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Syntheses and characterization of η^5-cyclopentadienyl and η^5-indenyl ruthenium(II) complexes of arylazoimidazoles: The molecular structure of the complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(C_6H_5\text{–}N{=}N\text{–}C_3H_3N_2)]^+$

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Abstract

The complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ (**1**) reacts with several arylazoimidazole (RaaiR′) ligands, viz., 2-(phenylazo)imidazole (Phai-H), 1-methyl-2-(phenylazo)imidazole (Phai-Me), 1-ethyl-2-(phenylazo)imidazole (Phai-Et), 2-(tolylazo)imidazole (Tai-H), 1-methyl-2-(tolylazo)imidazole (Tai-Me) and 1-ethyl-2-(tolylazo)imidazole (Tai-Et), gave complexes of the type $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(RaaiR')]^+$ {where R, R′ = H (**2**), R = H, R′ = CH_3 (**3**), R = H, R′ = C_2H_5 (**4**), R = CH_3, R′ = H (**5**), R, R′ = CH_3 (**6**), R = CH_3, R′ = C_2H_5 (**7**)}. The complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]^+$ (**8**) undergoes reactions with a series of *N*,*N*-donor azo ligands in methanol yielding complexes of the type $[(\eta^5\text{-}C_9H_7)$ $Ru(PPh_3)(RaaiR')]^+$ {where R, R′ = H (**9**), R = H, R′ = CH_3 (**10**), R = CH_3, R′ = H (**11**), R = CH_3, R′ = C_2H_5 (**12**)}, respectively. These complexes were characterized by FT IR and FT NMR spectroscopy as well as by analytical data. The molecular structure of the complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(C_6H_5\text{–}N{=}N\text{–}C_3H_3N_2)]^+$ (**2**) was established by single crystal X-ray diffraction study.

Keywords: Cyclopentadienyl; Indenyl; Arylazoimidazole ligands; Ruthenium complexes

1. Introduction

Cyclopentadienyl ruthenium(II) complexes have been mainly considered as useful model compounds and have recently been successfully employed as catalysts in a series of C-C bond forming reactions [1]. The chemistry of ruthenium with unsaturated nitrogen ligands [2–11] has been studied extensively in recent times, including the study of photophysical and photochemical properties. The major work has grown around *N*,*N*-chelating pyridine bases and related species [2–11]. The number of heteroatoms, the ring size, and the substituents in the heterocyclic ring significantly modify the π-acidity and regulate the physical and chemical properties of the compounds [12].

Recently, the design of molecular architectures with imidazole ligands has contributed to the understanding of biomolecular interactions with metal ions in biology and provides models for the active sites of metalloproteins [13–16]. Ruthenium–imidazole complexes are of interest for their antitumor activities [16]. The molecule bears the azoimine (–N=N–C=N–) functional group, and is an efficient π-acid system for the stabilization of

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low oxidation state metal ions. The chemistry of this functional group with platinum is also known in detail [17–19]. We had previously reported half-sandwich complexes of ruthenium with nitrogen-based ligands [20]. However, no reports are available on these half-sandwich ruthenium complexes with azoimine ligands. The complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ differs from its analogue $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ in certain aspects such as stability of the complex in solution. Reaction of the complex $[(\eta^5\text{-}C_9H_7)Ru\ (PPh_3)_2Cl]$ with N-donor bases in methanol yielded the complexes without the indenyl group, resulting in simple coordination compounds. However, insofar as our knowledge goes, the chemistry of bidentate nitrogen-chelating indenyl-ruthenium complexes remains relatively unexplored [21]. The ligands used in the present study are shown in Chart 1.

Herein, we present the syntheses of arylazoimidazole (RaaiR′) complexes of cyclopentadienyl-ruthenium(II) and indenyl-ruthenium(II). The single crystal X-ray structure analysis of the representative complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(C_6H_5\text{–}N{=}N\text{–}C_3H_3N_2)]^+$ (**2**) is also presented.

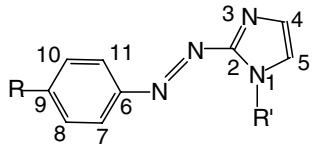
2. Experimental

2.1. Physical measurements

Elemental analysis was performed on a Perkin–Elmer-2400 CHN/O analyzer. Infrared spectra were recorded on a Perkin–Elmer-model 983 spectrophotometer with the sample prepared as KBr pellets. Electronic spectra were recorded on a Hitachi-300 spectrophotometer. The ^{1}H NMR and ^{13}C $\{^1H\}$ NMR spectra were recorded in $CDCl_3$ solvent with tetramethylsilane as internal standard and on Bruker AMX-400 (400 MHz) and Bruker ACF-300 (300 MHz) spectrometers, the coupling constants J being given in hertz. The ^{31}P $\{^1H\}$ NMR spectra was recorded in $CDCl_3$ solvent and on a Bruker AMX-400 (400 MHz), chemical shifts being recorded relative to H_3PO_4 (85%).

2.1.1. Materials and methods

All chemicals used were of reagent grade. All reactions were carried out in distilled and dried solvents.



R = H, CH_3

R' = H, CH_3, C_2H_5

Chart 1.

Ruthenium chloride trihydrate was purchased from Arora Matthey Ltd., and used as received. The ligands [17a,22] and the precursor complexes [23] were prepared by the following literature methods.

2.2. Synthesis of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(L)]PF_6$ {L = Phai-H (2), Phai-Me (3), Phai-Et (4), Tai-H (5), Tai-Me (6), Tai-Et (7)}

The following general procedure was used for preparing these compounds:

A mixture of complex **1** (100 mg, 0.138 mmol), the arylazo-imidazole (RaaiR′) ligand (0.165 mmol) and NH_4PF_6 (0.207 mmol) was refluxed in methanol (30 ml) under nitrogen atmosphere for 2 h. The yellow suspension gradually turned light green in color. The solvent was removed under reduced pressure. The light green solid was dissolved in 10 ml of CH_2Cl_2 and filtered to remove ammonium chloride. The filtrate was concentrated to 2 ml, whereupon addition of excess of hexane gave a greenish-brown precipitation. The greenish-brown colored product was washed with hexane 2–3 times and dried under vacuum. The product was dissolved in chloroform, when layering with hexane gave the crystalline product.

2. Yield: 85 mg (83%). IR (KBr pellets, cm^{-1}): $\nu_{(N\text{–}H)}$ 3423 (s), $\nu_{(N=N)}$ 1447 (s), $\nu_{(C=N)}$ 1633 (s), $\nu_{(P\text{–}F)}$ 850 (s).

^{1}H NMR ($CDCl_3$, δ): 4.83 (s, 5H, C_5H_5), 6.93–7.69 (m, 20H, Ph), 7.77 (d, 1H, $J_{H\text{–}H}$ = 7.68 Hz, imidazole), 7.95 (d, 1H, $J_{H\text{–}H}$ = 7.43 Hz, imidazole), 8.10 (b, 1H, NH).

^{13}C $\{^1H\}$ NMR ($CDCl_3$, δ): 81.32 (C_5H_5), 121.35, 123.56, 124.96, 126.37, 126.92, 127.83, 130.06, 132.42 (Ph), 134.26, 135.52, 152.17 (imidazole).

^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ): 45.05 (s).

Elemental Anal. Calc. for $C_{32}H_{28}N_4P_2F_6Ru$: C, 51.54; H, 3.78; N, 7.51. Found: C, 51.62; H, 3.39; N, 7.63%.

UV–Vis (CH_2Cl_2): λ_{max} = 460, 371, 362 nm.

3. Yield: 77 mg (74%). IR (KBr pellets, cm^{-1}): $\nu_{(N=N)}$ 1437 (s), $\nu_{(C=N)}$ 1629 (s), $\nu_{(P\text{–}F)}$ 850 (s).

^{1}H NMR ($CDCl_3$, δ): 3.74 (s, 3H, CH_3), 4.89 (s, 5H, C_5H_5), 7.00–7.44 (m, 20H, Ph), 7.75-7.79 (m, 2H, imidazole).

^{13}C $\{^1H\}$ NMR ($CDCl_3$, δ): 34.48 (CH_3), 81.65 (C_5H_5), 123.47, 126.19, 128.58, 129.58, 130.24, 131.91, 132.89, 133.60 (Ph), 135.51, 157.75, 158.25 (imidazole).

^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ): 45.16 (s).

Elemental Anal. Calc. for $C_{33}H_{30}N_4P_2F_6Ru$: C, 52.17; H, 3.97; N, 7.37. Found: C, 52.47; H, 4.02; N, 7.31%.

UV–Vis (CH_2Cl_2): λ_{max} = 581, 473, 378 nm.

4. Yield: 83 mg (78%). IR (KBr pellets, cm^{-1}): $\nu_{(N=N)}$ 1440 (s), $\nu_{(C=N)}$ 1626 (s), $\nu_{(P\text{–}F)}$ 850 (s).

^{1}H NMR ($CDCl_3$, δ): 1.41 (t, 3H, $J_{H\text{–}H}$ = 7.32 Hz, CH_3), 4.15 (q, 2H, $J_{H\text{–}H}$ = 6.80 Hz, CH_2), 4.89 (s, 5H,

C_5H_5), 6.99–7.42 (m, 20H, Ph), 7.75 (d, 1H, J_{H-H} = 7.48 Hz, imidazole), 7.83 (d, 1H, J_{H-H} = 7.38 Hz, imidazole).

^{13}C {^1H} NMR ($CDCl_3$, δ): 15.45 (CH_3), 43.32 (CH_2), 81.72 (C_5H_5), 123.46, 124.31, 128.63, 129.58, 130.87, 131.35, 132.17, 132.89 (Ph), 133.70, 135.52, 157.69 (imidazole).

^{31}P {^1H} NMR ($CDCl_3$, δ): 45.06 (s).

Elemental Anal. Calc. for $C_{34}H_{32}N_4P_2F_6Ru$: C, 52.78; H, 4.17; N, 7.24. Found: C, 52.43; H, 4.26; N, 7.22%.

UV–Vis (CH_2Cl_2): λ_{max} = 584, 474, 376 nm.

5. Yield: 85 mg (82%). IR (KBr pellets, cm^{-1}): $\nu_{(N-H)}$ 3409 (s), $\nu_{(N=N)}$ 1440 (s), $\nu_{(C=N)}$ 1600 (s), $\nu_{(P-F)}$ 850 (s).

^1H NMR ($CDCl_3$, δ): 2.41 (s, 3H, CH_3), 4.62 (s, 5H, C_5H_5), 6.92–7.44 (m, 19H, Ph), 7.49 (s, 1H, NH), 7.65 (d, 1H, J_{H-H} = 8.30 Hz, imidazole), 7.79 (d, 1H, J_{H-H} = 8.08 Hz, imidazole).

^{13}C {^1H} NMR ($CDCl_3$, δ): 31.60 (CH_3), 80.94 (C_5H_5), 123.42, 128.26, 128.70, 129.22, 129.92, 130.97, 131.21, 132.67 (Ph), 133.36, 142.47, 155.31 (imidazole).

^{31}P {^1H} NMR ($CDCl_3$, δ): 45.25 (s).

UV–Vis (CH_2Cl_2): λ_{max} = 566, 460, 401 nm.

Elemental Anal. Calc. for $C_{33}H_{30}N_4P_2F_6Ru$: C, 52.17; H, 3.97; N, 7.37. Found: C, 52.53; H, 3.84; N 7.41%.

6. Yield: 81 mg (76%). IR (KBr pellets, cm^{-1}): $\nu_{(N=N)}$ 1437 (s), $\nu_{(C=N)}$ 1629 (s), $\nu_{(P-F)}$ 849 (s).

^1H NMR ($CDCl_3$, δ): 2.43 (s, 3H, CH_3), 3.72 (s, 3H, CH_3), 4.87 (s, 5H, C_5H_5), 7.00–7.42 (m, 19H, Ph), 7.66–7.78 (m, 2H, imidazole).

^{13}C {^1H} NMR ($CDCl_3$, δ): 21.27 (CH_3), 34.45 (CH_3), 81.42 (C_5H_5), 123.44, 125.93, 128.56, 129.34, 130.18, 130.89, 132.02, 133.62 (Ph), 135.46, 142.42, 155.84 (imidazole).

^{31}P {^1H} NMR ($CDCl_3$, δ): 45.31 (s).

Elemental Anal. Calc. for $C_{34}H_{32}N_4P_2F_6Ru$: C, 52.78; H, 4.17; N, 7.24. Found: C, 52.37; H, 4.44; N, 7.35%.

UV–Vis (CH_2Cl_2): λ_{max} = 580, 471, 386 nm.

7. Yield: 87 mg (81%). IR (KBr pellets, cm^{-1}): $\nu_{(N=N)}$ 1440 (s), $\nu_{(C=N)}$ 1633 (s), $\nu_{(P-F)}$ 850 (s).

^1H NMR ($CDCl_3$, δ): 1.39 (t, 3H, J_{H-H} = 5.24 Hz, CH_3), 2.43 (s, 3H, CH_3), 4.09–4.14 (m, 2H, CH_2), 4.87 (s, 5H, C_5H_5), 6.98 (d, 2H, J_{H-H} = 8.64 Hz, Ph), 7.13 (d, 2H, J_{H-H} = 8.40 Hz, Ph), 6.98–7.80 (m, 17H, Ph and imidazole).

^{13}C {^1H} NMR ($CDCl_3$, δ): 22.67 (CH_3), 29.69 (CH_3), 54.34 (CH_2), 81.53 (C_5H_5), 122.25, 123.40, 124.07, 128.58, 129.28, 130.14, 130.82, 131.91 (Ph), 132.88, 133.65, 135.41 (imidazole).

^{31}P {^1H} NMR ($CDCl_3$, δ): 45.20 (s).

Elemental Anal. Calc. for $C_{35}H_{35}N_4P_2F_6Ru$: C, 53.30; H, 4.47; N, 7.10. Found: C, 53.42; H, 4.07; N, 6.96%.

UV–Vis (CH_2Cl_2): λ_{max} = 571, 469, 378 nm.

*2.3. Synthesis of [(η^5-C_9H_7)Ru(PPh_3)(L)]BF_4 {C_9H_7 = indenyl, L = Phai-H (**9**), Phai-Me (**10**), Tai-H (**11**), Tai-Et (**12**)}*

The following general procedure was used for preparing these compounds:

A mixture of the complex **8** [(η^5-C_9H_7)Ru-(PPh_3)$_2$(CH_3CN)]BF_4 (100 mg, 0.115 mmol) and the arylazoimidazole (RaaiR′) ligand (0.165 mmol) was refluxed in methanol (30 ml) under nitrogen atmosphere for 2 h. The yellow suspension gradually turned to brown in color. The solvent was removed under the reduced pressure. The brown solid was dissolved in dichloromethane and filtered. The filtrate was concentrated to 2 ml and addition of excess of hexane gave a brown precipitation. The brown colored product was washed with hexane and diethyl ether and dried under vacuum. The brown product was dissolved in chloroform, when layering with hexane gave the crystalline product.

9. Yield: 74 mg (87%). IR (KBr pellets, cm^{-1}): $\nu_{(N-H)}$ 3436 (s), $\nu_{(N=N)}$ 1434 (s), $\nu_{(C=N)}$ 1633 (s), $\nu_{(B-F)}$ 1082 (s).

^1H NMR ($CDCl_3$, δ): 4.93 (d, 2H, J_{H-H} = 4.38 Hz, indenyl), 5.34 (t, 1H, indenyl), 6.65 (d, 2H, J_{H-H} = 8.36 Hz, Ph), 6.87–7.47 (m, 22H, Ph), 7.66 (d, 1H, J_{H-H} = 6.78 Hz, imidazole), 7.79 (b, 1H, NH), 7.85 (d, 1H, J_{H-H} = 7.64 Hz, imidazole).

^{13}C {^1H} NMR ($CDCl_3$, δ): 64.55, 65.06, 88.97 (indenyl), 123.29, 124.02, 124.74, 125.43, 127.66, 128.58, 129.21, 130.24, 130.98, 131.60 (Ph), 133.88, 135.31, 156.56 (imidazole).

^{31}P {^1H} NMR ($CDCl_3$, δ): 50.77 (s).

Elemental Anal. Calc. for $C_{36}H_{29}N_4PBF_4Ru$: C, 58.71; H, 3.97; N, 7.61. Found: C, 58.39; H, 3.86; N, 7.56%.

UV–Vis (CH_2Cl_2): λ_{max} = 475, 391, 356, 292 nm.

10. Yield: 72 mg (83%). IR (KBr pellets, cm^{-1}): $\nu_{(N=N)}$ 1440 (s), $\nu_{(C=N)}$ 1600 (s), $\nu_{(B-F)}$ 1082 (s).

^1H NMR ($CDCl_3$, δ): 3.65 (s, 3H, CH_3), 4.98 (d, 2H, J_{H-H} = 13.40 Hz, indenyl), 5.70 (t, 1H, indenyl), 6.54 (d, 2H, J_{H-H} = 9.42 Hz, Ph), 6.81–7.48 (m, 22H, Ph), 7.83 (d, 1H, J_{H-H} = 7.52 Hz, imidazole), 7.67 (d, 1H, J_{H-H} = 7.48 Hz, imidazole).

^{13}C {^1H} NMR ($CDCl_3$, δ): 31.06 (CH_3), 62.43, 64.35, 87.68 (indenyl), 122.62, 123.36, 124.42, 125.03, 125.79, 127.34, 127.97, 129.21, 130.46, 132.24 (Ph), 134.05, 135.97, 153.27 (imidazole).

^{31}P {^1H} NMR ($CDCl_3$, δ): 50.86 (s).

Elemental Anal. Calc. for $C_{37}H_{31}N_4PBF_4Ru$: C, 59.21; H, 4.16; N, 7.47. Found: C, 59.57; H, 3.97; N, 7.16%.

UV–Vis (CH_2Cl_2): λ_{max} = 489, 376, 289 nm.

11. Yield: 75 mg (87%). IR (KBr pellets, cm^{-1}): $\nu_{(N-H)}$ 3423 (s), $\nu_{(N=N)}$ 1440 (s), $\nu_{(C=N)}$ 1600 (s), $\nu_{(BF)}$ 1082 (s).

^1H NMR ($CDCl_3$, δ): 2.45 (s, 3H, CH_3), 4.94 (d, 2H, indenyl), 5.31 (t, 1H, indenyl), 6.67 (d, 2H, J_{H-H} = 8.62

Hz, Ph), 6.86–7.43 (m, 21H, Ph), 7.66 (d, 1H, J_{H-H} = 4.36 Hz, imidazole), 7.78 (d, 1H, J_{H-H} = 8.08 Hz, imidazole), 7.80 (b, 1H, NH).

^{13}C {^1H} NMR ($CDCl_3$, δ): 22.15 (CH_3), 63.87, 65.26, 88.38 (indenyl), 121.06, 123.52, 124.48, 125.07, 125.72, 126.93, 128.31, 129.43, 130.04, 131.23 (Ph), 133.52, 134.62, 147.83 (imidazole).

^{31}P {^1H} NMR ($CDCl_3$, δ): 50.79 (s).

Elemental Anal. Calc. for $C_{37}H_{32}N_4PBF_4Ru$: C, 59.13; H, 4.29; N, 7.45. Found: C, 59.33; H, 4.26; N, 7.31%.

UV–Vis (CH_2Cl_2): λ_{max} = 472, 397, 389 nm.

12. Yield: 82 mg (92%). IR (KBr pellets, cm^{-1}): $\nu_{(N=N)}$ 1440 (s), $\nu_{(C=N)}$ 1626 (s), $\nu_{(B-F)}$ 1082 (s).

^1H NMR ($CDCl_3$, δ): 1.29 (t, 3H, J_{H-H} = 4.68 Hz, CH_3), 2.46 (s, 3H, CH_3), 4.03 (q, 2H, J_{H-H} = 7.46 Hz, CH_2), 4.94 (d, 2H, J_{H-H} = 4.14 Hz, indenyl), 5.69 (t, 1H, indenyl), 6.59 (d, 2H, J_{H-H} = 8.35 Hz, Ph), 7.14 (d, 2H, J_{H-H} = 8.39 Hz, Ph), 6.79–7.41 (m, 19H, Ph), 7.67 (d, 1H, J_{H-H} = 4.69 Hz, imidazole), 7.77 (d, 1H, J_{H-H} = 8.42 Hz, imidazole).

^{13}C {^1H} NMR ($CDCl_3$, δ): 15.37 (CH_3), 21.38 (CH_3), 43.00 (CH_2), 64.57, 65.99, 88.96 (indenyl), 123.01, 123.74, 124.49, 126.14, 127.38, 128.59, 128.97, 129.63, 130.79, 132.47 (Ph), 133.20, 133.81, 142.59 (imidazole).

^{31}P {^1H} NMR ($CDCl_3$, δ): 51.07 (s).

Elemental Anal. Calc. for $C_{39}H_{36}N_4PBF_4Ru$: C, 60.08; H, 4.65; N, 7.18. Found: C, 60.15; H, 4.42; N, 7.21%.

UV–Vis (CH_2Cl_2): λ_{max} = 484, 399, 292 nm.

3. Structure analysis and refinement

X-ray quality crystals of the complex **2**[PF_6] were grown by slow diffusion of hexane into chloroform solution. The green crystal of complex **2**[PF_6] was mounted on a Bruker Apex CCD diffractometer in a full reciprocal sphere equipped with a CCD detector and used for data collection. X-ray intensity data were collected with graphite monochromated Mo Kα radiation at 373 (2) K, with 0.3° ω scan mode and 10 s per frame. The intensity data were corrected for Lorentz and polarization effects. Absorption correction was done using the SAINT program [24]. A summary of the crystal data, data collection parameters and convergence results is compiled in Table 1. An empirical absorption correction was made by modeling a transmission surface by spherical harmonics, employing equivalent reflections with $I > 2\sigma(I)$ (program SADABS) [25]. The structure was solved by direct methods [26]. All the non-hydrogen atoms were refined anisotropically using the full-matrix least-squares technique on F^2 using the SHELXL 97 software [27]. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of an isotropic refinement and as per the "riding" model. Fig. 2 displays the ORTEP [28] representations of the molecule. Refinement converged at final R_1 values of 0.0405 (for observed data F) for compound **2**.

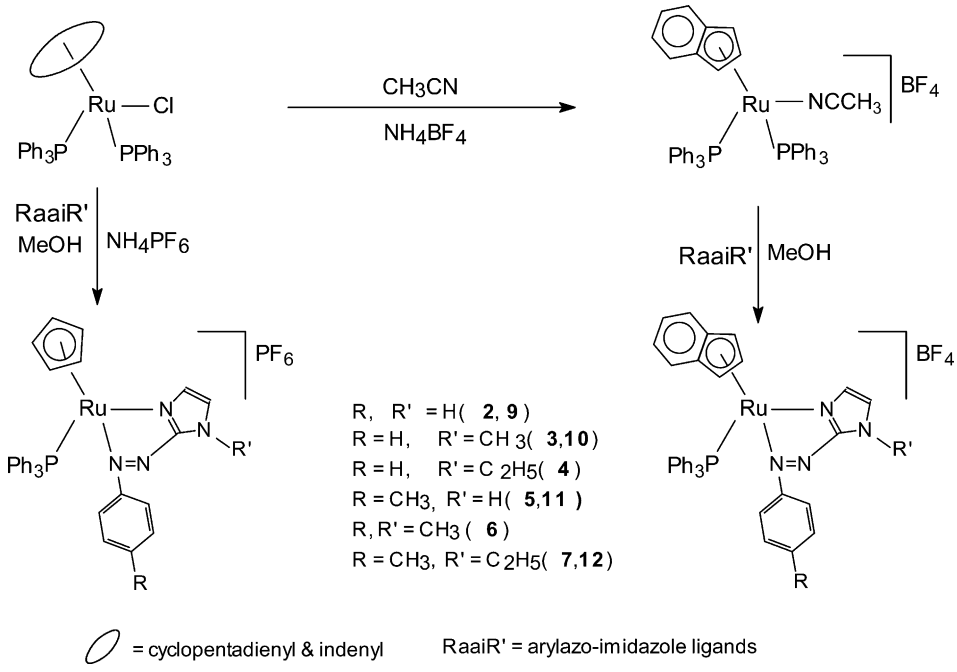
Table 1
Crystal data and structure refinement parameters for complex **2**[PF_6]$CHCl_3$

Formula	$C_{33}H_{29}Cl_3F_6N_4P_2Ru$
M_r	864.96
T (K)	373 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.9496(8)
b (Å)	11.7707(11)
c (Å)	16.6002(16)
α (°)	79.832(2)
β (°)	82.355(2)
γ (°)	82.0680(10)
V (Å^3)	1694.2 (3)
Z	4
D_{calc} (g cm^{-3})	1.696
μ (Mo Kα) (mm^{-1})	0.859
F(000)	868
θ (°)	2.31 to 28.30
Reflections collected	11073
Independent reflections	7974 [$R_{(int)}$ = 0.0159]
Completeness to θ	28.30 to 94.8
Data/restraints/parameters	7974/0/443
Goodness-of-fit on F^2	1.025
R_1 ($I > 2\sigma(I)$), wR_2	0.0405, 0.0976
R_1, R_2 (all data)	0.0460, 0.1007
Largest difference peak and hole (e Å^{-3})	+1.322 and −0.888

4. Results and discussion

1-Methyl-2-(arylazo)imidazole (aai-Me), 1-ethyl-2-(arylazo)imidazole (aai-Et) and 2-(arylazo)imidazole (aaiH) were synthesized by coupling the aryldiazonium ions with imidazole in aqueous sodium carbonate solution (pH 7) and purified by the reported method [22]. The alkylation was carried out by adding alkyl halide in dry THF solution to the corresponding 2-(arylazo) imidazole in the presence of sodium hydride [29].

The cyclopentadienyl and indenyl complexes such as [$CpRu(PPh_3)_2Cl$] (**1**) and [(indenyl)$Ru(PPh_3)_2(MeCN)]^+$ (**8**) reacted with arylazoimidazoles (RaaiR′) in the presence of ammonium salts in methanol to form the mononuclear cationic cyclo-pentadienyl and indenyl ruthenium complexes having the general formula [Cp′$Ru(PPh_3)$(RaaiR′)]$^+$ (Cp′ = cyclopentadienyl, indenyl) (Scheme 1). The cationic complexes **2**–**7** are brownish-green, while the complexes **9**–**12** are brown in color. These complexes are non-hygroscopic, air-stable, shiny crystalline solids. They are sparingly soluble in methanol and benzene; soluble in dichloromethane, chloroform,



Scheme 1.

acetone, acetonitrile, and insoluble in hexane, petroleum ether and diethyl ether.

4.1. Cyclopentadienyl-ruthenium complexes

The analytical data of these complexes are consistent with our formulations. The infrared spectra of the complexes **2**–**7** exhibit a chelated azoimine group as strong bands at 1437–1447 cm^{-1} and 1626–1633 cm^{-1} corresponding to $\nu_{(N=N)}$ and $\nu_{(C=N)}$, respectively [19,20]. In addition, the IR spectra contain a strong band at 850 cm^{-1} due to the ν_{P-F} of the PF_6 group. The proton NMR spectra of these complexes (**2**–**7**) exhibit a singlet at 4.62–4.89 ppm for the cyclopentadienyl ring protons, indicating a downfield shift from the starting complex **1**. Downfield shift in the position of the cyclopentadienyl protons might result from a change in electron density on the metal center due to chelation of the arylazo-imidazole ligand through its nitrogen atoms. The N–methyl (N–Me) protons of the complexes **3** and **6** appear as singlets at 3.74 and 3.72 ppm, respectively. The N–methylene (N–CH_2–) protons of the complexes **4** and **7** appear as triplets at 1.41 ppm (J_{H-H} = 7.32 Hz) and 1.39 ppm (J_{H-H} = 5.24 Hz), respectively. The imidazole 4H and 5H protons appear at 7.78–7.95 and 7.65–7.77 ppm, respectively. All these complexes show a multiplet in the range of 6.98–7.80 ppm due to the phenyl protons of the triphenylphosphine moiety and the aryl group of the azoimine ligands.

The ^{13}C {^1H} NMR spectrum of the complexes (**2**–**7**) contain resonances for the cyclopentadienyl ring carbons at around 81 ppm. The resonance observed at around 155 ppm may be due to the azoimine (C=N) carbon of the ligand. The spectra also show resonance in the range of 122.25–142.42 ppm for the aromatic carbons and carbons of imidazole C–H group. The ^{31}P {^1H} NMR of the complexes display a singlet at around 45 ppm due to the triphenylphosphine moiety as compared to 42 ppm observed in the neutral precursor complex [$CpRu(PPh_3)_2Cl$]. This downfield shift relative to the complex **1** indicates the cationic nature of these complexes. In all these complexes, ^{31}P nuclei exhibit a downfield shift as compared with those in the complex **1**. The ^{31}P nuclei of the counter ion PF_6^- appear as a septet around 145 (ppm) in the above complexes.

4.2. Indenyl-ruthenium complexes

The reaction of the complex **8** with ligands RaaiR′ in methanol yielded brown colored and air-stable cationic azoimine complexes of the type **9**–**12** (Scheme 1) by substitution of one of the triphenylphosphine and acetonitrile ligands. The IR spectra of these complexes show a strong band in the range of 3436 and 3426 cm^{-1} due to the $\nu_{(N-H)}$ mode for complexes **9** and **11**. In addition, the IR spectra contain strong bands at ~1440 and ~1600 cm^{-1}, corresponding to the $\nu_{(N=N)}$ and $\nu_{(C=N)}$ modes of the azoimine ligands [30], and a strong band 1082 cm^{-1} due to the $\nu_{(B-F)}$ mode of the BF_4 group.

The ^1H NMR spectra of the complexes **9**–**12** display a doublet at around 4.95 ppm and a triplet at 5.34–5.70 ppm for the cyclopentadienyl ring protons of the indenyl group. The CH group of imidazole appears as a doublet

in the range of 7.64–7.83 ppm. The NH protons of the complexes **9** and **11** exhibit a strong peak at ~8.0 ppm. All these complexes also show multiplets in the range of 6.54–7.48 ppm due to the phenyl protons of the triphenylphosphine moiety, the arene ring of the indenyl group and the aryl group of the azoimine ligands. The ^{13}C $\{^1H\}$ NMR spectrum also exhibits appropriate signals. The carbon attached to nitrogen (N1, see Chart 1) in the ligand (in the case of complexes **10** and **12**) exhibits signals around 31 and 43 ppm for the N–methyl and N–*C*H_2 groups, respectively. The methyl carbon of the N-ethyl group (N–CH_2–*C*H_3) of complex **12** exhibits a signal at 15.37 ppm. The cyclopentadienyl carbons of indenyl group appear around 62–89 ppm, while the imidazole carbons appear in the range between 133 and 156 ppm. The carbons of arene group are thus similar to those in other similar reported compounds [30]. The ^{31}P spectra of these complexes exhibit sharp resonance in the range of 50.77–51.07 ppm due to the triphenylphosphine moiety as compared to 46.5 ppm observed in the neutral complex [(η^5-C_9H_7)Ru-(PPh_3)$_2$Cl] [23b]. This downfield chemical shift indicates the cationic nature of these complexes following substitution of one chloride ion and one triphenylphosphine unit by the ligands.

4.3. Electronic spectra

The interaction of the filled dπ (t_2g) orbitals on ruthenium(II) with low lying π* orbitals on the azoimine ligands should provide a metal-to-ligand charge transfer (MLCT) transition (t_2g–π*) in the electronic spectra of these complexes [5,8,17], where the transition energy of these bands varies with the nature of the ligands acting as π-acceptors. The presence of an electron donating group (H, CH_3, and C_2H_5) in the imidazole nitrogen of the azoimine ligand should increase the energy of transition causing a red shift in the MLCT maxima [31], while an electron withdrawing group should decrease the transition energy. The electronic spectra of cyclopentadienyl-ruthenium(II) azoimine complexes (**2**–**7**) with the formulations [(η^5-C_5H_5)Ru(PPh_3)(RaaiR′)]$^+$ displayed very weak bands at 560–584 nm, a medium absorption band at ~460 nm and a very strong absorption band at ~360 nm (Fig. 1). The band at 460 nm has been assigned to a MLCT transition [t_2g {Ru(II) → π* (azoimine)}]. The λ_{max} values of this band is consistent with those of the azoimine ligand bound to the complexes of ruthenium(II) [32].

The free ligand itself shows intraligand charge-transfer transitions (n–π*, π–π*) of high intensity ($\varepsilon \sim 10^4$–10^5 $M^{-1}\,cm^{-1}$) at <400 nm. The transitions at ~380 nm and below are thus not considered further. Other two transitions at longer wavelength region (460–480 and 560–580 nm) differ in their intensities. The first transition (460–480 nm) is of moderate intensity and has been assigned to the MLCT band (dπ(Ru) → π* (azoimine)) in the complexes [17] or else from the hybrid orbitals composed of dπ(Ru) and π (Cp/indenyl) to the π* (azoimine) orbital of the ligand. The weak transition at 560–580 nm may originate from a singlet–triplet transition, particularly that allowed by the strong spin–orbit coupling in ruthenium [33], Because of better delocalization in the indenyl ring the CT bands are shifted to longer wavelength compared to cyclopentadienyl complexes.

Electronic spectra of indenyl complexes (**9**–**12**) display bands in the region 475–489, ~395 and ~350 nm. The broad medium intensity bands centering around 480 nm are assigned to MLCT bands arising from drift

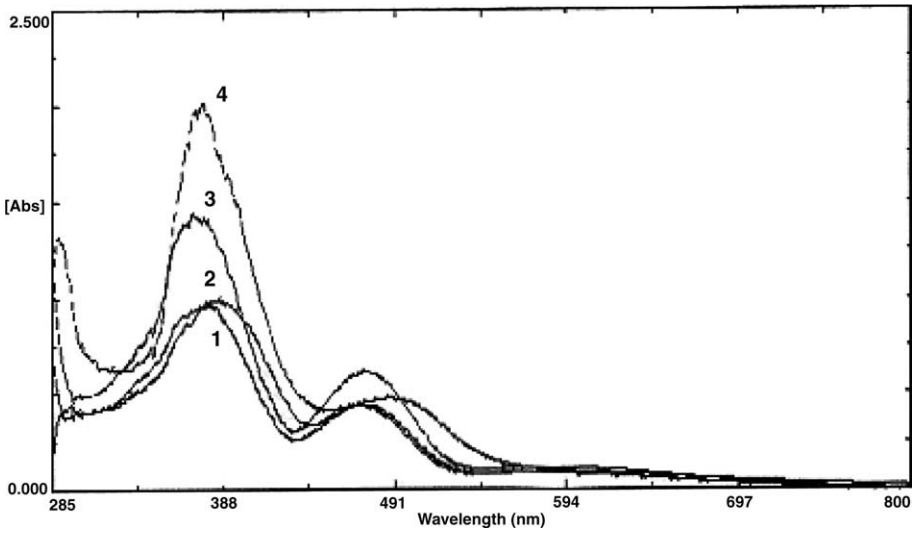


Fig. 1. Electronic spectra have taken in dichloromethane. *Key*: 1, represents complex [(η^5-C_5H_5)Ru(PPh_3)(Phai-H)]$^+$ (**3**); 2, represents complex [(η^5-C_5H_5)Ru(PPh_3)(Tai-Me)]$^+$ (**6**); 3, represents complex [(η^5-C_5H_5)Ru(PPh_3)(Phai-Et)]$^+$ (**4**) and 4, represents complex [(η^5-C_9H_7)Ru(PPh_3)(Phai-Me)]$^+$ (**10**).

of electron density from the filled Ru(II) → dπ(t_2g) orbitals to the low lying π* orbitals of the RaaiR′ ligand. The position of this band is consistent with those in other metal–azo complexes [34]. The band around 350 nm is assigned to an MLCT transition [Ru(II) → d* on the cyclopentadienyl ring].

5. Molecular structure

A summary of the single-crystal X-ray structure analysis is shown in Table 1. The ORTEP drawing of the compound **2** is shown in Fig. 2, with selected bond lengths and bond angles given in Table 2. The geometry around the ruthenium atom in the complex is octahedral, where the cyclopentadienyl ligand occupies three coordination positions.

The complex crystallizes in the triclinic space group $P\bar{1}$. The structure of the compound $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(C_6H_5\text{–}N{=}N\text{–}C_3H_3N_2)]PF_6 \cdot CHCl_3$ (**2**) consists of a ruthenium atom η^5-coordinated to a cyclopentadienyl molecule, to the two nitrogen atoms of the Phaai-H group, and to a triphenylphosphine ligand through the P atom, leading to a 'three-legged piano stool' type structure. The Phaai-H moiety acts as a chelating ligand to the ruthenium center in this complex. The two Ru–N distances 2.051(2) and 2.047(2) Å are slightly different, as found in related structures involving phosphine complexes (2.177(2) Å) [20d,21b,35]. The average Ru–C (cyclopentadienyl) distance is 2.21 Å. The Ru–P bond distance of 2.3291(7) Å is similar to those in ruthenium–phosphorus complexes reported earlier [19c,d,36]. The cyclopentadienyl ring is nearly planar and shows C–C bond distances that appear to be normal. The bond angles N(4)–Ru(1)–P(1), N(4)–Ru(1)–N(1) and N(1)–Ru(1)–P(1) are 91.16(6)°, 74.99(10)° and 94.06(7)°, respectively, indicating a piano stool type of structure around the ruthenium center. The N=N bond distance N(3)–N(4) is 1.307(3) Å, which is longer than the value for the free ligand (1.250 (1) Å) [37]. This refers to significant charge delocalization from the metal d-orbital, namely, the dπ(Ru) → π*(azo) transition in the coordinated Phaai-H.

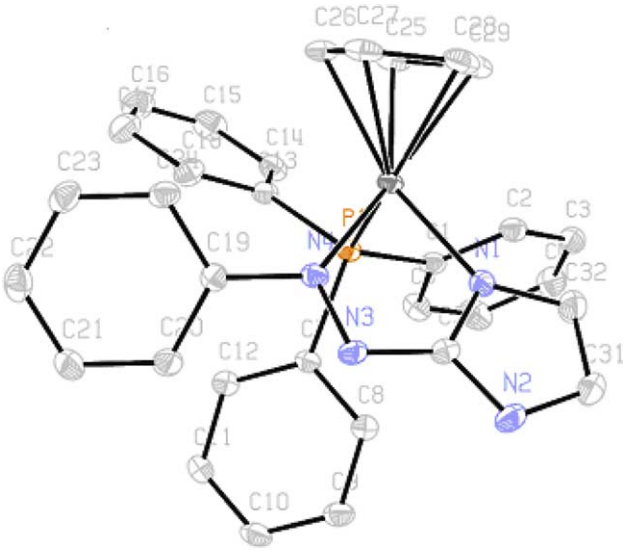


Fig. 2. ORTEP drawing of compound **2**. Hydrogen atoms, PF_6 and $CHCl_3$ omitted for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) for $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(C_6H_5\text{–}N{=}N\text{–}C_3H_3N_2)]PF_6 \cdot CHCl_3$ (**2**)

Bond lengths (Å)	
Ru(1)–C(25)	2.189(3)
Ru(1)–C(28)	2.223(3)
Ru(1)–N(4)	2.047(2)
N(1)–C(30)	1.337(3)
P(1)–C(7)	1.833(3)
Ru(1)–C[a]	2.21
Ru(1)–C(26)	2.206(3)
Ru(1)–C(29)	2.212(3)
Ru(1)–P(1)	2.3291(7)
N(1)–C(32)	1.375(3)
P(1)–C(1)	1.828(3)
Ru(1)–C(27)	2.220(3)
Ru(1)–N(1)	2.051(2)
N(4)–N(3)	1.307(3)
N(4)–C(19)	1.436(3)
P(1)–C(13)	1.834(3)
Bond angles (°)	
P(1)–Ru(1)–N(1)	94.06(7)
N(1)–Ru(1)–N(4)	74.99(10)
P(1)–Ru(1)–N(4)	91.16(6)

[a] Ruthenium to average distance of Cp.

6. Concluding remarks

We have prepared new η^5-cyclopentadienyl and η^5-indenyl ruthenium(II) complexes containing arylazoimidazole (RaaiR′) ligands. The complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ with arylazoimidazole (RaaiR′) in the presence of methanol gave complexes of the type $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(RaaiR')]^+$. The indenyl-ruthenium chloro complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ with arylazoimidazole ligands in the presence of methanol under refluxing conditions gave rise to a product without the organic fragment, while the indenyl-ruthenium acetonitrile complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(NCCH_3)]^+$ under similar conditions gave rise to complexes of the type $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(RaaiR')]^+$ due to the labile nature of the acetonitrile group.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 263827 for complex **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or on the web www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.04.042.

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