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Synthesis, characterisation and theoretical studies on some *piano-stool* ruthenium and rhodium complexes containing substituted phenyl imidazole ligands

Ashish Kumar Singh, Prashant Kumar, Mahendra Yadav, Daya Shankar Pandey *

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221005, UP, India

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ABSTRACT

Reactions of the chloro-bridged arene ruthenium complexes $[\{(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)_2\}]$ (η^6-arene = benzene, *p*-cymene) and structurally analogous rhodium complex $[\{(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)_2\}]$ with imidazole based ligands viz., 1-(4-nitro-phenyl)-imidazole (NOPI), 1-(4-formylphenyl)-imidazole (FPI) and 1-(4-hydroxyphenyl)-imidazole (HPI) have been investigated. The resulting complexes have been characterised by elemental analyses, IR, ^1H and ^{13}C NMR, electronic absorption and emission spectral studies. Crystal structure of the representative complex $[(\eta^5\text{-}C_5Me_5)RhCl_2(NOPI)]$ has been determined crystallographically. Geometrical optimisation on the complexes have been performed using exchange correlation functional B3LYP. Optimised bond lengths and angles of the complexes have been found to be in good agreement with our earlier reports and single crystal X-ray data of the complex $[(\eta^5\text{-}C_5Me_5)RhCl_2(NOPI)]$.

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1. Introduction

The dimeric chloro-bridged arene ruthenium $[\{(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl\}_2]$ (arene = benzene and their derivatives) and structurally analogous rhodium and iridium complexes $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh or Ir) imparting η^6-/η^5-cyclic hydrocarbon ligands are versatile and valuable synthetic intermediates that have seen many applications in coordination, organometallic chemistry and catalysis [1–6]. These complexes undergo a rich variety of chemistry *via* intermediacy of the chloro-bridge cleavage reactions leading to the formation of a series of interesting neutral and cationic mononuclear half-sandwich complexes [7–13]. Air-stable, water-soluble complexes containing (η^6-arene)Ru- and (η^5-C_5Me_5)Rh- moieties find wide applications in many areas including homogeneous catalysis, polymeric materials, nano-cages and nano-particle precursors [14–19]. These are also, being explored for their medicinal properties as anticancer agents [20–25]. Further, it have been shown that certain acceptor–donor molecules exhibit twisted internal charge transfer (TICT) which appears attractive for molecular switching, since there is an almost perfect orbital decoupling in the twisted internal charge transfer state. It is expected that the complexes in which redox sites are bridged by this type of molecule could be a good model to test the possibility of molecular switching. In this regard, 1-(4-cyanophenyl)-imidazole (CPI) have drawn special attention due to occurrence of twisted internal charge transfer (TICT) and its ability to behave as a good bridging ligand [26,27].

In this direction to develop the chemistry of CPI and related ligands, we have examined reactivity of the arene ruthenium complexes $[\{(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl\}_2]$ (arene = benzene, *p*-cymene) with 1-(4-cyanophenyl)-imidazole and have reported first examples of luminescent complexes containing (η^6-arene)Ru- moiety [27–29]. It is expected that the replacement of cyanophenyl group in CPI by nitro phenyl, phenyl carbaldehyde or phenolic group may lead to substantial changes in the properties of the resulting complexes. With this view-point we have examined reactivity of the arene ruthenium $[\{(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl\}_2]$ (arene = benzene, *p*-cymene) and rhodium complexes $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl\}_2]$ with 1-(4-nitrophenyl)-imidazole (NOPI), 1-(4-formylphenyl)-imidazole (FPI) and 1-(4-hydroxyphenyl)-imidazole (HPI). In this paper we report syntheses and spectral characterisation of a series of neutral mononuclear complexes containing (η^6-arene)Ru- and (η^5-C_5Me_5)Rh- moieties and aforesaid ligands. Also, we present herein crystal structure of the representative rhodium complex $[(\eta^5\text{-}C_5Me_5)RhCl_2(NOPI)]$.

2. Experimental

2.1. Materials and physical measurements

All the chemicals were obtained from commercial sources and used without further purifications. Pentamethylcyclopentadiene, hydrated rhodium(III) chloride, hydrated ruthenium(III) chloride,

* Corresponding author. Tel.: + 91 542 2307321 105.
E-mail address: dspbhu@bhu.ac.in (D.S. Pandey).

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4-fluronitrobenzene, 4-fluorobenzaldehyde, 4-imidazol-yl-phenol and imidazole were procured from Sigma–Aldrich. The ligands 1-(4-nitrophenyl)-imidazole (NOPI) [30], 1-(4-formylphenyl)-imidazole (FPI) [31] and precursor complexes [{(η^6-arene)Ru(μ-Cl)Cl}$_2$] (arene = benzene [32], *p*-cymene [33]), [{(η^5-C_5Me_5)Rh(μ-Cl)Cl}$_2$] [34] were prepared and purified following the literature procedures. Elemental analyses on the complexes were performed on an Exter CE-440 CHN Analyzer. IR and electronic absorption spectra were recorded on a Perkin Elmer-577 and Shimadzu-UV 1700 spectrophotometers, respectively. ^{1}H and ^{13}C NMR spectra of the complexes were recorded on a JEOL AL 300 FT-NMR machine in *d*-chloroform at 298 K using TMS as an internal reference. Emission spectra were recorded in dichloromethane on a Varian Carry Eclips spectrophotometer.

2.2. Syntheses

2.2.1. Preparation of [(η^6-C_6H_6)$RuCl_2$(NOPI)] **1**

To a solution of NOPI (95 mg, 0.50 mmol) in methanol (25 mL), the ruthenium complex [{(η^6-C_6H_6)RuCl(μ-Cl)$_2$] (125 mg, 0.25 mmol) was added and the resulting suspension was stirred at room temperature for 4 h. Clear pale red solution thus obtained was filtered through celite to remove any solid impurities. Addition of petroleum ether (60–80 °C) to the filtrate afforded pale red crystalline product. It was separated by filtration, washed with methanol (2 × 10 mL), diethyl ether (2 × 10 mL) and dried under vacuum. Yield: 176 mg, 80%. Microanalytical data: *Anal.* Calc. $C_{15}H_{13}N_3O_2Cl_2Ru$, requires: C, 41.02; H, 2.98; N, 9.57. Found: C, 40.82; H, 3.23; N, 9.43%. IR (KBr cm^{-1}): 3449 (vbr), 3086 (s), 1595 (vs), 1514 (s), 1432 (s), 1339 (vs), 1304 (vs) 1270 (vs), 1199 (w), 1111 (vs), 1064 (vs), 1008 (w), 957 (w), 845 (s), 747 (s), 688 (w), 621 (vs), 506 (w). ^{1}H NMR ($CDCl_3$, δ ppm): 8.48 (s, 1H), 8.09 (d, 2H, *J* = 9.3 Hz), 8.00 (d, 3H, *J* = 9.0 Hz), 7.55 (s, 1H), 6.61 (s, 6H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 146.2, 140.4, 139.4, 128.3, 125.5, 121.5, 118.6, 87.63(C η^6-C_6H_6). UV–vis. {CH_2Cl_2, λnm (ε)}:445 (1.58 × 10^3), 290 (2.13 × 10^4), 242 (1.76 × 10^4).

2.2.2. Preparation of [(η^6-$C_{10}H_{14}$)$RuCl_2$(NOPI)].1/2(Et_2O) **2**

This complex was prepared from NOPI (95 mg, 0.50 mmol) and [{(η^6-$C_{10}H_{14}$)RuCl(μ-Cl)$_2$] (153 mg, 0.25 mmol) following the method **1**. Yield: 196 mg, 79%. Microanalytical data: *Anal.* Calc. $C_{19}H_{21}N_3O_2Cl_2Ru$, requires: C, 46.07; H, 4.27; N, 8.48. Found: C, 45.93; H, 4.15; N, 8.27%. IR (KBr cm^{-1}): 3450 (vbr), 3099 (m), 2917 (w), 1598 (s), 1514 (s), 1339 (vs), 1302 (s), 1250 (w), 1111 (m), 1058 (s), 1023 (w), 848 (s), 754 (s), 686 (w), 509 (w). ^{1}H NMR ($CDCl_3$, δ ppm): 8.43 (s, 1H), 8.36 (d, 2H, *J* = 8.7 Hz), 7.54 (d, 3H, *J* = 9.0 Hz), 7.36 (s, 1H), 5.51 (d, 2H, *J* = 5.4 Hz), 5.35 (d, 2H, *J* = 5.4 Hz), 3.47 (q, 2H, *J* = 7.2 Hz), 3.01 (m, 1H), 2.24 (s, 3H), 1.32 (d, 6H, *J* = 6.9 Hz), 1.208 (t, 3H, *J* = 6.9 Hz). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 146.4, 140.1, 139.0, 128.5, 125.0, 122.1, 118.0 103.2, 96.9, 82.2, 81.0, 29.9($(CH_3)_2$***C***H), 23.0 ($(***C***H_3)_2$CH), 19.0 (***C***H_3). UV–vis. {CH_2Cl_2, λnm (ε)}: 442 (1.10 × 10^3), 290 (2.11 × 10^4), 241 (1.73 × 10^4).

2.2.3. Preparation of complex [(η^5-C_5Me_5)$RhCl_2$(NOPI)] **3**

This complex was prepared from NOPI (95 mg, 0.50 mmol) and [{(η^5-C_5Me_5)RhCl(μ-Cl)$_2$] (155 mg, 0.25 mmol) following the procedure for **1**. Yield: 202 mg, 81%. Microanalytical data: Anal. Calc. $C_{19}H_{22}N_3O_2Cl_2Rh$, requires: C, 45.81; H, 4.45; N, 8.43% Found: C, 45.65; H, 4.87; N, 8.22%. IR (KBr cm^{-1}): 3451 (vbr), 3140 (m), 2960 (w), 1602 (s), 1522 (s), 1463 (s), 1337 (vs), 1302 (s), 1267 (w), 1220 (s), 1109 (m), 1065 (s), 797 (s), 621 (w), 478 (w). ^{1}H NMR ($CDCl_3$, δ ppm): 8.52 (s, 1H), 8.37 (d, 2H, *J* = 9.0 Hz), 7.58 (d, 2H, *J* = 8.7 Hz), 7.42 (m, 2H), 1.61(s, 15H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 146.8, 140.5, 137.5, 132.2, 125.8, 121.4, 119.2, 93.9 (***C***–CH_3), 9.1 (C–***C***H_3). UV–vis. {CH_2Cl_2, λnm (ε)}: 400 (4.48 × 10^3), 289 (1.79 × 10^4), 258 (1.75 × 10^4).

2.2.4. Preparation of complex [(η^6-C_6H_6)$RuCl_2$(FPI)] **4**

It was prepared following the procedure for **1** using FPI (86 mg, 0.50 mmol) and [{(η^6-C_6H_6)RuCl(μ-Cl)$_2$] (125 mg, 0.25 mmol). Yield: 171 mg, 81%. Microanalytical data: *Anal.* Calc. $C_{16}H_{14}N_2OCl_2Ru$, requires: C, 45.51; H, 3.34; N, 6.63. Found: C, 45.37; H, 3.63; N, 6.52%. IR(KBr cm^{-1}): 3482 (vbr), 3122 (m), 2960 (w), 1698 (vs), 1601(vs), 1519 (s), 1487 (vs), 1375 (w), 1303 (vs), 1216 (w), 1171 (s), 1120 (m), 1056 (s), 957 (w), 828 (s), 510 (w). ^{1}H NMR ($CDCl_3$, δ ppm): 10.03 (s, 1H), 8.47 (s, 1H), 8.29 (d, 2H, *J* = 9.0 Hz), 7.58 (s, 1H), 7.52 (d, 2H, *J* = 6.6 Hz), 7.32 (s, 1H), 6.45 (s, 6H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 190.1, 140.0, 136.9, 135.6, 131.5, 122.3, 118.6, 87.3(C η^6-C_6H_6). UV–vis. {CH_2Cl_2, λnm (δ)}: 451 (1.43 × 10^3), 284 (1.88 × 10^4), 240 (1.69 × 10^4).

2.2.5. Preparation of complex [(η^6-$C_{10}H_{14}$)$RuCl_2$(FPI)] **5**

It was prepared following the method for **1** using FPI (86 mg, 0.50 mmol) and [{(η^6-$C_{10}H_{14}$)RuCl(μ-Cl)$_2$] (153 mg, 0.25 mmol). Yield: 187 mg, 78%. Microanalytical data: *Anal.* Calc. $C_{20}H_{22}N_2OCl_2Ru$, requires: C, 50.21; H, 4.64; N, 5.86. Found: C, 50.06; H, 4.55; N, 5.59%. IR (KBr cm^{-1}): 3455 (vbr), 3126 (m), 2918 (w), 1693 (vs), 1602 (vs), 1517 (s), 1490 (vs), 1376 (w), 1304 (vs), 1213 (w), 1168 (s), 1120 (m), 1061 (s), 829 (vs), 759 (w), 478 (w). ^{1}H NMR ($CDCl_3$, δ ppm): 10.07 (s, 1H), 8.52 (s, 1H), 8.45 (d, 2H, *J* = 8.7 Hz), 8.02 (d, 2H, *J* = 9.0 Hz), 7.55 (s, 1H), 7.37 (s, 1H), 5.61 (d, 2H, *J* = 5.7 Hz), 5.41 (d, 2H, *J* = 5.4 Hz), 3.00 (m, 1H), 2.26 (s, 3H), 1.38 (d, 6H, *J* = 6.6 Hz). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 190.5, 141.1, 137.8, 134.7, 132.4, 121.2, 119.1, 101.8, 97.9, 81.2, 79.6, 30.3($(CH_3)_2$***C***H), 23.3 ($(***C***H_3)_2$CH), 20.1 (***C***H_3). UV–vis. {CH_2Cl_2, λnm (ε)}: 446 (1.44 × 10^3), 290 (1.96 × 10^4), 241 (1.62 × 10^4).

2.2.6. Preparation of complex [(η^5-C_5Me_5)$RhCl_2$(FPI)] **6**

This complex was prepared using FPI (86 mg, 0.50 mmol) and [{(η^5-C_5Me_5)RhCl(μ-Cl)$_2$] (155 mg, 0.25 mmol) following the method for **1**. Yield: 197 mg, 82%. Microanalytical data: *Anal.* Calc. $C_{20}H_{23}N_2OCl_2Rh$, requires: C, 49.92; H, 4.82; N, 5.82. Found: C, 49.71; H, 4.57; N, 5.63%. IR (KBr cm^{-1}): 3478 (vbr), 3123 (m), 3060 (w), 2960 (br), 1698 (vs), 1600 (vs), 1519 (vs), 1485 (m), 1376 (w), 1302 (vs) 1215 (vs), 1170 (s), 1118 (s), 1055 (vs), 826 (s), 509 (w). ^{1}H NMR ($CDCl_3$, δ ppm): 10.05 (s, 1H), 8.50 (s, 1H), 8.02 (d, 2H, *J* = 8.4 Hz), 7.57 (d, 2H, *J* = 8.4 Hz), 7.44 (s, 1H), 7.37 (s, 1H), 1.58 (s, 15H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm):190.6, 140.3, 137.5, 135.6, 131.7, 121.3, 119.0, 93.9 (***C***–CH_3), 9.1(C–***C***H_3). UV–vis. {CH_2Cl_2, λnm (ε)}: 402 (3.44 × 10^3), 282 (1.77 × 10^4), 254 (1.80 × 10^4).

2.2.7. Preparation of complex [(η^6-C_6H_6)$RuCl_2$(HPI)] **7**

It was prepared from HPI (80 mg, 0.50 mmol) and [{(η^6-C_6H_6)RuCl(μ-Cl)$_2$] (125 mg, 0.25 mmol) following the method for **1**.Yield: 164 mg, 80%. Microanalytical data: *Anal.* Calc. $C_{15}H_{14}N_2OCl_2Ru$, requires: C, 43.91; H, 3.44; N, 6.83. Found: C, 43.68; H, 3.22; N, 6.76%. IR (KBr cm^{-1}): 3543 (vbr), 3145 (m), 2940 (br), 1602 (vs), 1522 (s), 1425 (br), 1391 (vs), 1310 (vs) 1265 (vs), 1185 (w), 1120 (vs), 1066 (vs), 965 (w), 842 (s), 771 (s), 661 (w), 622 (vs), 565 (w). ^{1}H NMR ($CDCl_3$, δ ppm): 9.95 (s, 1H, O***H***), 8.52(s, 1H), 8.37 (d, 2H, *J* = 8.7 Hz), 7.61 (s, 1H), 7.52 (d, 2H, *J* = 6.6 Hz), 7.32 (s, 1H), 5.85 (s, 15H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 157.2, 137.5, 131.9, 128.3, 122.7, 118.5, 117.0, 88.1(C η^6-C_6H_6).

2.2.8. Preparation of complex [(η^6-$C_{10}H_{14}$)$RuCl_2$(HPI)] **8**

This complex was prepared from HPI (80 mg, 0.50 mmol) and [{(η^6-$C_{10}H_{14}$)RuCl(μ-Cl)$_2$] (153 mg, 0.25 mmol) following the same procedure as employed for **1**. Yield: 189 mg, 81%. Microanalytical

data: *Anal.* Calc. $C_{19}H_{22}N_2OCl_2Ru$, requires: C, 48.93; H, 4.94; N, 5.97. Found: C, 48.82; H, 4.75; N, 5.86%. IR (KBr cm^{-1}); 3540 (vbr), 3141 (m), 2925 (br), 1597 (vs), 1525 (s), 1422 (br), 1388 (vs), 1310 (vs) 1268 (vs), 1184 (w), 1125 (vs), 1070 (vs), 964 (w), 839 (s), 773 (s), 656 (w), 623 (vs), 560 (w). ^{1}H NMR ($CDCl_3$, δ ppm): 9.86(s, 1H, O*H*), 8.37(s, 1H), 8.06 (d, 2H, *J* = 8.7 Hz), 7.59 (d, 2H, *J* = 9.0 Hz), 7.36 (d, 2H, *J* = 8.7 Hz), 5.72 (d, 2H, *J* = 6.3 Hz), 5.55 (d, 2H, *J* = 6.6 Hz), 3.06(s, 1H), 2.32 (s, 3H), 1.39(d, 6H, *J* = 6.6 Hz). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 157.0, 138.0, 132.4, 128.1, 122.3, 119.1, 116.6, 102.8, 97.5, 82.7, 81.4, 30.7($(CH_3)_2$***C***H), 22.2 (($***C***H_3)_2$CH), 18.7 (***C***H_3).

2.2.9. Preparation of complex [(η^5-C_5Me_5)$RhCl_2$(HPI)] ***9***

It was prepared following exactly the same procedure as employed for **1** starting from HPI (80 mg, 0.50 mmol) and [{(η^5-C_5Me_5)RhCl(μ-Cl}$_2$] (155 mg, 0.25 mmol) in methanol.. Yield: 185 mg, 79%. Microanalytical data: *Anal.* Calc. $C_{19}H_{23}N_2OCl_2Rh$, requires: C, 48.64; H, 4.94; N, 5.97. Found: C, 48.30; H, 4.15; N, 6.16%. IR (KBr cm^{-1}): 3440 (vbr), 2932 (br), 1599 (vs), 1525 (s), 1425 (br), 1385 (vs), 1323 (vs), 1274 (vs), 1190 (w), 1120 (vs), 1065 (vs), 963 (w), 835 (s), 763 (s), 650 (w), 624 (vs), 565 (w). ^{1}H NMR ($CDCl_3$, δ ppm): 9.90(s, 1H, O*H*), 8.49(s, 1H), 8.37 (d, 2H, *J* = 9.0 Hz), 7.58 (d, 2H, *J* = 8.7 Hz), 7.42 (m, 2H), 1.61(s, 15H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 157.1, 137.5, 132.2, 128.1, 122.7, 118.6, 116.9, 94.2 (***C***–CH_3), 9.3(C–***C***H_3).

2.3. X-ray crystallography

2.3.1. Details of single crystal X-ray diffraction study

Details about the data collection, solution and refinement are summarised in Section 2.3.2. Intensity data for 3 were collected on a Rigaku AFC-7R diffractometer equipped with graphite Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. The structure was solved by direct methods (SHELXS 97) and refined by full-matrix least squares procedure based on F^2 (SHELX 97) [35]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located at calculated positions and refined using a riding model with isotropic thermal parameters fixed at 1.2 times the U_{eq} value of the appropriate carrier atom.

2.3.2. Selected crystallographic data of ***3***

Formula = $C_{19}H_{22}Cl_2N_3O_2Rh$, Mw = 498.21, specimen 0.15 mm × 0.13 mm × 0.12 mm, Triclinic space group $P\bar{1}$, *a* = 12.306(3) Å, *b* = 12.503(3) Å, *c* = 13.912(3) Å, α = 90.00°, β = 102.39(3)°, γ = 90.00°, *V* = 2090.9(7) Å^3, *Z* = 4, D_{calc} = 1.583, *F*(0 0 0) = 1008, μ = 1.091, T(*K*) = 293(2), λ = 0.71073, $R_{(all)}$ = 0.0446, R($I > 2\sigma(I)$) = 0.0308, wR_2 = 0.0644, wR_2 [$I > 2\sigma(I)$] = 0.0612, GOF = 1.249.

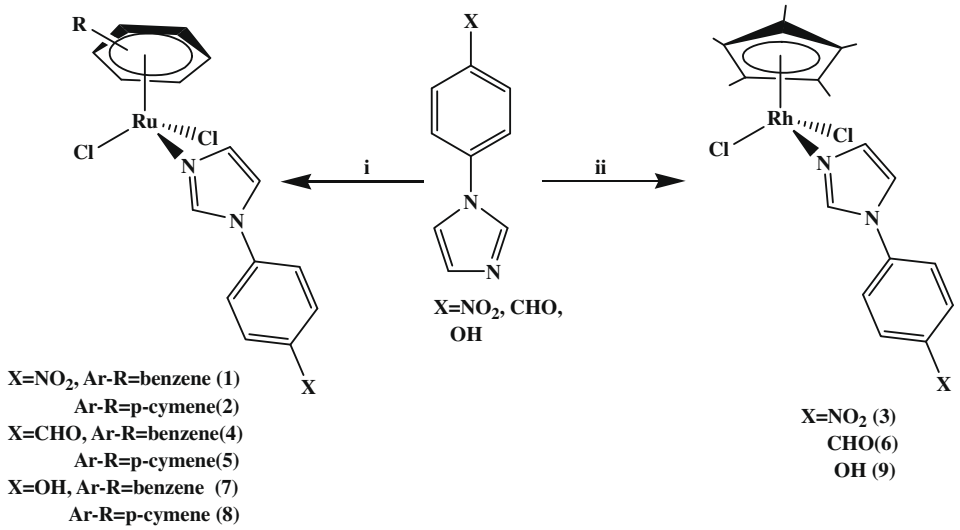
2.4. Computational methods

Calculations were performed using hybrid B3LYP density functional method which uses Becke's 3-parameter non-local exchange functionals mixed with the exact (Hartree–Fock) exchange functional and Lee–Yang–Parr's non-local correlation functional [36,37]. Geometries of the complexes were optimised without any symmetry restrictions with standard 6-31G** basis sets [38,39] for N, C, H, O and Cl elements and LANL2DZ [40–42] for Ru and Rh which combines quasi-relativistic effective core potentials with a valence double-basis set. Frequency calculations were performed to determine whether the optimised geometries were minima on the potential energy surface. The electronic structure of the complexes were examined by natural charges at each atom computed using Kohn–Sham orbitals obtained from DFT calculations [43]. 6-31G** basis sets for N, C, H, O and Cl elements and LANL2DZ for Ru and Rh elements. The calculations were performed using GAUSSIAN 03 program [44].

3. Results and discussion

Reactions of the chloro-bridged dimeric arene ruthenium complexes [{(η^6-arene)RuCl(μ-Cl}$_2$] (arene = benzene, *p*-cymene) and rhodium complex [{(η^5-C_5Me_5)RhCl(μ-Cl}$_2$] with imidazole containing ligands 1-(4-nitrophenyl)-imidazole (NOPI), 1-(4-formylphenyl)-imidazole (FPI) and 1-(4-hydroxyphenyl)-imidazole (HPI) were carried out in methanol under stirring conditions at RT. These reactions afforded neutral mononuclear complexes [(η^6-C_6H_6)$RuCl_2$(NOPI)] (**1**), [(η^6-$C_{10}H_{14}$)$RuCl_2$(NOPI)] (**2**), [(η^5-C_5Me_5)-$RhCl_2$(NOPI)] (**3**), [(η^6-C_6H_6)$RuCl_2$(FPI)] (**4**), [(η^6-$C_{10}H_{14}$)$RuCl_2$-(FPI)] (**5**), [(η^5-C_5Me_5)$RhCl_2$(FPI)] (**6**), [(η^6-C_6H_6)$RuCl_2$(HPI)] (**7**), [(η^6-$C_{10}H_{14}$)$RuCl_2$(HPI)] (**8**), [(η^5-C_5Me_5)$RhCl_2$(HPI)] (**9**) reasonably good yields. A simple scheme showing the synthesis of the complexes is depicted in Scheme 1.

All the complexes are air-stable solid and not shows any sign of decomposition when placed in air for several days. All the complexes are of crystalline nature. They are soluble in common organic solvent like dichloromethane, acetone, acetonitrile,



Scheme 1. Synthesis of complexes **1**–**9** (i)[{η^6-arene)RuCl(μ-Cl)}$_2$] (arene = C_6H_6, $C_{10}H_{14}$) (ii)[{η^5-C_5Me_5)RhCl(μ-Cl)}$_2$].

dimethylsulphoxide (DMSO) and dimethylformamide (DMF) but insoluble in *n*-hexane, diethyl ether, benzene and toluene. The complexes have been characterised by elemental analyses, IR, NMR and electronic spectral studies. Density functional theoretical calculations have been performed to authenticate the structures and electronic structure of these complexes.

In the IR spectra of respective complexes characteristic bands corresponding to $\nu_{N=O,}$ $\nu_{C=O}$ and ν_{O-H} of the coordinated NOPI, FPI and HPI were displayed at ~1339, 1598 and 3550 cm^{-1}, respectively [30–34]. The band corresponding to imidazole ring vibrations appeared at ~1600 cm^{-1} as compared to that in the free ligand (1610 cm^{-1} in NOPI, 1615 cm^{-1} in FPI and 1608 cm^{-1} in HPI). The shift in the position of $\nu_{C=N}$ bands suggested coordination of the ligand to metal centre through imidazole nitrogen. IR spectra of the complexes also exhibited characteristic bands associated with η^6-C_6H_6, η^6-$C_{10}H_{14}$ and η^5-C_5Me_5 rings at their usual positions.

^{1}H NMR spectral data of the complexes are recorded in $CDCl_3$ and presented in the experimental section. Position and integrated intensity of the various signals corresponding to ligands and the arene precursors corroborated well to a system involving coordination of ligands with ruthenium/rhodium centres. The ^{1}H NMR spectrum of the complexes displayed resonances between 7.2–8.5 ppm corresponding to the protons of the coordinated ligand, while characteristic signals due to aldehyde and phenol appeared at ~9–11 ppm and 8–10 ppm, respectively. Downfield shift in the position of peak corresponding to the imidazole ring suggested coordination of the metal through imidazolyl nitrogen. Peaks corresponding to the arene precursors appeared at almost the same position as in the precursor complexes without any significant change. Peaks corresponding to the η^6-C_6H_6 protons appeared at ~6 ppm and the one corresponding to the η^5-C_5Me_5 protons at ~1.5 ppm. As expected the protons associated with η^6-*p*-cymene also appeared in the normal range [33].

^{13}C NMR spectra also supported formulations of the respective complexes. Resulting data are summarised in the experimental section and representative spectra of the complexes **1**, **3**, **6** and **8** are depicted in Figs. S1–S4. Resonances associated with aromatic carbons of phenyl and imidazolyl groups of ligands are observed between 115–150 ppm while characteristic peak of aldehyde group of ligand FPI observed at ~190 ppm and peak corresponding to **C**–OH of HPI observed at ~157 ppm. Similarly, In (η^5-C_5Me_5)Rh-related complexes, pentamethylcyclopentadienyl carbons resonated at 8.6(C–CH_3), 94.8(C_5Me_5) ppm, for (η^6-C_6H_6)Ru- related complexes carbons resonated at ~87 ppm (Figs. S1–S3). Similarly, Peaks associated with carbon of η^6-*p*-cymene also appeared in the normal range (Fig. S4).

The electronic absorption spectra of complexes **1**–**6** were recorded in acetonitrile solutions at room temperature and resulting data are summarised in the experimental section. The low spin d^6 orbitals on ruthenium(II)/Rhodium(III) provides filled metal orbitals of proper symmetry to interact with relatively low lying π^* orbitals on the ligand. It is expected to give a band associated with metal to ligand charge transfer (MLCT) transition ($t_1g \rightarrow \pi^*$) whose position varies with nature of the metal ion and ligands acting as π acceptor. Electronic spectra of the complexes **1**–**6** displayed MLCT bands at ~450 and ~400 nm for Ru and Rh complexes, respectively (Fig. 1). Peaks around 290 nm and 230 nm ascribed as intra-ligand transition [45,46]. On the basis of its position and intensity the low energy bands in the region 400–450 nm has been assigned to MLCT transitions [Ru(II)/Rh(III) $\rightarrow \pi^*$ orbital of L] while, the absorptions in the region 247–293 nm has been attributed to the ligand field

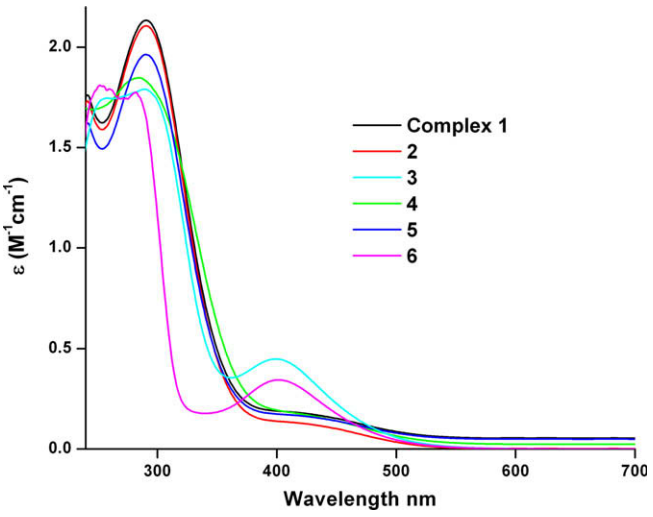


Fig. 1. UV–vis spectra of complexes **1**–**6**.

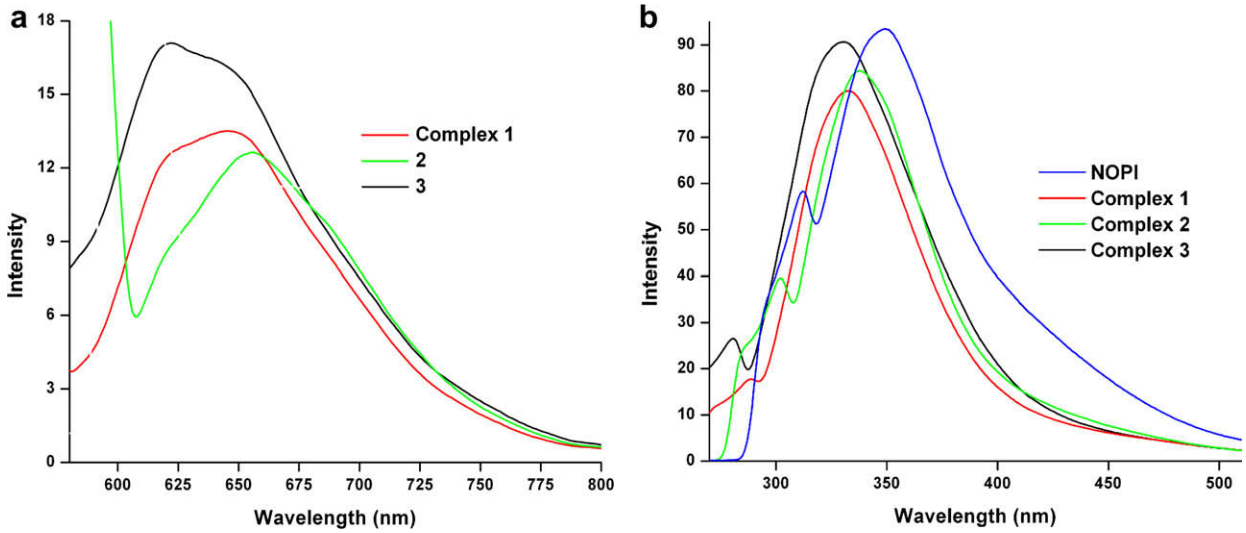


Fig. 2. Emission spectra of complex **1**–**3** upon excitation (a) at MLCT band (b) at intra-ligand transition.

or intra-ligand transitions ($\pi \rightarrow \pi^*$). Presence of MLCT bands support formation of the complexes [25,47,48].

Emission spectra of the complexes **1**–**3** were acquired in dichloromethane at room temperature and the resulting spectra are shown in (Figs. 2a and b). Upon excitation at the respective MLCT bands, complexes **1**–**3** results moderate emissions [655, 445 nm (exc), **1**; 650, 442 nm (exc), **2** and 622, 400 nm (exc), **3**. (Fig. 2a) These bands may be due to triplet metal-to-ligand charge transfer state (^{3}MLCT). In addition, these exhibited strong emissions in the region 320–350 nm upon excitation at ~290 nm.(Fig. 2b) It has been ascribed to ligand based transitions, which originate from NOPI. Hence, these compounds are luminescent materials.

Molecular structure of **3** has been determined crystallographically. Details about the data collection, solution and refinement are summarised in crystallographic section, selected geometrical parameters are gathered in Table S1 and ORTEP view at 30% thermal ellipsoid probability is depicted in Fig. 3. The metal centre rhodium in this complex adopted typical *piano-stool* geometry. Coordination geometry about the metal centre rhodium is completed by imidazolyl nitrogen, two chloro- groups and C_5Me_5 ring coordinated in η^5-manner. The Rh–N and Rh–Cl bond distances [Rh–N1 = 2.107 Å, Rh–Cl1 = 2.399 Å, Rh–Cl2 = 2.418 Å) are normal [49]. The Cl–Rh–Cl and N–Rh–Cl angles are less than 90° which are consistent with the "piano-stool" arrangement of various groups about the metal centre (Table S1) [49]. The η^5-C_5Me_5 ring is essentially planar and coordinated to rhodium centre with an average bond distance of 2.145 Å [range 2.134(3)–2.251(3) Å] and metal to centroid of η^5-C_5Me_5 distance of 1.766 Å) [49].

Weak interaction studies on the complex **3** revealed that two C–H···O intermolecular contacts (C16–H16···O1 = 3.632 Å, C8–H8B···O2 = 3.407 Å[50]) between hydrogen of the phenyl group of NOPI and oxygen of the nitro group results in a structural motif having slipper shaped cavities along the crystallographic-'*c*'-axis with the dimensions of 14.813 × 11.118 Å (Fig. 4). Significant interaction parameters along with the symmetry are listed in Table 1.

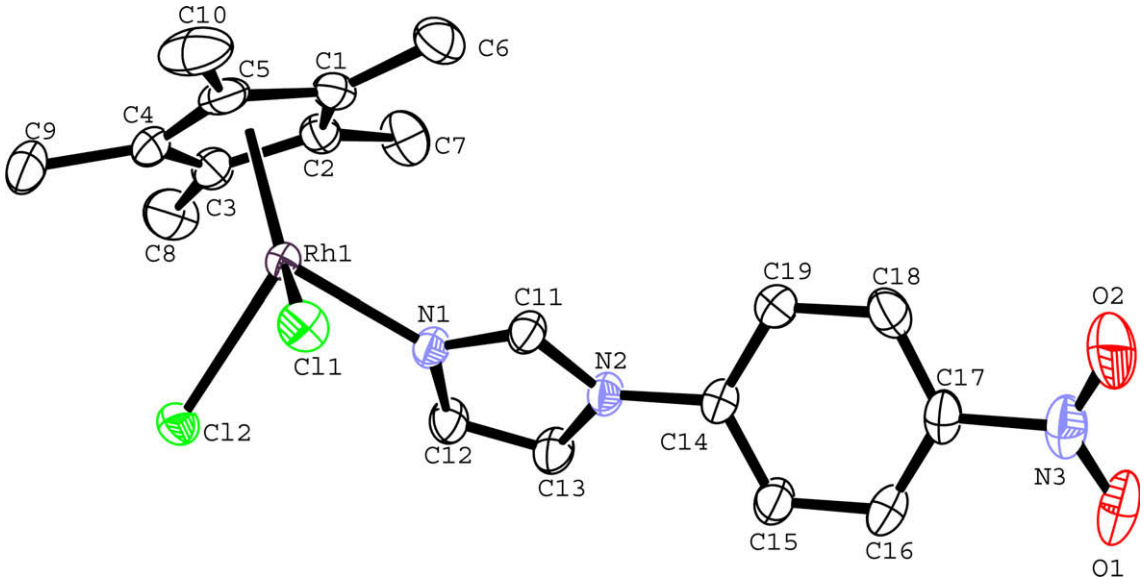


Fig. 3. Molecular structure of complex **3**.

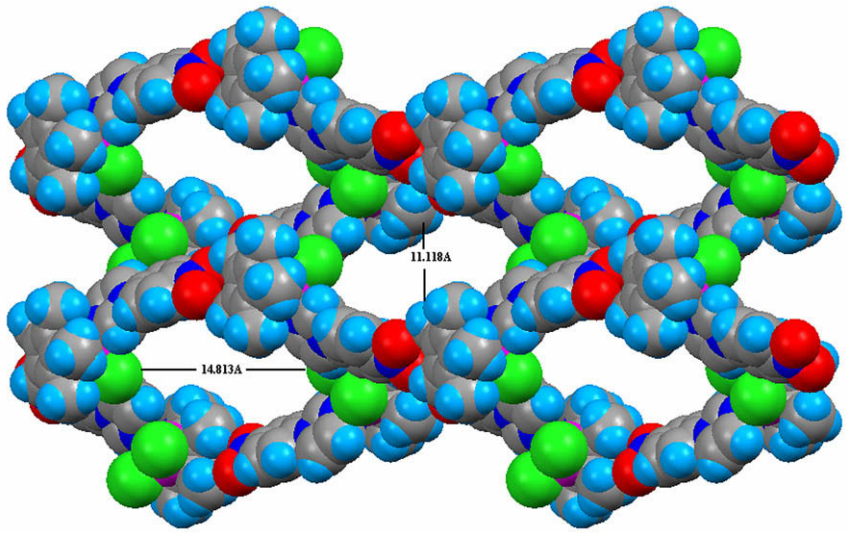


Fig. 4. Cavity resulting from H-bonding interaction in **3**.

Table 1
Matrices for weak-interactions in **3**.

Complex **1**				
Donor–H···acceptor	D–H	H···A	D···A	D–H···A
1 C(13)–H(13)···Cl(2)[a]	0.93	2.83	3.734	164
1 C(11)–H(11)···Cl(1)[b]	0.93	2.92	3.831	165
1 C(16)–H(16)···O(1)[c]	0.93	2.72	3.632	168
1 C(8)–H(8B)···O(2)[d]	0.96	2.71	3.407	130
1 C(6)–H(6A)···Cl(2)[e]	0.96	2.95	3.891	168
1 C(7)–H(7B)···Cl(2)[e]	0.96	2.86	3.761	157
1 C(19)–H(19)···Cl(2)[e]	0.96	2.78	3.453	130

[a] = 2 − *x*, −1/2 + y, 1/2 − z.
[b] = 2 − *x*,1 − *y*,−*z*.
[c] =3 − *x*, −*y*, −*z*.
[d] =−1 + *x*, 1/2 − *y*, 1/2 + z.
[e] =*x*, 1/2 − *y*, −1/2 + *z*.

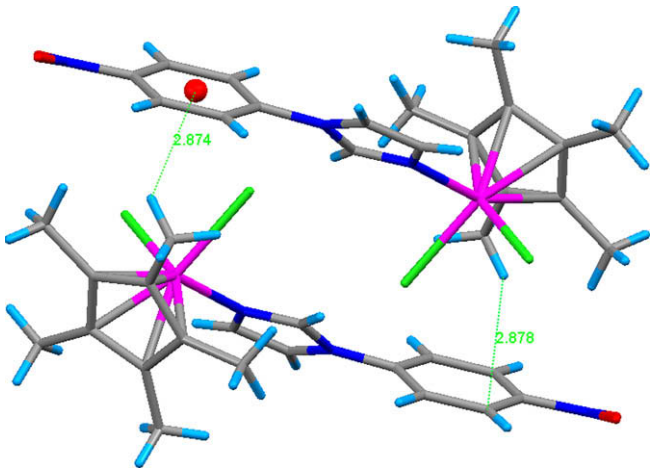


Fig. 5. C–H···π interaction in **3**.

Furthermore, the methyl protons of C_5Me_5 ring are intramolecularly involved in long range C–H···π interactions with the phenyl ring. The methyl hydrogen H10C approaches C17 of the phenyl ring resulting in C–H···π interactions with a contact distance of 2.878 Å (H10C to centroid distance 2.874 Å) (Fig. 5) [50]. Further, crystal structure of **3** revealed the presence of extensive inter-molecular C–H···Cl interactions (C13–H13···Cl2 = 3.734 Å, C11–H11···Cl1 = 3.831 Å, C6–H6A···Cl2 = 3.891 Å, C7–H7B···Cl2 = 3.761 Å, C19–H19···Cl2 = 3.453 Å). Various interaction distances are consistent with the values reported in the literature [50].

3.1. Theoretical calculations

3.1.1. Optimised geometries

To establish the structure and verify geometrical parameters (bond length and bond angles) geometrical optimisations were performed on the complexes **1**–**9**. Optimised geometries of all the complexes are shown in Figs. S5–S13. One can see that optimised bond lengths and bond angles for **3** are in excellent agreement with the data from X-ray diffraction analyses (Table S3). Structures of other complexes too, have been authenticated by optimisation of the expected structures and comparing the geometrical parameters with analogous complexes reported by us [28]. In addition, frequency calculations have also been performed to check whether the optimised geometries are minima on potential energy surface or not.

3.1.2. Bonding analysis

We begin the analysis of the bonding situation in the complexes with a discussion of natural atomic charges. Natural bond orbital (NBO) charge distributions are presented in the Scheme S1. One can see that the calculated NPA charge distributions for the metals (Ru/Rh), arene/cyclopentadiene and imidazolyl based ligands are positive, while that for the chloro groups are negative. It is noteworthy that the charge distribution in all the complexes are similar hence, their electronic properties. To visualise the Ru/Rh–N1, Ru/Rh–Cl1, Ru/Rh–Cl2, Ru–(η5-$C_{10}H_{14}$) bonding, envelope plots of some of the relevant molecular orbitals of **2** are depicted in Fig. S14. Similar conclusions may be extended to other complexes under study

4. Conclusions

In the present work we have described synthesis, spectral and structural characterisation of characterisation of a series of neutral mononuclear complexes containing (η^6-arene)Ru- and (η^5-C_5Me_5)Rh- moieties and imidazole based ligands. To compare the geometrical parameters from theoretical studies with the single crystal X-ray data, theoretical studies have performed. NBO calculations suggested that there is an overall charge flow in the direction M → L.

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Appendix A. Supplementary material

CCDC 742147 contains the supplementary crystallographic data for complex **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <www.ccdc.cam.ac.uk/data_request/cif>. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.011.

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