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Ruthenium(II), rhodium(III) and iridium(III) based effective catalysts for hydrogenation under aerobic conditions

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ABSTRACT

The new cationic mononuclear complexes [(η^6-arene)Ru(Ph-BIAN)Cl]BF_4 [η^6-arene = benzene (**1**), *p*-cymene (**2**)], [(η^5-C_5H_5)Ru(Ph-BIAN)PPh_3]BF_4 (**3**) and [(η^5-C_5Me_5)M(Ph-BIAN)Cl]BF_4 [M = Rh (**4**), Ir (**5**)] incorporating 1,2-bis(phenylimino)acenaphthene (Ph-BIAN) are reported. The complexes have been fully characterized by analytical and spectral (IR, NMR, FAB-MS, electronic and emission) studies. The molecular structure of the representative iridium complex [(η^5-C_5Me_5)Ir(Ph-BIAN)Cl]BF_4 has been determined crystallographically. Complexes **1**–**5** effectively catalyze the reduction of terephthalaldehyde in the presence of HCOOH/CH_3COONa in water under aerobic conditions and, among these complexes the rhodium complex [(η^5-C_5Me_5)Rh(Ph-BIAN)Cl]BF_4 (**4**) displays the most effective catalytic activity.

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1. Introduction

There has been intense research interest amongst the scientific community in the chemistry of transition metal complexes containing mono/bi/polydentate ligands [1]. In this regard, highly conjugated diimine ligands based on acenaphthene quinone (bian) have drawn considerable recent attention [2]. The extensive π-electron system of acenaphthene and two conjugated imine functions enables these substituted acenaphthene quinone based ligands to act as a better σ-donor and π-acceptor, comparable to the commonly used diimine ligands viz., bipy, phen, etc. [3]. These combined properties and rigidity of the acenaphthene ring makes them a better chelating ligand to coordinate with metal centres. Complexes based on substituted acenaphthene quinone derivative ligands with late transition metals are being used as efficient catalysts for various important reactions [4]. A number of complexes of Pd, Pt, Zn, Ni and Cu containing acenaphthene quinone ligands have been prepared and well studied, however the chemistry of these ligands with arene ruthenium or rhodium complexes have scarcely been explored [2,5].

Furthermore, remarkable efforts have been devoted towards the development of catalysts based on organometallic complexes for hydrogenation reactions [6]. One of the major problems associated with the practical application of theses catalysts is the necessity of anhydrous reaction conditions. The use of organometallic complexes as catalysts under aqueous and aerobic conditions in the hydrogenation of aldehyde and ketones has received considerable current interest [7]. It has been observed that by using water as the solvent, the catalytic reactions can be considerably accelerated [8,9]. Encouraged by recent reports on hydrogenation reactions by organometallic complexes, we have evaluated the catalytic potential of the *piano-stool* complexes **1**–**5** in the reduction of terephthalaldehyde in air under aqueous conditions.

We describe herein the synthetic and spectral features of the *piano-stool* arene ruthenium(II) complexes [(η^6-arene)Ru(Ph-BIAN)Cl]BF_4 [η^6-arene = benzene (**1**), *p*-cymene (**2**)], the cyclopentadienyl complex [(η^5-C_5H_5)Ru(Ph-BIAN)PPh_3]BF_4 (**3**) and the pentamethylcylcopentadienyl rhodium(III) and iridium(III) complexes [(η^5-C_5Me_5)M(Ph-BIAN)Cl]BF_4 [M = Rh (**4**), Ir (**5**)]. Also, we describe herein the reduction of terephthalaldehyde in the presence of the complexes **1**–**5**.

2. Experimental

2.1. General

All the synthetic manipulations were performed under a nitrogen atmosphere. Analar grade chemicals were used throughout. Solvents were dried and distilled prior to use [10]. Hydrated ruthenium(III) chloride, ammonium tetrafluoroborate, acenaphthenequinone, aniline and hydroxylamine hydrochloride were procured from

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Aldrich Chemical Company, Inc. USA and were used as received. The precursor complexes $[\{(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)\}_2]$, $[(\eta^6\text{-arene})RuCl_2\text{-}(PyCN)]$ (arene = benzene and *p*-cymene), $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ and $[(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)\}_2]$ (M = Rh and Ir) and the ligand (1,2-diphenylimino)acenaphthene (Ph-BIAN) were prepared and purified according to the published procedures [11,5f]. Microanalysis and FAB mass spectra were acquired from the Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow. Electronic and luminescence spectra were recorded on a Shimadzu UV-1601 and Perkin–Elmer LS-45 spectrofluorophotometers, respectively. NMR spectra were acquired on a JEOL AL 300 MHz spectrometer, where chemical shifts were referenced to internal tetramethylsilane for ^{1}H NMR and phosphorous trichloride for ^{31}P NMR at room temperature.

2.2. Synthesis and characterization of $[(\eta^6\text{-}C_6H_6)RuCl(Ph\text{-}BIAN)]BF_4$ (**1**)

(a) To a suspension of the chloro-bridged dimeric ruthenium complex $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ (0.502 g, 1.0 mmol) in methanol (25 mL), Ph-BIAN (0.664 g, 2.0 mmol) was added and the suspension was stirred at room temperature for ~10.0 h. Slowly it dissolved and gave a clear brown-black solution. It was filtered through Celite to remove any solid impurities. The filtrate was treated with NH_4BF_4 dissolved in methanol and left for slow crystallization. The dark brown product thus obtained was separated by filtration, washed with diethyl ether and dried under *vacuum*. It was further recrystallized from dichloromethane/diethyl ether. Yield: 0.471 g (68 %). *Anal.* Calc. (%) for $C_{30}ClF_4H_{22}N_2BRu$: C, 52.02; H, 3.18; N, 4.05. Found: C, 51.94; H, 2.83; N, 4.24%. FAB-MS: m/z = 547 (547) [M$^+$]; 512 (512) [M−Cl$^+$]. ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$, 298 K): 8.05 (d, 2H, J = 7.5 Hz), 7.99 (d, 2H, J = 7.2 Hz), 7.85 (d, 2H, J = 6.9 Hz), 7.73 (t, 2H, J = 6.6 Hz), 7.61 (m, 4H, J = 8.1 Hz), 7.44 (t, 2H, J = 7.5 Hz), 6.92 (d, 2H, J = 7.2 Hz), 5.58 (s, 6H). UV–Vis: λ_{max} (ε, dm^3 mol^{-1} cm^{-1}) = 706 (5.8×10^3), 446 (1.9×10^4), 300 (3.9×10^4), 256 (4.1×10^4) nm. Emission: λ_{em} (λ_{ex}, $\Phi/10^{-6}$) = 577 (446, 1.9) nm.

(b) Alternately, complex **1** can be synthesized by the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2(PyCN)]$ with Ph-BIAN in methanol under stirring conditions at room temperature.

2.3. Synthesis and characterization of $[(\eta^6\text{-}C_{10}H_{14})RuCl(Ph\text{-}BIAN)]BF_4$ (**2**)

This was prepared following the above synthetic procedure for **1** using $[\{(\eta^6\text{-}C_{10}H_{14})RuCl(\mu\text{-}Cl)\}_2]$ (0.612 g, 1.0 mmol) in place of $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$. Red brown, Yield: 0.531 g (71 %). *Anal.* Calc. (%) for $BC_{34}ClF_4H_{30}N_2Ru$: C, 54.55; H, 4.01; N, 3.74. Found: C, 53.88; H, 3.82; N, 3.57%. FAB-MS: m/z = 603 (603) [M$^+$]; 568 (568) [M−Cl$^+$]. ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$, 298 K): 7.99 (d, 2H, J = 8.1 Hz), 7.93 (d, 2H, J = 6.6 Hz), 7.82 (d, 2H, J = 6.3 Hz), 7.74 (t, 2H, J = 6.9 Hz), 7.62 (m, 4H), 7.43 (t, 2H, J = 8.1 Hz), 6.89 (d, 2H, J = 6.9 Hz), 5.33 (s, 4H), 2.51 (sep., 1H, J = 6.9 Hz), 1.99 (s, 3H), 1.09 (d, 6H, J = 6.9Hz). UV–Vis: λ_{max} (ε, dm^3 mol^{-1} cm^{-1}) = 462 (2.3×10^4), 310 (3.9×10^4), 255 (4.1×10^4) nm. Emission: λ_{em} (λ_{ex}, $\Phi/10^{-6}$) = 547 (462, 1.8) nm.

2.4. Synthesis and characterization of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(Ph\text{-}BIAN)]BF_4$ (**3**)

A suspension of the ruthenium complex $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ (0.728 g, 1.0 mmol) in methanol (25 mL) was treated with Ph-BIAN (0.332 g, 1.0 mmol) and the solution was refluxed for ~10.0 h. The resulting dark purple-black solution was filtered through Celite, and a saturated methanolic solution of NH_4BF_4 was added to the filtrate and left for slow crystallization. The dark purple-black product thus obtained was filtered and washed with diethyl ether and dried under vacuum. The product was further recrystallized from dichloromethane/diethyl ether. Yield: 0.584 g (69 %). *Anal.* Calc. (%) for $BC_{47}F_4H_{36}N_2PRu$: C, 66.58; H, 4.25; N, 3.30. Found: C, 65.98; H, 4.11; N, 3.87%. FAB-MS: m/z = 763 (760) [M$^+$]; 500 (498) [M−PPh$_3^+$]. ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$, 298 K): 8.13 (d, J = 8.1 Hz), 8.01 (d, J = 7.0 Hz), 7.91 (t, J = 7.1 Hz), 7.71 (t, J = 6.9 Hz), 7.60 (m), 4.65 (s). ^{31}P NMR (δ ppm, 120 MHz, $CDCl_3$): 43.29 (s). UV–Vis: λ_{max} (ε, dm^3 mol^{-1} cm^{-1}) = 561 (1.9×10^4), 323 (2.6×10^4), 244 (4.1×10^4) nm. Emission: λ_{em} (λ_{ex}, $\Phi/10^{-6}$) = 617 (561, 0.9) nm.

2.5. Synthesis and characterization of $[(\eta^5\text{-}C_5(CH_3)_5)RhCl(Ph\text{-}BIAN)]BF_4$ (**4**)

This was prepared following the above synthetic procedure for **1** using $[\{(\eta^5\text{-}C_5(CH_3)_5)RhCl(\mu\text{-}Cl)\}_2]$ (0.618 g, 1.0 mmol) in place of $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$. Red brown, Yield: 0.499 g (72 %). *Anal.* Calc. (%) for $BC_{34}ClF_4H_{31}N_2Rh$: C, 58.87; H, 4.47; N, 4.04. Found: C, 58.68; H, 4.82; N, 4.37%. ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$, 298 K): 7.98 (d, 2H, J = 8.1 Hz), 7.95 (d, 2H, J = 7.8 Hz), 7.83 (d, 2H, J = 7.5 Hz), 7.71–7.52 (m, 6H), 7.41 (t, 1H, J = 8.1Hz), 6.91 (d, 2H, J = 6.9 Hz), 1.33 (s, 15H). UV–Vis: λ_{max} (ε, dm^3 mol^{-1} cm^{-1}) = 375 (3.5×10^4), 314 (3.9×10^3), 257 (4.1×10^4) nm.

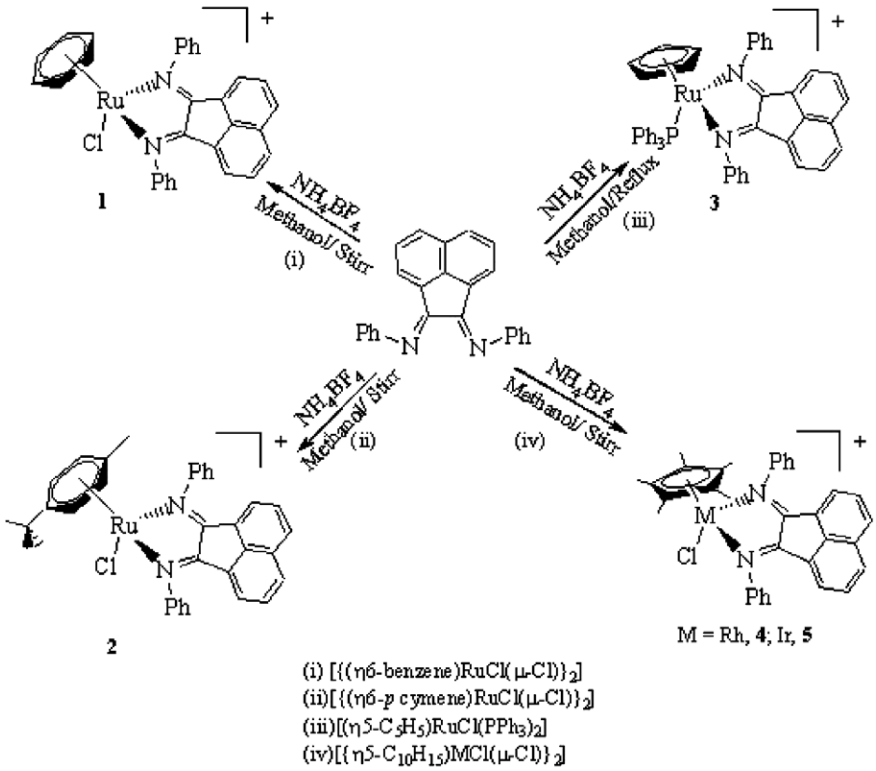
2.6. Synthesis and characterization of $[(\eta^5\text{-}C_5(CH_3)_5)IrCl(Ph\text{-}BIAN)]BF_4$ (**5**)

This was prepared following the above synthetic procedure for **1** using $[\{(\eta^5\text{-}C_5(CH_3)_5)IrCl(\mu\text{-}Cl)\}_2]$ (0.796 g, 1.0 mmol) in place of $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$. Red brown, Yield: 0.547 g (70 %). *Anal.* Calc. (%) for $BC_{34}ClF_4H_{31}N_2Ir$: C, 52.17; H, 3.96; N, 3.58. Found: C, 52.31; H, 3.82; N, 3.77%. ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$, 298K): 8.02 (d, 2H, J = 8.1 Hz), 7.99 (d, 2H, J = 6.9 Hz), 7.78 (d, 2H, J = 7.8 Hz), 7.71–7.52 (m, 6H), 7.43 (t, 2H, J = 7.8 Hz), 6.99 (d, 2H, J = 7.5 Hz), 1.31 (s, 15H). UV–Vis: λ_{max} (ε, dm^3 mol^{-1} cm^{-1}) = 435 (2.2×10^4), 319 (3.9×10^4), 244 (4.0×10^4) nm.

3. Results and discussion

3.1. Synthesis and characterization of the complexes **1**–**5**

The cationic mononuclear complexes $[(\eta^6\text{-arene})Ru(Ph\text{-}BIAN)Cl]^+$ (η^6-arene = benzene, **1** and *p*-cymene, **2**) (Scheme 1) have been synthesized by the reactions of the arene ruthenium precursor complexes $[\{(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)\}_2]$ with Ph-BIAN in methanol at room temperature. Complexes **1** and **2** were also prepared by the reaction of the complexes $[(\eta^6\text{-arene})RuCl_2(PyCN)]$ (η^6-arene = benzene **1**, *p*-cymene, **2**; PyCN = 4-cyanopyridine) with Ph-BIAN in methanol. It was observed that in the reactions of the arene ruthenium complexes containing 4-cyanopyridine $[(\eta^6\text{-arene})\text{-}RuCl_2(PyCN)]$ with Ph-BIAN, the coordinated 4-cyanopyridine gets substituted by Ph-BIAN to afford the complexes **1** and **2**. This observation is consistent with our earlier findings on the analogous arene ruthenium $[(\eta^6\text{-arene})RuCl_2(PyCN)]$ and 3:3-bis allyl ruthenium complexes $[(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})RuCl_2(PyCN)]$ incorporating 4-cyanopyridine, where the respective bases (EPh_3, E = P, As, Sb; bipy, phen) displaced the metal bound 4-cyanopyridine [12]. Treatment of $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ with Ph-BIAN in refluxing methanol led to the formation of the cationic ruthenium complex $[(\eta^5\text{-}C_5H_5)Ru(Ph\text{-}BIAN)(PPh_3)]^+$ (Scheme 1), which was isolated as the BF_4^- salt.



Scheme 1.

The pentamethylcyclopentadienyl complexes $[(\eta^5\text{-}C_5Me_5)M(\text{Ph-BIAN})Cl]^+$ [M = Rh (**4**), Ir (**5**)] were obtained by the reactions of the chloro-bridged dimeric complexes $[\{(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)\}_2]$ [M = Rh and Ir] with two equivalents of Ph-BIAN in methanol and these were isolated as BF_4^- salts.

Spectral and analytical data of complexes **1**–**5** corroborate well to the proposed formulations. FAB-MS spectra of the complexes displayed prominent peaks corresponding to the molecular ion fragment. Representative spectra of **1**–**3** are shown in Fig. 1. Complexes **1** and **2** displayed the loss of chloride in the first step, whereas **3** displayed the loss of the coordinated triphenylphosphine. In these complexes the metal to Ph-BIAN bond is stronger and remains intact. The FAB-MS spectral results corroborate well to the proposed formulation of the complexes.

^{1}H NMR spectral data of the complexes, along with their assignments, are recorded in the experimental section. In the ^{1}H NMR spectra of complexes **1** and **2**, the protons associated with the arene moiety and Ph-BIAN displayed downfield shifts as compared to that in the precursor complexes and uncoordinated ligand, respectively. The ^{1}H NMR spectrum of complex **1** exhibited resonances at δ 8.05 (d, 2H), 7.99 (d, 2H), 7.85 (d, 2H), 7.73 (t, 2H), 7.62 (t, 4H), 7.44 (t, 2H) and 6.92 (d, 2H) ppm corresponding to Ph-BIAN protons and at δ 5.58 (s) ppm corresponding to the coordinated $\eta^6\text{-}C_6H_6$ ring protons. Similarly, in the ^{1}H NMR spectrum of complex **2** Ph-BIAN protons resonated at δ 7.99 (d, 2H, 8.1 Hz), 7.93 (d, 2H, 6.6 Hz), 7.82 (d, 2H, 6.3 Hz), 7.74 (t, 2H, 6.9 Hz), 7.62 (m, 4H), 7.43 (t, 2H, 8.1 Hz) and 6.89 (d, 2H, 6.9 Hz) ppm, while the protons associated with the *p*-cymene ring resonated at δ 5.33 (s, 4H), 2.51 (sep, 1H, 6.9 Hz), 1.99 (s, 3H) and 1.09 (d, 6H, 6.9 Hz) ppm. It was observed that the protons corresponding to Ph-BIAN resonated at almost same position in all the complexes. Further, the protons associated with the $\eta^5\text{-}C_5H_5$ ring in complex **3** resonated at 4.65 ppm and the methyl protons corresponding to the pentamethylcyclopentadienyl rings in complexes **4** and **5** appeared as a singlet at ~1.30 ppm. The position and integrated intensity of the various signals corresponded well to the formulation of respective complexes. In the ^{31}P NMR spectrum of complex **3**, the ^{31}P nuclei of the coordinated triphenylphosphine resonated as a singlet in the normal range at 43.29 ppm.

Electronic and emission spectral data for all the complexes are recorded in the experimental section. Comparative electronic spectra for the mononuclear complexes **1**–**5** are shown in Fig. 2. The electronic spectra of the ruthenium complexes **1** and **2** displayed bands at ~446, 310 and 255 nm. On the basis of its intensity and position, the lower energy absorption band at 446 nm has been assigned to a [Ru(II) → π^* Ph-BIAN] metal-to-ligand charge transfer (MLCT), where the high-lying filled orbital is localized on the metal centre and the low-lying empty orbital is localized on Ph-BIAN. Bands at around 300 nm could be attributed to intra-ligand π–π^* transitions. Similar trends of absorptions have been observed in the electronic spectra of complexes **3**–**5**.

The luminescence properties of complexes **1**–**3** were examined at room temperature in dichloromethane, Fig. 3. Upon excitation at their respective excitation bands (in parentheses), the complexes exhibited moderate emissions [577 nm (446 nm) for **1**, 547 nm (462 nm) for **2** and 617 nm (561 nm) for **3**]. The emission spectra were found to be parallel to their respective absorption bands, therefore these bands may be assigned to the ^{3}MLCT energy state of $Ru_{d\pi}\text{-}BIAN_{\pi^*}$. The observed results could be attributed to the fact that the excited state energy can be fine tuned with different substituents on the ligands that can be either electron donating or electron withdrawing [1c,1d,1e,13]. Emission from arene ruthenium complexes is often quenched following a non-radiative deactivation pathway [14]. Further, the non-radiative decay could be hindered by a judicious choice of ligands that controls the energy gap between the lowest excited energy state and the ground state (Table 1).

3.2. Solid-state characterization of complex *5*

Suitable crystals with distinct morphology were grown from a dichloromethane solution and diethylether by slow diffusion. The

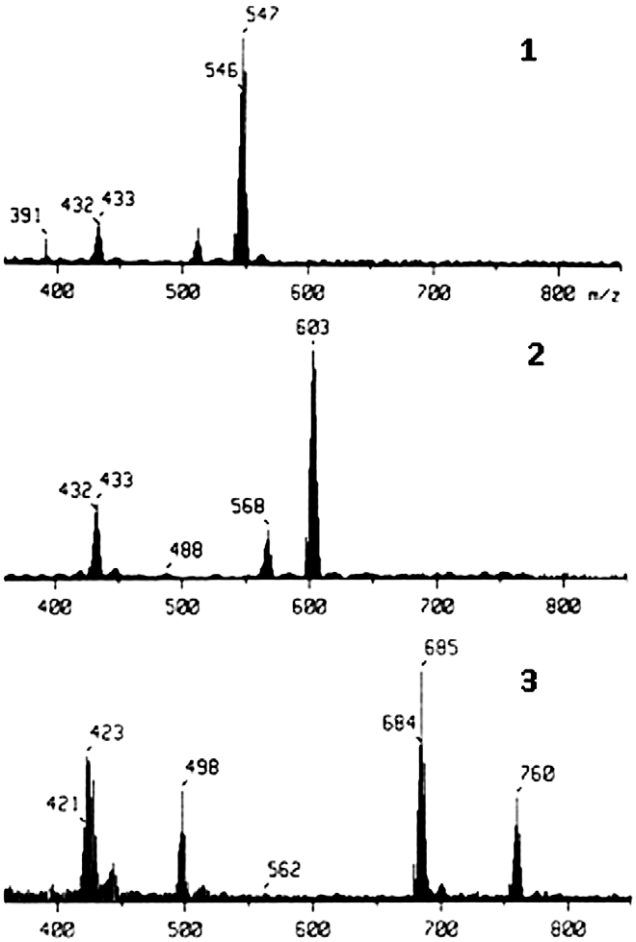


Fig. 1. FAB mass spectra of **1**–**3**.

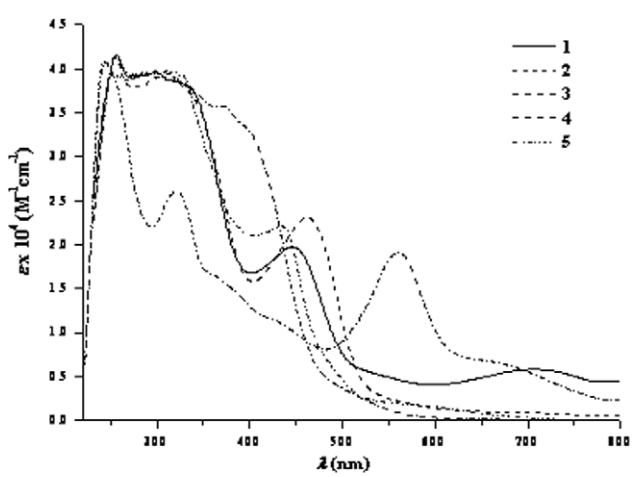


Fig. 2. Electronic spectra of **1**–**5** in dichloromethane.

ORTEP [15] depiction, including the atom-numbering scheme for the complex cation of **5**, is shown in Fig. 4, and the selected crystallographic data and bond parameters are listed in Tables 2 and 3, respectively. Complex **5** crystallizes in the orthorhombic crystal system with the *Pnma* space group. The coordination geometry about the metal centre Ir(1) is completed by nitrogen N(1) of PhBIAN, chloride ligand Cl(1) and $C_5Me_5(Cp^*)$ in η^5-coordination mode. Considering C_5Me_5 as a single coordination site, the overall

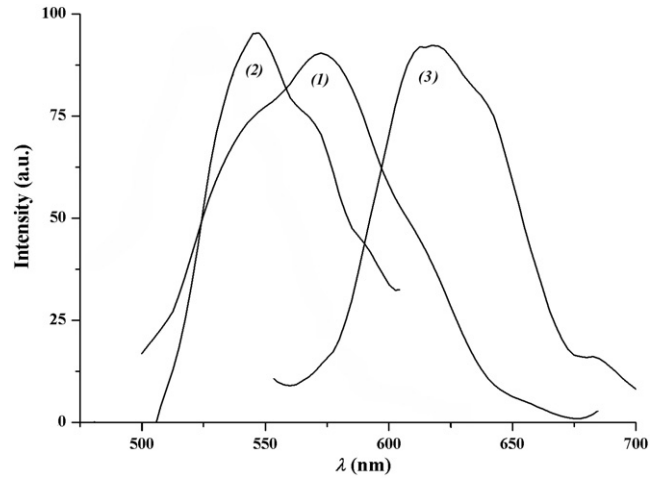


Fig. 3. Emission spectra of **1**–**3** in dichloromethane solution.

Table 1
Crystallographic data for **5**

Empirical formula	$C_{6.18}H_{5.64}B_{0.18}Cl_{0.18}F_{0.73}Ir_{0.18}N_{0.36}$
Formula weight	142.19
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	*Pnma*
Unit cell dimensions	
a (Å)	12.073(2)
b (Å)	16.432(3)
c (Å)	15.775(3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	3129.4(11)
Z	22
D_{calc} (Mg/m^3)	1.660
Reflections collected/unique (R_{int})	28 948/3706 (0.0730)
Data/restraints/parameters	3706/0/211
Goodness-of-fit on F^2	0.998
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0431$, $wR_2 = 0.1164$
R indices (all data)	$R_1 = 0.0488$, $wR_2 = 0.1210$

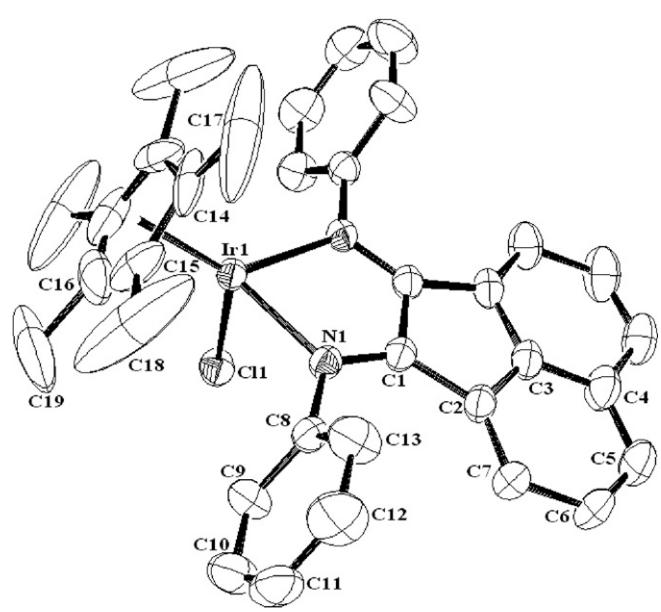
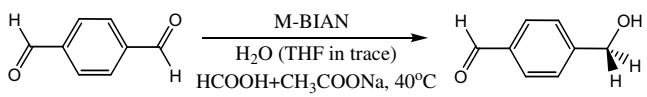


Fig. 4. ORTEP view of **5** with 30% ellipsoid probability.

Table 2
Important bond parameters (Å, °) for **5**

Ir(1)–N(1)	2.101(4)
Ir(1)–C(14)	2.133(8)
Ir(1)–C(16)	2.145(7)
Ir(1)–C(15)	2.166(6)
Ir–Ccp*	2.151
Ir–Cct	2.151
Ir(1)–Cl(1)	2.4047(18)
C–C(C5Me5)	1.368
C(C5Me5)–C(C5*Me*5)	1.473
C(1)–N(1)	1.299(7)
C(1)–C(2)	1.467(7)
C(1)–C(1)#1	1.473(10)
N(1)–Ir(1)–N(1)	76.9

Table 3
Hydrogenation of terephthalaldehyde with M-BIAN in H_2O at a S/C ratio of 100



Catalyst	% Con	*t* (h)	TOF[a] (h^{-1})
RuB-BIAN (**1**)	>99	7	14
RuPC-BIAN (**2**)	>99	3	33
RuCP-BIAN (**3**)	>99	10	10
Rh-BIAN (**4**)	>99	0.75	133
Ir-BIAN (**5**)	>99	2	50

[a] Based on >99 % conversion.

coordination geometry about the metal centre is a typical *piano-stool* geometry. The average Ir—C_{cp^*} distance is 2.151 Å (range 2.133–2.166 Å; Ir–C_{ct} 1.810 Å) [16,17a]. The Ir–Cl and Ir–N distances are normal and have values of 2.4047 and 2.101 Å, respectively [16a–18]. The chelating N–Ir–N bite for the coordination of the imino nitrogen of Ph-BIAN is 76.9°. The arrangement of phenyl rings with respect to the acenaphthene ring is almost orthogonal, with a dihedral angle of 71.97°. The acenaphthene ring is planar with a deviation of 0.76°. The C–C(C_5Me_5) bond lengths in C_5Me_5 are in the range 1.25–1.472 Å, with an average value of 1.368 Å, and the exterior C(C_5Me_5)–C(C_5Me_5) average bond length is 1.473 Å. The C–C bond lengths within the Cp^* ring and the C–CH_3 bond lengths are normal [19].

3.3. Catalytic application of complexes *1*–*5*

To evaluate the selectivity and efficiency of complexes **1**–**5** as catalysts towards the reduction of the mono/di-formyl group, terephthalaldehyde was used as a model substrate. Hydrogenation was initiated by introducing formic acid–sodium acetate and terephthalaldehyde (1.0 mmol) in water (a few drops of freshly distilled THF was used to dissolve the catalyst) and air at 40 °C with 1% catalyst. All the complexes were found to catalyze the hydrogenation of terephthalaldehyde to produce 4-hydroxymethybenzaldehyde in aqueous solution (Table 3). It was observed that in all cases only one formyl group of terephthalaldehyde was selectively reduced. Further, we found that the rhodium complex Rh-BIAN (**4**) led to almost complete conversion of terephthalaldehyde into 4-hydroxymethybenzaldehyde in 45 min. The analogous iridium complex Ir-BIAN (**5**) was less active as compared to the rhodium complex Rh-BIAN (**4**) and complete conversion of the substrate took place in 2 h. RuPC-BIAN (**2**) required 3 h for the same reduction and RuCP-BIAN (**3**) is least effective in this regard. Among the ruthenium *p*-cymeme and benzene complexes, the ruthenium *p*-cymene complex (**2**) is more effective than its benzene (**1**) analogue. This may be due to the inductive effect of the isopropyl and methyl substituents on the capped arene ligand. Further, Rh-BIAN was also found to catalyze the hydrogenation of 2-acetyl-naphthalene, however only 20% conversion was achieved even after 10 h.

4. Conclusion

In conclusion, in this work a new series of mononuclear *piano-stool* complexes [(η^6-arene)Ru(Ph-BIAN)Cl]BF_4 [η^6-arene = C_6H_6 (**1**), $C_{10}H_{14}$ (**2**)], [(η^5-C_5H_5)Ru(Ph-BIAN)PPh_3]BF_4 (**3**) and [(η^5-C_5Me_5)M(Ph-BIAN)Cl]BF_4 [M = Rh (**4**), Ir (**5**)] have been synthesized using a highly conjugated diimine ligand with a rigid acenaphthene skeleton. Apart from the non-radiative nature of arene ruthenium complexes, the reported complexes were found to be luminescent at room temperature in dichloromethane. Furthermore, it has been shown that complexes **1**–**5** effectively catalyze the reduction of terephthalaldehyde, and among these the rhodium complex [(η^5-C_5Me_5)Rh(Ph-BIAN)Cl]BF_4 (**4**) is an effective hydrogenating catalyst for use in water and air, and delivers faster rates without requiring inert gas protection or substrate solubility in water.

Crystallographic data: Crystals suitable for single crystal X-ray diffraction analyses for **5** were grown from dichloromethane and diethyl ether at room temperature using the diffusion technique. Preliminary data on the space group and unit cell dimensions as well as intensity data were collected on a R-AXIS RAPID II diffractometer using graphite monochromatized Mo Kα radiation. The structure was solved by direct methods and refined using SHELX 97 [20]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The H-atoms attached to carbon atoms were included as a fixed contribution and were geometrically calculated and refined using the SHELX riding model.

5. Supplementary data

CCDC 670670 contains the supplementary crystallographic data for complex **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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