		3	0.5	15	90

[a]Conditions: 1 mmol of substrate, 1 mmol of KOH, 1 mmol of glycerol, 5 mL of water, temperature 110 °C. [b]Conversion determined with NMR.

The Rh(III) complex **2** is more efficient as a catalyst relative to the corresponding Ru(II) and Ir(III) analogues (**1** and **3**). When the transfer hydrogenation reactions catalyzed with **2** were monitored with ^{1}H NMR spectra, a broad singlet was noticed around δ −10.7 ppm after 1 h. This signal is a characteristic of metal hydride formation, which probably

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occurs due to M−Cl bond cleavage or its very considerable weakening to make available on the metal center a coordination site for formation of an intermediate containing a M−H bond.[27] Therefore, the present catalytic reactions with **1**−**3** probably progress via formation of alkoxide and metal hydride intermediates.[28] With a deficiency of NH groups in the system, transfer hydrogenation catalyzed with **1**−**3** appears to pursue a conventional mechanism.[28] The Rh(III) complex **2** appears to be a somewhat better catalyst than the Ru(II)/Ir(III) analogues (**1**/**3**) (Table 2), as in case of the Ru or Ir complexes for conversions comparable with that of the Rh analogue with the same catalyst loading, a somewhat longer reaction time is needed. DFT calculations (see below) are consistent with the better efficiency of the Rh complex **2**.

It is pertinent to compare the present catalytic activations with the reported procedures carried out in water or in which the hydrogen source is glycerol, as there is no example of the use of glycerol as a source of hydrogen in aqueous medium to our knowledge. Iridium(III) complexes[18d,19b] of NHC-based ligands have been reported for catalytic activation of TH in glycerol, but the catalyst loading required is 2.5 mol % higher than those of **1**−**3** (0.5−1.0 mol %). The time needed for 99% conversion is also 7 h, except in one case, where it is 1.5 h. Several Ru(II) complexes[11,14,15] have been explored for TH in water using HCOOH/HCOONa as the hydrogen source. Apart from mandatory pH control, the reaction time for good conversion (>80%) in many cases is more than 12 h more than the time required for **1**−**3**. However, our catalytic system may be faster than the reported systems due to temperature of 110 °C selected in the present case for TH, which is higher than the 70−90 °C used in some earlier reported catalytic systems.[14−17] Ir(III) and Rh(III) complexes have been relatively less explored for TH in water.[4,5,16,17] An (η^5-Cp*)Ir^{III} complex with a pyridine-based ligand gives 98% conversion in 12 h at 0.1 mol % catalyst loading using water as solvent.[5e] The catalyst loading is somewhat lower than that of the present Ir complex but use of formic acid as the H source has made the protocol pH dependent. The Rh-TsCYDN complex gives 99% conversion in 15 min when 1 mol % of catalyst is used in water with HCOOH as a H source.[4a] The Rh TsDPEN complex causes catalytic TH in water in a very short time (30 min) at a catalyst loading of 1 mol %, but the process is pH dependent, as the hydrogen source is HCOOH.[4e]

Homogeneous vs Heterogeneous Catalysis in Transfer Hydrogenation. When transfer hydrogenation is catalyzed with iridium complexes in glycerol under microwave conditions, formation of Ir nanoparticles (NPs) has been reported, which affect the catalytic process.[20b] Thus, it is significant to understand whether the present transfer hydrogenation catalysis is homogeneous or heterogeneous. In order to know whether such metal NPs are formed with the present complexes and also have some influence on catalysis, a mercury poisoning test[29] has been executed. The presence of mercury in the TH of acetophenone with glycerol using **1**−**3** as catalysts showed no significant inhibition of conversion (Table 3). A PPh_3 poisoning test has also been carried out.[30] In the presence of 5 equiv of PPh_3 the catalytic reaction occurred with only a 6% decrease in percent conversion (Table 4). Thus, the catalysis is homogeneous in nature. Furthermore, there was no visible sign of NP formation.

DFT Calculations. Density functional theory (DFT) calculations were executed on all three complexes **1**−**3**, in order to support structure and catalytic activity related

Table 3. Mercury Test for the Catalytic Transfer Hydrogenation[a]

entry	catalyst/Hg	time (h)	conversion (%)[b]
1[c]	1/0	5	98
2[d]	1/0	4	99
3[e]	1/0	6	95
4[c]	1/400	5	90
5[d]	1/400	4	95
6[e]	1/400	6	88

[a]Conditions: 1 mmol of benzaldehyde, 1 mmol of KOH, 1 mmol of glycerol, catalyst 0.5 mol %, water 5 mL, 110 °C, in air. [b]Determined by NMR. [c]Ru complex **1**. [d]Rh complex **2**. [e]Ir complex **3**.

Table 4. PPh_3 Poisoning Test for the Catalytic Transfer Hydrogenation[a]

entry	catalyst/PPh_3	time (h)	conversion (%)[b]
1[c]	1/0	5	98
2[d]	1/0	4	99
3[e]	1/0	6	95
4[c]	1/5	5	92
5[d]	1/5	4	94
6[e]	1/5	6	90

[a]Conditions: 1 mmol of benzaldehyde, 1 mmol of KOH, 1 mmol of glycerol, catalyst 0.5 mol %, water 5 mL, 110 °C. [b]Determined by NMR. [c]Ru complex **1**. [d]Rh complex **2**. [e]Ir complex **3**.

experimental results. The HOMOs (highest occupied molecular orbitals) of all complexes are essentially similar and are positioned primarily over Ru, Rh, or Ir and the benzene/Cp* ring, with some contribution toward S, N, and Cl donor atoms. The d orbitals of Ru(II)/Rh(III)/Ir(III) interacting with π orbitals of η^5-Cp*/η^6-benzene ring and p orbitals of chlorine, nitrogen, and sulfur atoms compose their HOMO (Figure 6). Detailed calculated bond length and angle parameters are given in Table 5. The concurrence between the observed and calculated bonding parameters is better for M−Cl and M−arene(centroid). There is some variation between calculated and observed M−S bond distances. The calculated and experimentally found bond angles are also reasonably close (Table 5), except in few cases: e.g., Cl−Ru−N1.

The HOMO−LUMO energy gap (lowest unoccupied molecular orbital) of a complex may be correlated with its chemical reactivity.[31] Generally, a large gap reflects low reactivity. The HOMO−LUMO energy gaps of **1**−**3** differ sufficiently (Figure 6). It is lowest for the Rh complex, indicating that most likely its catalytic activity has to be greater than those of the Ru and Ir complexes. This is consistent with the observed catalytic efficiency of complexes **1**−**3** (Table 2).

CONCLUSIONS

The half-sandwich complexes [(η^6-C_6H_6)Ru(**L**)Cl][PF_6], [(η^5-Cp*)Rh(**L**)Cl][PF_6], and [(η^5-Cp*)Ir(**L**)Cl][PF_6] (**1**−**3**, respectively) of 2-((2-pyridyl)methylthio)benzoic acid (**L**) have been synthesized and characterized by multinuclear NMR, HR-MS, and X-ray crystallography. The compounds are water soluble, due to the presence of a −COOH group in the ligand. They efficiently catalyze pH-independent transfer hydrogenation of carbonyl compounds in water using glycerol as a hydrogen donor. Glycerol has been explored for TH in water for the first time. The insensitivity of the three complexes to air and moisture is an additional advantage. The catalytic

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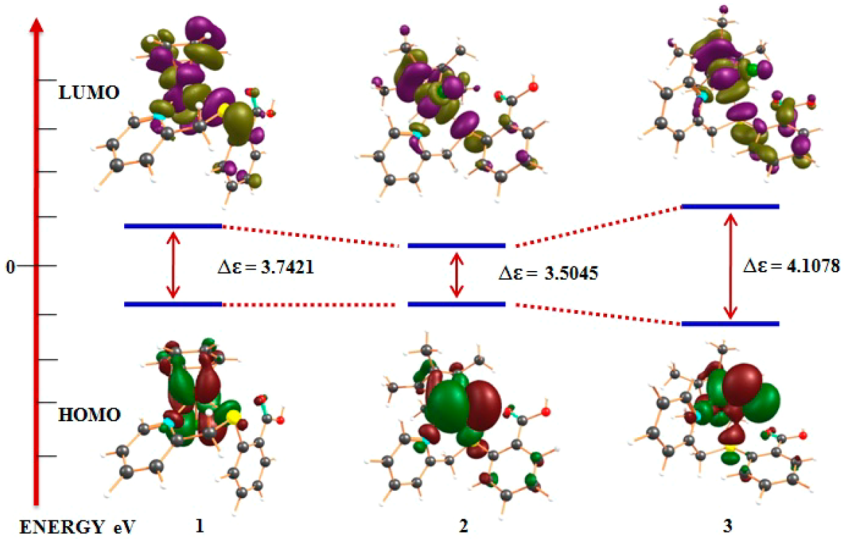

Figure 6. HOMO−LUMO energy gap of **1**−**3**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) of 1−3 Determined Experimentally and Optimized with DFT

1			2			3		
	bond length/ angle	optimized value		bond length/ angle	optimized value		bond length/ angle	optimized value
Ru−S(1)	2.4079(6)	2.505	Rh−S(1)	2.3989(10)	2.555	Ir−S(1)	2.3637(14)	2.541
Ru−Cl(1)	2.3842(6)	2.402	Rh−Cl(1)	2.3724(10)	2.410	Ir−Cl(1)	2.3791(15)	2.424
Ru−N(1)	2.103(2)	2.142	Rh−N(1)	2.107(3)	2.179	Ir−N(1)	2.099(4)	2.151
Ru−C[a]	1.688(1)	1.779	Rh−C[a]	1.858(0)	1.785	Ir−C[a]	1.805(1)	1.842
S1−Ru−N1	80.16(6)	81.45	S1−Rh−N1	81.37(9)	80.22	S1−Ir−N1	81.78(14)	79.97
S1−Ru−Cl	91.95(2)	91.04	S1−Rh−Cl	93.44(5)	92.88	S1−Ir−Cl	93.44(5)	91.60
Cl−Ru−N1	86.67(6)	83.14	Cl−Rh−N1	85.33(13)	85.88	Cl−Ir−N1	85.33(13)	84.57
O1−C7−O2	122.9(2)	122.08	O1−C7−O2	121.8(4)	121.96	O1−C7−O2	122.9(7)	122.14

[a]C = centroid.

efficiency is highest for the Rh complex, which is corroborated by DFT studies. There is no evidence for NP formation in the catalytic process, which appears to be homogeneous. The formation of a M−H bond favors a conventional mechanism for the present transfer hydrogenation via alkoxide formation. The experimental bond lengths and angles are consistent with DFT results.

EXPERIMENTAL SECTION

Physical Measurements. All reactions have been performed in glassware dried in an oven, under ambient conditions except for the synthesis of **L**. 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. The nitrogen atmosphere, when required, was created using Schlenk techniques. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300.13 and 75.47 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 with ^{1}H NMR). IR spectra in the range 4000−400 cm^{-1} were recorded as KBr pellets. For single-crystal structures the data were collected using Mo Kα (0.71073 Å) radiation at 298(2) K. The software SADABS[32] was used for absorption correction (if needed) and SHELXTL for space group, structure determination, and refinements.[33] 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, sodium formate as reference compound), with sample taken in CH_3CN. The C, H, and N analyses were carried out with a C, H, and N analyzer.

Chemicals and Reagents. Thiosalicylic acid, (2-chloromethyl)-pyridine hydrochloride, and ammonium hexafluorophosphate were used as received. The ligand **L** was prepared as reported earlier.[22] [(η^6-C_6H_6)RuCl(μ-Cl)]$_2$,[34] [(η^5-Cp*)RhCl(μ-Cl)]$_2$,[35] and [(η^5-Cp*)IrCl-(μ-Cl)]$_2$[36] were synthesized according to literature procedures. Common reagents and chemicals available locally were used. All of the solvents were dried and distilled before use by standard procedures.[37]

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-03 program.[38] The geometry of complexes **1**−**3** was optimized at the B3LYP[39] level using an SDD basis set for the metal and S atom and 6-31G* basis sets for C, N, Cl, and H. 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 prepared using the Chemcraft program package (http://www.chemcraftprog.com).

Synthesis of Complex 1. The ligand **L** (0.2 mmol) and solid [(η^6-C_6H_6)RuCl$_2$]$_2$ (0.1 mmol) dissolved in CH_3OH (15 cm^3) were stirred together for 8 h at room temperature. The resulting yellow solution was filtered, and the volume of the filtrate was reduced to ∼7 cm^3 with a rotary evaporator. The concentrate was treated with solid NH_4PF_6 (0.2 mmol), and the resulting yellow microcrystalline solid **1** was filtered, washed with 10 cm^3 of ice-cold CH_3OH, and dried in vacuo. The single crystal of **1** was obtained by diffusion of diethyl ether into their solutions (4 cm^3) made up in a mixture of CH_3OH and CH_3CN

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(1/4). Yield: 0.102 g, ∼85%. Anal. Calcd for $C_{19}H_{17}ClNO_2RuS·[PF_6]$: C, 37.73; H, 2.83; N, 2.32. Found: C, 37.32; H, 2.92; N, 2.48. Mp: 180 °C. ^{1}H NMR (CD_3CN, 25 °C vs Me_4Si; δ (ppm)): 4.74−4.96 (m, 2H, H_8), 5.78 (s, 6H, Ru-Ar-H), 6.83 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, H_{10}) 7.38−7.44 (m, 3H, H_2, H_{11-12}), 7.84−7.87 (m, 1H, H_3), 7.98−8.07 (m, 2H, H_4, H_{13}), 8.88−8.89 (m, 1H, H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_4Si; δ (ppm)): 45.8 (C_8), 87.8 (Ru-Ar-C), 123.8 (C_{10}), 124.8 (C_{12}), 128.2 (C_3), 128.5 (C_2), 129.8 (C_6), 130.1 (C_5), 131.7 (C_4), 134.4 (C_{11}), 140.1 (C_1), 157.0 (C_{13}), 159.8 (C_9), 166.0 (C_7 COOH). HR-MS (CH_3CN): $[M]^+$ m/z 459.9705; calculated value for $C_{19}H_{17}ClNO_2RuS$ 459.9708 (δ −0.7 ppm). IR (KBr; cm^{-1}): 3101 (m; ν_{C-H}(aromatic)), 2923 (s; ν_{C-H}(aliphatic)), 1691 (m; $\nu_{C=N}$), 1439 (m; $\nu_{C=C}$(aromatic)), 835 (s; ν_{P-F}), 767 (m; ν_{C-H}(aromatic)).

Synthesis of Complex 2. The solid $[(\eta^5\text{-Cp*})RhCl(\mu\text{-Cl})]_2$ (0.1 mmol) and ligand **L** (0.2 mmol) dissolved in CH_3OH (15 cm^3) were mixed. 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 (0.2 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 **2** were obtained by diffusion of diethyl ether into its solution (4 cm^3) made in a mixture (1/4) of CH_3OH and CH_3CN. Yield: 0.120 g, ∼90%. Anal. Calcd for $C_{23}H_{26}ClNO_2RhS·[PF_6]$: C, 41.61; H, 3.95; N, 2.11. Found: C, 41.69; H, 3.85; N, 2.21. Mp: 205 °C. ^{1}H NMR (CD_3CN, 25 °C vs Me_4Si; δ (ppm)): 1.74 (s, 15H, Rh-Cp*-H), 4.50−4.97 (m, 2H, H_8), 6.92−6.95 (m, 1H, H10), 7.37−7.50 (m, 3H, H_2, H_{11-12}), 7.89−7.92 (m, 1H, H_3), 8.03−8.06 (m, 2H, H_4, H_{13}), 8.45 (d, $^3J_{H-H}$ = 5.4 Hz, 1H, H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_4Si; δ (ppm)): 8.5 (Rh-Cp*-C) 43.5 (C_8), 99.3 (Rh-Cp-C), 124.7 (C_{10}), 125.7 (C_{12}), 126.8 (C_3), 128.3 (C_2), 129.8 (C_6), 130.4 (C_5), 131.1 (C_4), 133.0 (C_{11}), 140.2 (C_1), 154.2 (C_{13}), 159.7 (C_9), 166.3 (C_7 COOH). HR-MS (CH_3CN): $[M - (Cl + H)]^+$ m/z 482.0655; calculated value for $C_{23}H_{25}NO_2RhS$ 482.656 (δ −0.8 ppm). IR (KBr; cm^{-1}): 3100 (m; ν_{C-H}(aromatic)), 2974 (s; ν_{C-H}(aliphatic)), 1686 (m; $\nu_{C=N}$), 1443 (m; $\nu_{C=C}$(aromatic)), 843 (s; ν_{P-F}), 752 (m; ν_{C-H}(aromatic)).

Synthesis of Complex 3. A mixture of solid $[(\eta^5\text{-Cp*})IrCl(\mu\text{-Cl})]_2$ (0.1 mmol) and **L** (0.2 mmol) dissolved in CH_3OH (15 cm^3) was stirred for 10 h at room temperature. The resulting yellow solution was filtered. After workup, as described for **2**, single crystals of **3** were obtained by diffusion of diethyl ether into its solution (4 cm^3) made in a mixture (1/4) of CH_3OH and CH_3CN. Yield: 0.130 g, ∼86%. Anal. Calcd for $C_{23}H_{26}ClNO_2IrS·[PF_6]$: C, 36.68; H, 3.48; N, 1.86. Found: C, 36.60; H, 3.23; N, 2.01. Mp: 210 °C. ^{1}H NMR (CD_3CN, 25 °C vs Me_4Si; δ (ppm)): 1.73 (s, 15H, Ir-Cp*-H), 4.30−5.07 (m, 2H, H_8), 6.96 (m, 1H, H10), 7.40−7.45 (m, 3H, H_2, H_{11-12}), 8.03−8.08 (m, 3H, H_{3-4}, H_{13}), 8.47 (d, $^3J_{H-H}$ = 5.7 Hz, 1H, H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_4Si; δ (ppm)): 7.4 (Ir-Cp*-C) 45.7 (C_8), 92.0 (Ir-Cp-C), 123.8 (C_{10}), 125.9 (C_{12}), 127.6 (C_3), 128.4 (C_2), 128.5 (C_6), 130.1 (C_5), 130.7 (C_4), 132.9 (C_{11}), 140.2 (C_1), 154.0 (C_{13}), 160.1 (C_9), 165.9 (C_7 COOH). HR-MS (CH_3CN): $[M]^+$ m/z 608.0958; calculated value for $C_{23}H_{26}ClIrNO_2S$ 608.0988 (δ 4.9 ppm). IR (KBr; cm^{-1}): 3089 (m; ν_{C-H}(aromatic)), 2983 (s; ν_{C-H}(aliphatic)), 1608 (m; $\nu_{C=N}$), 1473 (m; $\nu_{C=C}$(aromatic)), 842 (s; ν_{P-F}), 756 (m; ν_{C-H}(aromatic)).

Procedure for Catalytic Transfer Hydrogenation of Carbonyl Compounds. A round-bottom flask fitted with a water condenser (with a stopper) and containing a magnetic bar was charged with a mixture of the substrate (1 mmol), glycerol (1 mmol), KOH (1 mmol), water (5 cm^3), and **1**, **2**, or **3** (0.5−1 mol %), stirred and heated to 110 °C for the appropriate time. The reaction was followed by ^{1}H NMR spectroscopy. After completion of the reaction, the reaction mixture was cooled to room temperature. The mixture was extracted with diethyl ether (3 × 20 cm^3), and the solvent was removed on a rotary evaporator. The resulting semisolid extract was passed through a short column (∼8 cm 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. The ^{1}H NMR spectra authenticating these products are reported in the Supporting Information (Figures S12−S19).

Hg Poisoning Test. In a reaction vessel was placed an excess of Hg (Hg/(Ru/Rh/Ir) 400/1). The aqueous transfer hydrogenation reaction of benzaldehyde (1.0 mmol) with glycerol (1.0 mmol) using **1**, **2**, or **3** (0.5 mol %) as catalyst was carried out in the vessel under optimum conditions. Conversion of ∼95% was observed after 4−6 h of reaction.

PPh_3 Poisoning Test. To a catalytic transfer hydrogenation reaction mixture of benzaldehyde in water with glycerol (1.0 mmol) was added PPh_3 (5 mol %) under optimum conditions after addition of catalyst **1**, **2**, or **3** (1 mol %). After 4−6 h of reaction ∼94% of the product was obtained.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF and xyz files giving crystallographic and refinement data, bond lengths and angles, secondary interaction distances, NMR and mass spectra, and Cartesian coordinates (CCDC Nos. 986289, 986290, and 986291, respectively, for **1**−**3**). 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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