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Author: Saravanan Thangavel Subramaniam Boopathi N. Mahadevaiah Ponmalai Kolandaivel Pramod Pansuriya Holger B. Friedrich

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Highlights

- ➤ Ir(III), Rh(III) and Ru(II) complexes show pseudo octahedral "piano-tool" geometry
- > Catalytic activity for benzyl alcohol oxidation demonstrated by all three complexes
- > Ir and Ru complexes show best conversion of primary aromatic alcohols to aldehydes
- > DFT studies carried out on the complexes
- > Proposed reaction mechanism is supported by DFT

Catalytic Oxidation of Primary Aromatic Alcohols Using Half Sandwich Ir(III), Rh(III) and Ru(II) Complexes: A DFT Study

Saravanan Thangavel^a, Subramaniam Boopathi^b, N. Mahadevaiah^a, Ponmalai Kolandaivel^b, Pramod Pansuriya^a, Holger B. Friedrich^{*a}

^aSchool of Chemistry and Physics, University of KwaZulu-Natal, Durban 4000, South Africa.

^bDepartment of Physics, Bharathiar University, Coimbatore-641 046, Tamilnadu, India.

* Corresponding author: E-mail address: friedric@ukzn.ac.za; Tel: +27 31 2603107; Fax: +27 31 2603091.

Graphical abstract



Catalytic Oxidation of Primary Aromatic Alcohols Using Half Sandwich Ir(III), Rh(III) and Ru(II) Complexes: A Practical and Theoretical study.

Saravanan Thangavel^a, Subramaniam Boopathi^b, N. Mahadevaiah^a, Ponmalai Kolandaivel^b, Pramod Pansuriya^a, Holger B. Friedrich^{*a}

^aSchool of Chemistry and Physics, University of KwaZulu-Natal, Durban 4000, South Africa.
^bDepartment of Physics, Bharathiar University, Coimbatore-641 046, Tamilnadu, India.
*Corresponding author: E-mail address: friedric@ukzn.ac.za; Tel: +27 31 2603107; Fax: +27 31 2603091.

Abstract

The complexes $[Cp*IrCl(N-(pyridin-2-ylmethylene)aniline)]PF_6$ (1), [Cp*RhCl(N-(pyridin-2-ylmethylene)aniline)] PF_6 (2), (where $Cp^* = 1, 2, 3, 4, 5$ -pentamethylcyclopentadiene) and $[n^6$ -areneRuCl(N-(pyridin-2-ylmethylene)aniline)]PF₆ (3) have been synthesized and the structure and purity of these were confirmed by single crystal XRD and elemental analyses. Iridium and rhodium complexes exhibit the P21/n space group, the ruthenium complex the P21/c space group and all three complexes show the expected pseudo octahedral "piano-stool" geometry. The catalytic performance of these complexes for the dehydrogenation of primary alcohols to their respective aldehydes with different bases and solvents was investigated. The complexes of iridium and ruthenium give good conversions in different alkaline solutions. Density functional theory was applied to determine the respective MO energy levels, bond lengths, bond angles and binding energies of all the metal complexes. It was also used to study the activity, stability and intermediates of the complexes. A Gibbs free energy (ΔG) DFT calculation was carried out to help understand the reaction mechanism / catalytic cycle of the Rh complex (2). The energy barrier for oxidation of aromatic alcohols by the rhodium hydride complex is much lower (-8.50 Kcal/mol) than the barrier for hydride transfer of the corresponding Rh benzyloxo species (21.41 Kcal/mol), in agreement with mechanisms proposed for related systems.

Keywords: Catalytic oxidation; N, N' bidentate ligand; half sandwich metal complexes; primary alcohols; DFT.

1. Introduction

Oxidation of primary aromatic alcohols to their respective aldehydes is an important chemical transformation in synthetic chemistry [1]. Alcohols are generally inactive and require harsh methods to activate the hydroxyl group present [2-5]. In transition metal chemistry, the metal can mediate the dehydrogenation of alcohols to yield the aldehydes [5-9] and there are many reports on the oxidation of alcohols to aldehydes and ketones. Indeed, metal catalyzed versions of the oxidation reaction are recognized as one of the greener methods [10-13]. There are several water soluble homogeneous metal complexes that have been reported for the oxidation of alcohols, such as those of copper, palladium and gold [14, 15]. Many classical methods and reagents are available for these reactions, like "activated DMSO" methods, NaOCI/TEMPO (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxyl), hypervalent iodine reagents and chromium and manganese oxides [16-18].

To explore the metal complex systems, researchers also have developed eco-friendly and efficient catalytic metal complex systems for the oxidation of alcohols using less toxic oxidants such as oxygen, hydrogen peroxide and acetone [19-21].

In a homogeneous catalytic system, the borrowing of hydrogen and hydrogen auto transfer reactions usually occur via the formation of a metal hydride intermediate to complete the catalytic cycle [22, 23]. In recent years the hydrogen gas evolved alcohol dehydrogenation process has generated great interest from the view point of atom economy [22, 23]. There are different homogeneous catalytic systems which effectively dehydrogenate primary alcohols to their respective aldehydes, which include metals such as iridium, rhodium and ruthenium [24-26]. In the present work, we report comparative catalytic studies using iridium, rhodium and ruthenium in N, N' functional bidentate N-(pyridin-2-ylmethylene)aniline ligand complexes for the oxidation of primary aromatic alcohols to their respective aldehydes using inexpensive bases such as Cs_2CO_3 , K_2CO_3 , Na_2CO_3 and $NaHCO_3$. We also report a DFT modelling study of the complexes, HOMO-LUMO energy differences and reactivity.

2. Experimental Section

2.1. Methods and analysis

Unless otherwise noted, all manipulations were performed using standard Schlenk tube techniques under argon atmosphere. The reagents and solvents were purchased from Sigma-Aldrich, Fluka and Merck and used without further purification. The solvents were dried by standard procedures and distilled prior to use. Gas chromatography (GC) analysis was performed using a Perkin-Elmer Clarus 500 GC with a HP-Pona-50 m x 0.2 mm, 0.5 micron capillary column.

Single-crystal X-ray diffraction data were collected on a Bruker KAPPA APEX II DUO diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Data collection was carried out at 173(2) K. Temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). Cell refinement and data reduction were performed using the program SAINT [27]. The data were scaled and absorption corrections performed using SADABS. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods based on F² using SHELXL-97 [28]. For the structures and graphics, ORTEP-3 [29] and DIAMOND [30] programs were used. The crystals of all the metal complexes were obtained by slow evaporation of a mixture of hexane and acetonitrile at ambient temperature. The electronic absorption spectroscopy (UV-Vis) studies were recorded using a Perkin Elmer precisely Lambda35 instrument. The TGA-DSC analyses were performed using a Thermal Analyser SDT Q600 instrument and a heating rate of 10 °C.min⁻¹ and nitrogen flow of 100 ml.min⁻¹. The metal precursors (IrCl₂Cp*)₂, (RhCl₂Cp*)₂ and (RuCl₂C₆H₆)₂ were prepared according to the reported methods [31-33].

2.2. DFT Calculations

All the calculations were performed using the Guassian 09 program package [34]. The structural and energetic results calculated using M05-2X were more consistent with the experimental observations [35]. The hybrid exchange-correlation functional M05-2X, developed by Zhao and Truhlar [36, 37], have been shown to describe weak bonding interaction better than the other density functionals such as M06 classes, M05, B3LYP, and PBE functional. So, all the complex structures were optimized at M05-2X level of theory using the LANL2DZ basis set. Frequency calculation was carried out at the same level of theory and no negative frequency was observed. The absence of imaginary frequencies confirmed that all complex structures had stable

minima. The HOMO and LUMO energy gap was calculated from the DFT method. The frontier molecular orbital plot using the chemcraft was drawn program package (http://www.chemcraftprog.com). Using Gaussian NBO (ver. 3.1), natural population analysis (NPA) and natural bond orbital (NBO) analysis has been performed to investigate the change in electron density from proton donor to proton acceptor for optimized metal complexes at the M05-2X/LANL2DZ level of theory. Second order perturbation energy $(E^{(2)})$ was used to estimate the magnitude of electron delocalization [38].

2.3. General procedure for the oxidation of benzyl alcohol

Benzyl alcohol (1 mmol), catalyst (2 mol%), base (5 mol%) and solvent (20 mmol) were placed in a Schlenk tube under argon or nitrogen atmosphere. The mixture was stirred magnetically under reflux over the specified time. The yield of the benzaldehyde was determined by GC analysis using chlorobenzene as an internal standard.

2.4. Procedure for the oxidation of benzyl alcohol derivatives catalysed by complexes 1 and 3

The benzyl alcohol derivatives (1 mmol), catalyst 1 or 3 (2 mol%), base (5 mol%) and toluene or p-xylene (20 mmol) were added to a Schlenk tube under argon or nitrogen atmosphere. The mixture was stirred magnetically at reflux temperature. The yields of the products were analyzed by GC chromatography using chlorobenzene as an internal standard.

3. Results and discussion

3.1. Synthesis of ligand and metal complexes

The N, N' bidentate ligand precursor N-(pyridin-2-ylmethylene)aniline and metal complexes of iridium, rhodium and ruthenium were synthesised according to methods discussed elsewhere [39-41]. The structure and purity of the synthesized metal complexes, along with the ligands were confirmed by single crystal XRD, NMR, IR and electronic absorption spectral studies. The thermal stability of the prepared compounds was confirmed by TGA analysis. The structures of the metal complexes are shown (Fig.1).



Fig. 1. The metal complexes of Ir(III) (1), Rh(III) (2) and Ru(II) (3).

3.2. X – Ray Crystallography

The crystallographic data of complexes 1-3 are given in Table 1. The ORTEP view of the metal complexes iridium (1), rhodium (2) and ruthenium (3) are shown in Fig. 2a-c. In complexes 1 and 2, the iridium and rhodium metal centers are coordinated via the nitrogen atoms of the ligand, five carbon atoms of the Cp* moiety and Cl of the metal center. In complex (3), the ruthenium metal is coordinated via the nitrogen atoms of the ligand, via η^6 coordination to the benzene ring and to chlorine. This gives pseudo-octahedral half sandwich "piano-stool" structures around the iridium, rhodium and ruthenium metal centers in the complexes [41]. The Cp*/arene moieties of complexes 1, 2 and 3 occupy a triangular face of an octahedron. The N1, N2 nitrogen atoms form a five membered chelate ring with the metal center. A chloride completes the coordination sphere. The M-Cl bond length in complexes 1-3 are 2.400(10) Å, 2.393(8) Å and 2.393(10) Å, respectively. These values are consistent with related reported metal complexes in literature, like $[(\eta^5-C_5Me_5)IrCl(C_5H_5N-2-CH=NC_6H_4-P-NO_2)]PF_6$ [40], $[(\eta^5-C_5Me_5N-2-CH=NC_6H_4-P-NO_2)]PF_6$ [40], $[(\eta^5-C_5Me_5N-2-CH=NC_6H_4-P-NC_6H$ CH₃)]PF₆ [41]. The M-C (Cp*/arene) bond lengths in the complexes are 2.153(3) - 2.205(3) Å (1), 2.136(3) - 2.192(3) Å (2) and 2.171(4) - 2.192(4) Å (3), respectively. Non-covalent interactions of C-H...F and C-H...Cl bonds in the complexes of 1, 2 and 3 are observed. In the crystal structure of complexes 1-3 C-H...Cl and C-H...F non-covalent intra and inter-molecular interactions are seen (Fig. 3a-c). In all three complexes, the counter ion PF₆ is involved in C-H...F non-covalent inter-molecular interactions. The P-F... π inter-molecular interaction is observed in complexes 1 and 3 and C-H... π inter-molecule interaction is observed in complex 2 (Tables 2 & 3).

Table 1

Crystallographic data and summary of structural refinement of the metal complexes 1, 2 and 3.

	1	2	3
Empirical formula	C ₂₂ H ₂₅ ClF ₆ IrN ₂ P	C ₂₂ H ₂₅ ClF ₆ N ₂ PRh	C ₁₈ H ₁₆ ClF ₆ N ₂ PRu
Formula weight	690.06	600.77	541.82
Crystal colour	Orange	Yellow	Yellow
Temperature/K	173(2)	173(2)	173(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	8.694(4)	8.7080(4)	7.7407(3)
b (Å)	13.312(6)	13.2046(3)	17.0759(4)
c (Å)	20.664(9)	20.6563(8)	15.3185(6)
α (°)	90.00	90.00	90.00
β (°)	94.244(9)	94.4670(10)	101.7610(10)
γ (°)	90.00	90.00	90.00
Volume (Å ³)	2385.0(18)	2367.96(15)	1982.28(12)
Z	4	4	4
$\rho_{calc} (mg/mm^3)$	1.922	1.685	1.816
$\mu(MoK\alpha) [mm^{-1}]$	5.837	0.962	1.068
F(000)	1336.0	1208.0	1072.0
Crystal size/mm ³	$0.16 \times 0.14 \times 0.12$	$0.18 \times 0.14 \times 0.11$	$0.16 \times 0.12 \times 0.11$
20 range for data collection	3.96 to 57.26°	7.34 to 54.92°	7.22 to 55.76°
Reflections collected	81251	94755	94614
Independent reflections	6006[R(int) = 0.0495]	5403[R(int) = 0.0806]	4716[R(int) = 0.0847]
Data/restraints/parameters	6006/0/303	5403/0/303	4716/0/262
Goodness-of-fit on F ²	1.034	1.072	1.132
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0225, wR_2 = 0.0458$	$R_1 = 0.0344, wR_2 = 0.0692$	$R_1 = 0.0450, wR_2 = 0.0960$
Final R indexes [all data]	$R_1 = 0.0374, wR_2 = 0.0514$	$R_1 = 0.0656, wR_2 = 0.0807$	$R_1 = 0.0751, wR_2 = 0.1109$
Largest diff. peak/hole (e $Å^{-3}$)	1.31/-0.68	1.20/-0.66	1.59/-0.77

Table 2

C-H...X intermolecular interactions in complexes 1-3.

С-НХ	D-H	НА	DA	D-HA
Complex 1				
C(8)-H(8a)F(4)	0.98	2.54	3.502(4)	167
C(10)-H(10C)F(1)	0.98	2.44	3.332(5)	151
C(11)-H(11)F(2)	0.95	2.35	3.093(5)	135
C(13)-H(13)Cl(1)	0.95	2.79	3.622(4)	146
C(14)-H(14)F(5)	0.95	2.50	3.235(4)	134
C(21)-H(21)F(2)	0.95	2.54	3.313(4)	138
Complex 2				
C(10)-H(10A)F(6)	0.98	2.43	3.341(4)	154
C(11)-H(11)F(5)	0.95	2.35	3.122(4)	137
C(13)-H(13)Cl(1)	0.95	2.79	3.607(3)	145
C(14)-H(14)F(2)	0.95	2.51	3.227(4)	132
C(21)-H(21)F(5)	0.95	2.54	3.315(4)	139
Complex 3				
C(4)-H(4)F(6)	0.95	2.35	3.295(6)	172
C(17)-H(17)F(5)	0.95	2.48	3.374(6)	157

Table 3

Y-X... π intermolecular interactions in complexes 1-3.

Y-XCg(Pi-Ring)	XCg (Bond length (Å))	Y-XCg (Bond angles (°))
Complex 1		
P(1)-F(1)Cg(2)	3.111(3)	128.00(13)
Complex 2 (C-HCg)		
C(7)-H(7B)Cg(3)	2.89	137
Complex 3		
P(1)-F(5)Cg(1)	3.329(4)	129.22(18)
P(1)-F(6)Cg(3)	3.755(4)	141.34(17)



Fig. 2a. ORTEP view of the metal complex **1** with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for the clarity.



Fig. 2b. ORTEP view of the metal complex 2 with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for the clarity.



Fig. 2c. ORTEP view of the metal complex **3** with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for the clarity.



Fig. 3a. Non-covalent C-H...F interactions in the metal complex 1.



Fig. 3b. Non-covalent C-H...F and C-H...Cl interactions in the metal complex 2.



Fig. 3c. Non-covalent π ... π and C-H...F interactions in the metal complex 3.

3.3. Electronic absorption spectroscopy

The electronic absorption spectra of all the metal complexes were recorded by preparing a 10 μ M (v/v DCM) solution. The resulting spectra of the metal complexes are depicted in the wavelength range between 200 nm to 600 nm (Fig. 4). The intense low energy bands of the metal complexes appeared at 382.92 nm (1), 369.77 nm (2), 416.27 nm (3) and the conjugated intra ligand based π - π * and metal ligand charge transfer (MLCT) transitions were observed in the region of 315.23 nm to 284.92 nm for (1), 324.17 nm to 274.82 nm for (2) and 313.87 nm to 261.25 nm for (3) [43].



Fig. 4. UV-Visible spectrum of the metal complexes 1, 2 and 3 (Dichloromethane, 10μ M, v/v).

3.4. TG-DSC studies

TG patterns of all complexes are shown in Fig. 5a. In the TG traces, no degradation was observed until ~270° C, which indicates the high inherent stability of complexes 1-3. The calculated weight loss of the complexes at ~270 °C was 2.28% (1), 3.12% (2) and 7.85% (3) respectively. The DSC traces of exothermic peaks associated with the melting point of the complexes were at 290 °C (1), 280 °C (2) and 270 °C (3). The clear exothermic peak in the DSC trace (Fig. 5b) further confirms the crystalline nature of the metal complexes [44].



Fig. 5a. TGA curves of the complexes 1, 2 and 3. Heating rate 10 °C min⁻¹.



Fig. 5b. DSC curves of the complexes **1**, **2** and **3**. Heating rate 10 °C min⁻¹.

3.5. Catalytic activity studies

3.5.1. Oxidation of primary alcohols

The oxidation of benzyl alcohol under reflux conditions was carried out with various bases and solvents using the three complexes of iridium (1), rhodium (2) and ruthenium (3)

(Table 4). No benzyl alcohol conversion was achieved in the absence of catalysts **1-3**. In the presence of catalysts **1-3** (1 mol% or 2 mol%) and bases (5 mol%) in toluene under reflux, benzyl alcohol to benzaldehyde conversion reached up to 90% (Table 4). In the presence of the catalyst **1** (2 mol%) and the bases (5 mol%) Na₂CO₃, NaHCO₃, K₂CO₃ and Cs₂CO₃, the yield of benzaldehyde reached 44%, 33%, 63% and 89% respectively (Entries 3-6). In the presence of catalysts **2** (2 mol%) and **3** (2 mol%) with Na₂CO₃ as the base in toluene, the benzaldehyde yield obtained was 49% and 44% respectively (Entries 9 and 15). For catalyst **3** with NaHCO₃, the yield further increased to 58% (Entry 16). When catalysts **2** (2 mol%) and **3** (2 mol%) were refluxed with K₂CO₃ as the base in toluene, a 60% yield of the benzaldehyde was achieved in both systems (Entries 11 and 17). However, overall catalyst **1** with Cs₂CO₃ as base under reflux in toluene gave the best yield to benzaldehyde (89%) (Entry 6).

When the reaction was carried out with different solvents, the benzaldehyde yield varied. In the presence of K_2CO_3 as base and *p*-xylene as a solvent, the maximum benzaldehyde yields of 29% and 56% were achieved over catalysts **1** and **2** respectively (Entries 19 and 22). In the presence of all three catalysts, the use of 1,4 dioxane and DMSO as solvents gave a lower yield of benzaldehyde. The yield of benzaldehyde obtained from all the reactions using different solvents and K_2CO_3 as base are summarized in Table 4 (Entries 19-27). However, in the case of catalyst **3**, the yield of benzaldehyde was as high as 76% (Entry 25), likely due to the higher solubility of catalyst **3** in *p*-xylene than catalysts **1** and **2**.

Table 4

Screening and optimization for the oxidation of benzyl alcohol^a.

ОН	catalyst (2 mol%) base (5 mol%)	O H
	toluene, Under reflux	

Benzyl alcohol			Benzaldehyde			
Entry	Catalyst	Base	Conversion (%) ^c	Yield $(\%)^c$	TON	
1	1	None	24 ^b	24	24	
2	1	None	39	39	20	
3	1	Na ₂ CO ₃	44	44	22	
4	1	NaHCO ₃	34	33	17	
5	1	K_2CO_3	64	63	32	
6	1	Cs_2CO_3	90	89	45	
7	2	None	36 ^b	36	36	
8	2	None	38	38	19	
9	2	Na ₂ CO ₃	52	49	26	
10	2	NaHCO ₃	26	25	13	
11	2	K_2CO_3	63	60	32	
12	2	Cs_2CO_3	62	60	31	
13	3	None	16 ^b	16	16	
14	3	None	26	26	13	
15	3	Na ₂ CO ₃	48	44	24	
16	3	NaHCO ₃	60	58	30	
17	3	K_2CO_3	63	60	32	
18	3	Cs ₂ CO ₃	46	45	23	
19	1	K_2CO_3	31 ^d	29	16	
20	1	K_2CO_3	9 ^e	8	5	
21	1	K_2CO_3	25^{f}	23	13	
22	2	K_2CO_3	58 ^d	56	29	
23	2	K_2CO_3	24 ^e	20	12	

24	2	K ₂ CO ₃	22^{f}	21	11
25	3	K_2CO_3	78 ^d	76	39
26	3	K ₂ CO ₃	27 ^e	24	14
27	3	K ₂ CO ₃	$40^{\rm f}$	37	20

^a Benzyl alcohol (1 mmol) and catalyst (2 mol%) in toluene (20 mmol) under reflux 48 hrs.

^b Benzyl alcohol (1 mmol) and catalyst (1 mol%) in toluene (20 mmol) under reflux 48 hrs.

^c Determined by GC (average by two runs). ^d*p*-xylene (20 mmol). ^e 1,4 dioxane (20 mmol).

^f DMSO (20 mmol). Turnover number (TON) = [(mol of product)/(mol of catalyst)].

3.5.2. Effect of substituents on the oxidation of benzyl alcohol over the catalysts 1 and 3

Catalyst **1** showed good activity for oxidizing substituted benzyl alcohols in the presence of Cs_2CO_3 as base and toluene as solvent (Table 5). It is evident that substrates with groups present in the *para* position (Entries 2, 5, 7 and 8) were oxidized much faster than those with *ortho* substituted groups present in benzyl alcohol, in the presence of base [24, 44] (Entries 3 and 6), likely due to steric effects. The bulky *ortho* substitution could cause a decrease in the benzyl alcohol oxidation rate [46] (Entries 2 and 5). On the other hand, bulky 3,4 and 2,5-OCH₃ group substituted benzyl alcohol also showed moderate conversion with catalyst **1** (Entries 9 - 11). In contrast, *para* dimethylamino benzyl alcohol showed lower conversion due to the high electron donating ability of dimethylamino group on the aromatic ring (Entry 12). The electronic nature of the aromatic ring present in the substrate plays a big role in oxidation reactions. The efficient catalytic activity of the iridium complex (1) could be explained by the electronic effect of the ligand on the iridium metal. The N,N' ligand gives a greater donor strength than in the rhodium and ruthenium complexes [47]. The theoretical natural atomic populations study for the iridium complex coincides well with this statement (Section 3.6). Catalyst **1** showed 100% and 97% (Entries 2 and 8) conversion of electron rich and poor benzyl alcohols.

Table 5

Catalytic oxidation of benzyl alcohol derivatives mediated by catalyst 1^a.

R II OH	catalyst 1 (2 mol%) Cs ₂ CO ₃ (5 mol%)	ОН
	toluene, under reflux	R

Benzyl alcohol derivatives

Benzaldehyde derivatives

Entry	Benzyl alcohol	Conversion	Yield (%) ^c	TON
	derivaties	$(\%)^{c}$		
1	R – H	90 ^b	89	45
2	R4-NO ₂	100	98	50
3	R –2-NO ₂	83 ^b	80	42
4	R –2-OH	100	95	50
5	R –4-Cl	91	89	46
6	R –2-Cl	80^{b}	78	40
7	R –4-CH ₃	90	89	45
8	R –4-OCH ₃	97	96	49
9	R –3,4 –OCH ₃	72 ^b	70	36
10	R –2,5 –OCH ₃	48 ^b	46	24
11	R –4-OH 3–OCH ₃	64	62	32
12	R -4-N(CH ₃) ₂	33 ^b	30	17

^a Substrate (1 mmol) in toluene (20 mmol) under reflux 24 hrs. ^b Substrate (1 mmol) in toluene (20 mmol) under reflux 48 hrs. ^c Determined by GC (average by two runs). Turnover number (TON) = [(mol of product)/(mol of catalyst)].

Catalyst **3** showed up to 96% (Entry 4, Table 6) conversion in the oxidation of primary alcohols to their corresponding aldehydes using K_2CO_3 as base with *p*-xylene as the solvent (Table 6). In this catalytic system, the electron rich *para* substituted benzyl alcohols (Entries 7, 8 and 11) oxidized faster than electron poor *para* substituted benzyl alcohols (Entries 2 and 5). The bulky groups present in the *ortho* position of benzyl alcohol caused lower conversion of these

substituted benzyl alcohols (Entries 3, 6 and 10). A plausible coordination site for the substrate is the electronically unsaturated ruthenium center, which is generated after liberation of the labile chloride atom. The base K_2CO_3 is expected to promote the formation of the metal-alkoxide species, which could then undergo β -hydride elimination to form a ruthenium-hydride complex [48, 49]. A faster oxidation rate of the *ortho*-hydroxy benzyl alcohol to the corresponding aldehyde in both catalytic systems **1** and **3** was observed (Entry 4, Table 5 and Entry 4, Table 6).

Table 6

	R II OH K ₂ CO ₃	t 3 (2 mol%) (5 mol%)		`Н
	p-xyler	ne, under reflux	K -	
	Benzyl alcohol derivatives		Benzaldehyde	derivatives
Entry	Benzyl alcohol	Conversion (%) ^c	Yield $(\%)^c$	TON
	derivatives			
1	R –H	78 ^b	76	39
2	R4-NO ₂	45 ^b	44	23
3	R –2-NO ₂	40 ^b	37	20
4	R –2-OH	96	92	48
5	R –4-Cl	65 ^b	63	33
6	R –2-Cl	50 ^b	47	25
7	R –4-CH ₃	77	76	39
8	R –4-OCH ₃	85	84	43
9	R – <i>3</i> , <i>4</i> –OCH ₃	68 ^b	64	34
10	R –2,5-OCH ₃	51 ^b	48	26
11	R4-OH 3OCH ₃	91	90	46
12	$R - 4 - N(CH_3)_2$	no reaction ^b	-	-

Catalytic oxidation of benzyl alcohol derivatives mediated by catalyst 3^{a}

^a Substrate (1 mmol) in *p*-xylene (20 mmol) under reflux for 24 hrs. ^b Substrate (1 mmol) in *p*-xylene (20 mmol) under reflux for 48 hrs. ^c Determined by GC (average by two runs). Turnover number (TON) = [(mol of product)/(mol of catalyst)].

3.5.3. Proposed catalytic reaction mechanism for oxidation of primary alcohols

A proposed reaction mechanism (supported by theoretical calculations, Section 3.6) for the oxidation of primary alcohols by catalysts 1-3 is illustrated in Scheme 1. The initial step of this reaction cycle is the formation of a weakly bound metal complex with benzyl alcohol (A) formed from the free metal complex and benzyl alcohol. Step 1 of this catalytic cycle is the generation of the metal benzyloxo species (A)TS₁ from the active complex (A). In step 2, β hydrogen elimination occurs to form the dehydrogenated product of benzaldehyde and a metal hydride (B) complex. After this metal-hydride step, two possible transition states could be involved in this reaction cycle. In step 3, the metal hydride (B) intermediate promotes a protonolysis to form a favored transition state of the metal complex (C)TS₂ intermediate. Alternatively, hydride release from the metal hydride complex (B) could form the disfavored transition state involving $16e^{-1}$ species (D)TS₃ in step 4. The key steps of this catalytic cycle are the generation of the metal hydride intermediate in step 2. A similar kind of iridium hydride intermediate has been characterized and reported by Heiden et al. [50] and Fujita et al. [46]. Thus, the overall catalytic cycle involves two important steps: the formation of the metal benzyloxo species (A)TS₁ and the metal hydride species (B). The Gibbs free energy profile diagram is presented in Fig. 9.



M = Ir, Rh and Ru arene = Cp* or benzene

Scheme 1. Proposed reaction mechanism of an oxidation of primary alcohol by catalysts 1-3

3.6. Density Functional Theory (DFT) Calculations

DFT calculations were carried out to understand structural properties, such as type of molecular energy levels, bond lengths, bond angles and the binding nature of the metal complexes. A Gibbs free energy calculation on the rhodium catalytic cycle was carried out to support the proposed mechanism given in Scheme 1. The energy difference between the HOMO (highest occupied molecular orbitals) and the LUMO (lowest unoccupied molecular orbitals) orbitals is called the energy gap, which is important to understand the stability of the structures of the metal complexes. The analysis of the orbitals indicates that the electron absorption corresponds to the transition state from the ground state to the first excited state, which mainly describes the one electron excitation from the HOMO to the LUMO, which is correlated to the energy gap and the chemical reactivity. A larger energy gap between HOMO and LUMO indicates good stability of the structure and lower reactivity, and a smaller energy gap difference implies higher reactivity of the complexes [51] (Figs. 6 and 8).

The HOMO is highly concentrated over the metal centers, benzene or the Cp* ring, but with a small contribution from the Cl atom. Consequently, the LUMO is localized over the N1 and N2 atoms. The HOMO is constituted of a π -orbital in the Cp* ring or benzene. The LUMO is dominated by the π^* orbital of the pyridine ring. This suggests that the higher value of the HOMO of a d orbital of the metal has a tendency to donate electrons to the p orbital of the N1, N2 acceptor atoms. Calculated bond lengths and bond angles are given in the Table 7. The experimentally obtained results of bond distances and bond angles are close to the theoretical values, except for the angle C(5)-Ir(1)-Cl(1). The lone pair electrons of the Cl coordinated with the iridium center are placed closer to the N1 and N2 atoms, as compared to the rhodium (2) and ruthenium (3) complexes, which causes repulsion between Cl and the nitrogen atoms. Thus, the DFT method could not predict the C(5)-Ir(1)-Cl(1) bond angle accurately, due to the presence of the lone pair electrons of the Cl [52].

The calculated energy gaps from HOMO-LUMO for the iridium complex (1), rhodium complex (2) and ruthenium complex (3) were 120.59 Kcal/mol, 130.67 Kcal/mol and 124.49 Kcal/mol respectively. The higher energy gap of the rhodium complex (2) indicates that it is more stable and less reactive when compared to the iridium and ruthenium complexes. Lowest

vibrational frequency calculations have been carried out to predict the minimum energy structure with the lowest vibrational frequency for the Ir(III) complex (17.731 cm⁻¹), the Rh(III) complex (30.332 cm^{-1}) and the Ru(II) complex (3.797 cm^{-1}) and this is shown in the Supporting Information S2.

NPA analysis describes the charge transfer from chloride or nitrogen atoms to the metal (Ir(III), Rh(III) and Ru(II)) ions, which plays a pivotal role in determining metal complex properties (Fig. 7). The atomic charges of each atom in the complexes collected from NPA are presented in the supporting information S3, the metal ions gain charges of 2.79e (Ir(III)), 2.73e (Rh(III)) and 1.94e (Ru(II)) in the metal complexes. The positive charge of the metal ions decreases significantly in all the complexes and especially the iridium metal ion is strongly coordinated with neighboring atoms. The bidentate ligand N,N' donor electron strength on the iridium (N1 = -0.441 & N2 = -0.405) is higher than on rhodium and ruthenium and this would account for the iridium complex being more reactive than the other complexes. On the complexes **1-3**, the chloride group transfers higher charges of 0.66e to the Ru(II) metal ion when compared with lesser charge transfer from chloride (0.59e) to the Rh(III) and 0.61e to the Ir(III) metal ion (S5, Table 3). The electron densities of the Cl group attached to the iridium (0.273). These electron density values confirm that the Rh-Cl (**2**) bond is stronger and this would account for it being a less reactive complex compared to the latter two complexes [53].

The proposed reaction mechanism for the complexes is given in Scheme 1 and its frontier orbital diagram is shown in Fig. 8. The iridium benzyloxo (**A**) complex has a higher energy gap (116.59 Kcal/mol) than the iridium hydride (**B**) complex (106.83 Kcal/mol), which indicates that A is more stable (less reactive) than complex **B**. A similar iridium hydride (**B**) complex has been studied and reported as being a highly active species by Fujita et al. [46].

Gibbs free energy calculations of the rhodium catalytic cycle thus support the proposed mechanism (Scheme 1). The result of the Gibbs free-energy (ΔG) DFT calculation for the reaction mechanism of catalyst **2** is shown in Fig. 9. Gibbs free-energy (ΔG) profile calculations rationalize the stability and reactivity of various transformations of catalyst **2** as per the proposed

mechanism. In the reaction mechanism, the Rh-H step was processed via β -hydride elimination (TS₁) with a high activation free energy barrier of 15.19 Kcal/mol. The calculated activation free energy barrier of the Rh-H intermediate (B) was lower (10.32 Kcal/mol) than the corresponding Rh-benzyloxo (A) species, which correlates to the rate-determining step of the proposed reaction cycle. The Rh-H intermediate is the thermodynamically more favored stable state in the proposed reaction mechanism. The calculated Gibbs free energy barrier for the Rh-H species (10.32 Kcal/mol) was in good agreement with a reported value for a similar species [53]. The calculated activation free energy barrier of the 16e⁻ Rh complex (D)TS₃ was higher (31.85 Kcal/mol) than the respective Rh complex (C)TS₂ (20.34 Kcal/mol), which indicates that the proposed reaction mechanism is more favorable through the (C)TS₂ transition state than the (D)TS₃ $16e^{-}$ Rh complex (D)TS₃. The calculated Gibbs free energy values of the reaction intermediates are in the sequence: $TS_1 > B$ (stable state) < (C) TS_2 < (D) TS_3 , which confirms that the calculated low activation free energy transition intermediates (Rh-H species) can facilitate the oxidation of aromatic benzyl alcohols to their respective aldehydes. The Gibbs free-energy profile (ΔG) and the structures of the optimized rhodium catalytic cycle transition states are given in the supporting information S14.



Fig. 6. Molecular orbital diagrams of the metal complexes 1, 2 and 3.



Fig. 7. Natural atomic populations charges of complexes 1, 2 and 3.



Fig. 8. Molecular orbital diagrams of catalyst 1 reaction intermediates.



Fig. 9. Gibbs free energy profile of the Rh catalyst (2) catalyzed reaction mechanism shown in Scheme 1.

Table 7

Selected bond lengths (Å), bond angles (°) and calculated DFT data for metal complexes 1, 2 and

3.

Complex 1	Crystal data	DFT	Complex 2	Crystal data	DFT	Complex 3	Crystal data	DFT
Distances (Å)			Distances (Å)			Distances (Å)		
Ir(1) – C1 (Cp*)	2.174(3)	2.229	Rh(1) – C1 (Cp*)	2.157(3)	2.267	Ru(1) – C1 (arene)	2.192(4)	2.42
Ir(1) – C2 (Cp*)	2.204(3)	2.265	Rh(1) – C2 (Cp*)	2.192(3)	2.286	Ru(1) – C2 (arene)	2.192(4)	2.405
Ir(1) – C3 (Cp*)	2.205(3)	2.233	Rh(1) – C3 (Cp*)	2.192(3)	2.271	Ru(1) – C3 (arene)	2.185(4)	2.387
Ir(1) – C4 (Cp*)	2.153(3)	2.256	Rh(1) – C4 (Cp*)	2.136(3)	2.224	Ru(1) – C4 (arene)	2.192(4)	2.393
Ir(1) – C5 (Cp*)	2.171(3)	2.268	Rh(1) – C5 (Cp*)	2.157(3)	2.275	Ru(1) – C5 (arene)	2.171(4)	2.374
Ir(1) – Centroid (Cp*)	1.803	1.858	Rh(1) – Centroid (Cp*)	1.789	1.970	Ru(1) – C6 (arene)	2.192(4)	2.388
$\operatorname{Ir}(1) - \operatorname{Cl}(1)$	2.400(10)	2.468	Rh(1) - Cl(1)	2.393(8)	2.439	Ru(1) – Centroid (arene)	1.681	1.766
Ir(1) - N(1)	2.096(3)	2.077	Rh(1) - N(1)	2.106(2)	2.064	$\operatorname{Ru}(1) - \operatorname{Cl}(1)$	2.393(10)	2.426
Ir(1) – N(2)	2.106(2)	2.059	Rh(1) - N(2)	2.119(2)	2.085	Ru(1) - N(1)	2.093(3)	2.063
						Ru(1) – N(2)	2.084(3)	2.049
Angles (°)			Angles (°)			Angles (°)		
N(1)-Ir(1)-Cl(1)	84.76(7)	84.251	N(1)-Rh(1)-Cl(1)	85.88(7)	86.533	N(1)-Ru(1)-Cl(1)	86.34(9)	83.31
N(2)-Ir(1)-Cl(1)	86.67(8)	86.710	N(2)-Rh(1)-Cl(1)	87.74(6)	91.300	N(2)-Ru(1)-Cl(1)	86.12(9)	86.807
N(1)-Ir(1)-N(2)	76.21(10)	77.117	N(1)-Rh(1)-N(2)	76.58(9)	77.932	N(1)-Ru(1)-N(2)	76.99(12)	78.165
C(1)-Ir(1)-Cl(1)	155.43(9)	156.906	C(1)-Rh(1)-Cl(1)	155.14(8)	153.452	C(1)-Ru(1)-Cl(1)	123.09(14)	120.139
C(2)-Ir(1)-Cl(1)	116.77(9)	122.115	C(2)-Rh(1)-Cl(1)	116.74(8)	117.742	C(2)-Ru(1)-Cl(1)	94.29(13)	93.505
C(3)-Ir(1)-Cl(1)	93.29(8)	93.316	C(3)-Rh(1)-Cl(1)	92.76(8)	91.904	C(3)-Ru(1)-Cl(1)	89.23(14)	90.532
C(4)-Ir(1)-Cl(1)	103.85(9)	97.505	C(4)-Rh(1)-Cl(1)	103.32(8)	100.223	C(4)-Ru(1)-Cl(1)	112.12(16)	113.687
C(5)-Ir(1)-Cl(1)	141.65(8)	131.308	C(5)-Rh(1)-Cl(1)	141.06(8)	136.014	C(5)-Ru(1)-Cl(1)	149.46(16)	148.727
Centroid (Cp*)-Ir(1)- Cl(1)	126.13	122.930	Centroid (Cp*)-Rh(1)- Cl(1)	125.68	124.258	C(6)-Ru(1)-Cl(1)	160.77(13)	154.42
						Centroid (arene)- Ru(1)-Cl(1)	127.19	127.429

4. Conclusions

In summary, the catalytic activity of half sandwich Ir(III), Rh(III) and Ru(II) complexes in the oxidation of primary aromatic alcohols to their respective aldehydes was demonstrated. It is clear that the Ir(III) complex in the presence of Cs_2CO_3 and the Ru(II) complex in the presence of K_2CO_3 improved the oxidation of benzyl alcohol significantly. In the proposed reaction mechanism, the iridium-hydride intermediate was more reactive than iridium-benzyloxo species, which is supported by HOMO and LUMO energy gap differences. DFT calculation of selected bond lengths and angles essentially matched the obtained crystal data. Furthermore, the calculated electron density of the metal complexes and the calculated energy differences between the HOMO and LUMO energy gap difference of complex 1 is lower than those of 2 and 3, which indicates the following order of reactivity: 1 > 3 > 2. Gibbs free energy calculations on the proposed reaction mechanism catalysed by Rh(III) further confirmed the proposed reaction mechanism involving a Rh-H intermediate.

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Appendix A. Supplementary Information

CCDC-1020802 (1), CCDC-1020803 (2), and CCDC-1020804 (3) contain the supplementary crystallographic data in this paper. These data can be obtained free of charge from the Cambridge crystallographic data center via www.ccdc.cam.ac.uk/data_request/cif.

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