

New pentamethylcyclopentadienyl rhodium and iridium complexes containing arylazoimidazole ligands: Crystal and molecular structure of the complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\text{Me-C}_6\text{H}_4\text{-N=N-C}_3\text{H}_3\text{N}_2)]^+$

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Abstract

The dimeric $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\mu\text{-Cl})\text{Cl}]_2$ complexes ($\eta^5\text{-C}_5\text{Me}_5$ = pentamethylcyclopentadienyl; M = Rh and Ir) react 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), to afford complexes of the type $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}(\text{RaaiR}')]^+$ where M = Rh or Ir; R, R' = H (**1**, **7**), R = H, R' = CH₃ (**2**, **8**), R = H, R' = C₂H₅ (**3**, **9**), R = CH₃, R' = H (**4**, **10**), R, R' = CH₃ (**5**, **11**), R = CH₃, R' = C₂H₅ (**6**, **12**), respectively. These complexes have been characterized by FT IR, FT NMR spectroscopy as well as by analytical data. The molecular structure of the hexafluorophosphate salt of the complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\text{Me-C}_6\text{H}_4\text{-N=N-C}_3\text{H}_3\text{N}_2)]^+ 4[\text{PF}_6]^-$ has been established by single crystal X-ray diffraction study.

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1. Introduction

The dimeric chloro bridged complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\mu\text{-Cl})\text{Cl}]_2$ (M = Rh or Ir) have been the subject of investigation by many research groups as these are very useful starting materials [1]. The complexes undergo rich variety of chemistry via the intermediacy of chloro bridge cleavage reactions leading to the formation of series of interesting neutral and cationic mononuclear complexes

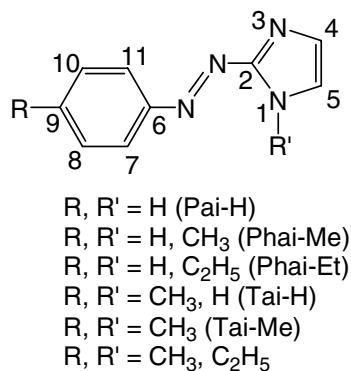
[2]. Despite extensive studies on the complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\mu\text{-Cl})\text{Cl}]_2$, its reactivity with arylazoimidazole ligands (RaaiR') are yet to be explored. Recently, the design of molecular architectures with imidazole ligands has contributed to the understanding of biomolecular interactions with metal ions in biology and provides models for the active sites of metalloproteins [3–6]. The molecule bears the azoimine (-N=N-C=N-) functional group, and is an efficient π -acid system for the stabilization of low oxidation state metal ions. The chemistry of this functional group with platinum is also known in detail [7–9]. The ligands used in the present study are shown in Scheme 1.

We had reported previously the synthesis of cyclopentadienyl and arene-ruthenium complexes containing N,N-donor arylazoimidazole ligands [10]. We also reported

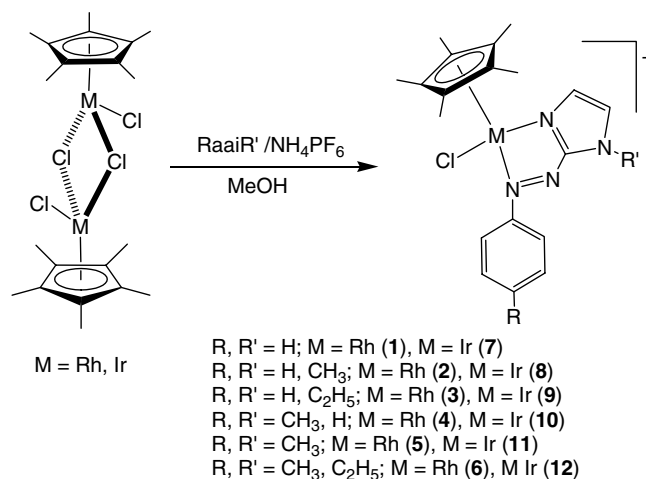
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¹ X-ray crystallography.



Scheme 1.



Scheme 2.

synthesis of cyclopentadienyl ruthenium [11], indenyl-ruthenium [12] and arene-ruthenium [13] complexes with a variety of nitrogen-based ligands. However, the analogous pentamethylcyclopentadienyl rhodium(III) and iridium(III) azo complexes have not been explored as much as the corresponding isoelectronic cyclopentadienyl and arene-ruthenium(II) complexes. As a part of our continuing study, we would like to report herein the syntheses and characterization of new cationic pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with N,N-donor arylazoimidazole ligands.

2. Results and discussion

1-Methyl-2-(arylo)imidazole (aai-Me), 1-ethyl-2-(arylo)imidazole (aai-Et) and 2-(arylo)imidazole (aai-H) were synthesized by coupling the aryldiazonium ions with imidazole in aqueous sodium carbonate solution (pH 7) and purified by the reported method [26]. The alkylation was carried out by adding alkyl halide in dry THF solution to the corresponding 2-(arylo)imidazole in the presence of sodium hydride [14].

Six arylazoimidazole (RaaiR') (see Scheme 1) ligands have been used in this work. Ligands are unsymmetrical N,N'-bidentate chelates, where N and N' abbreviated to N (imidazole) and N' (azo) donor centers, respectively. The pentamethylcyclopentadienyl rhodium and iridium dimers [$(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\mu\text{-Cl})\text{Cl}_2$] where M = Rh and Ir reacted with arylazoimidazoles (RaaiR') in the presence of ammonium salts in methanol to form mononuclear cationic complexes having the general formula $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}(\text{RaaiR}')^+]$ (C₅Me₅ = pentamethylcyclopentadienyl; M = Rh or Ir) (Scheme 2). The cationic complexes 1–6 are orange, while the complexes 7–12 are brown in colour. These complexes are non-hygroscopic, air-stable, shiny crystalline solids. They are sparingly soluble in methanol and benzene, soluble in dichloromethane, chloroform, acetone, acetonitrile, and insoluble in hexane, petroleum ether and diethyl ether.

The analytical data of these complexes are consistent with the formulations (Table 1). The formation of cationic complexes 1–6 and 7–12 are confirmed by the appearance

of the strong band at around 840 cm⁻¹ due to the $\nu_{(\text{P-F})}$ of the PF₆⁻ anion. The bands appearing at around 1600 and 1400 cm⁻¹ are assigned for $\nu_{(\text{C=N})}$ and $\nu_{(\text{N=N})}$, respectively, of the ligand [15].

The ¹H NMR spectrum of complexes shows a singlet for the pentamethylcyclopentadienyl protons in the range 1.38–1.71 ppm, indicating downfield shift from the starting dimeric complexes. A downfield shift in the position of the pentamethylcyclopentadienyl protons might result from a change in electron density on the metal center due to chelation of the arylazoimidazole ligand through its nitrogen atoms. The N–H proton of complexes 1, 4, 7 and 10 is exhibited a singlet in the range 8.2–9.2 ppm. The N-methyl protons (N-Me) of complexes 2, 5, 8 and 11 appear as a singlet at 3.82–4.19 ppm. The N-methylene proton (N-CH₂) of complexes 3, 6, 9 and 12 appears as a quartet in the range 4.14–4.55 ppm. All these complexes show doublet and multiplet in the range of 5.75–7.96 ppm due to the phenyl protons of the azoimine ligand.

The ¹³C {¹H} NMR spectrum of complexes 1–6 and 7–12 contain resonances for the pentamethylcyclopentadienyl ring carbons at around 90 ppm. The resonance observed at 155 ppm may be due to the azoimine (C=N) carbon of the ligand. The spectra also show resonances in the range of 122.1–162.2 ppm for the aromatic carbons and carbons of imidazole C–H group.

2.1. Electronic spectra

The low spin d⁶ configuration of the mononuclear complexes provides filled orbitals of proper symmetry, which can interact with low lying π^* orbitals of the arylazoimidazole ligands (RaaiR'). A band attributable to the MLCT ($t_{2g} \rightarrow \pi^*$) transition is therefore expected in the electronic spectra [16], where the transition energy of these bands varies with the nature of the ligands acting as π -acceptors. The presence of electron donating groups (H, CH₃, C₂H₅) on the imidazole nitrogen of the azoimine ligand should decrease the energy of transition, causing a red shift in

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