

Study of new mononuclear platinum group metal complexes containing η^5 and η^6 – Carbocyclic ligands and nitrogen based derivatives and formation of helices due to N–H...Cl interactions

Gajendra Gupta^a, Sairem Gloria^a, Babulal Das^b, Kollipara Mohan Rao^{a,*}

^a Department of Chemistry, North Eastern Hill University, Shillong 793 022, India

^b Department of Chemistry, Indian Institute of Technology, Guwahati, India

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ABSTRACT

A quite general approach for the preparation of η^5 - and η^6 -cyclichydrocarbon platinum group metal complexes is reported. The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ (arene = C_6H_6 , $\text{C}_{10}\text{H}_{14}$ and C_6Me_6) and η^5 -pentamethylcyclopentadienyl rhodium and iridium complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\mu\text{-Cl})\text{Cl}]_2$ (M = Rh and Ir) reacts with two equivalents of the ligands 2-chloro-3-(pyrazolyl)quinoxaline (**L**₁) and di-(2-pyridyl)amine (**L**₂) in presence of NH_4PF_6 to afford the corresponding mononuclear complexes of the type $[(\eta^6\text{-arene})\text{Ru}(\text{L}_1)\text{Cl}]\text{PF}_6$ {arene = C_6H_6 (**1**), $\text{C}_{10}\text{H}_{14}$ (**2**) and C_6Me_6 (**3**)}, $[(\eta^6\text{-arene})\text{Ru}(\text{L}_2)\text{Cl}]\text{PF}_6$ {arene = C_6H_6 (**4**), $\text{C}_{10}\text{H}_{14}$ (**5**) and C_6Me_6 (**6**)}, and $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{L}_1)\text{Cl}]\text{PF}_6$ {M = Rh (**7**), Ir (**8**)} and $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{L}_2)\text{Cl}]\text{PF}_6$ {M = Rh (**9**), Ir (**10**)}. However the mononuclear η^5 -cyclopentadienyl analogues such as $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$, $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{PPh}_3)_2\text{Br}]$, $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ and $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ complexes react in presence of one equivalent of ligands 2-chloro-3-(pyrazolyl)quinoxaline (**L**₁) and di-(2-pyridyl)amine (**L**₂) and one equivalent of NH_4PF_6 in methanol yielded mononuclear complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{L}_1)]\text{PF}_6$ (**11**), $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{PPh}_3)(\text{L}_1)]\text{PF}_6$ (**12**), $[(\eta^5\text{-C}_5\text{Me}_5)\text{-Ru}(\text{PPh}_3)(\text{L}_1)]\text{PF}_6$ (**13**) and $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)(\text{L}_1)]\text{PF}_6$ (**14**) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{L}_2)]\text{PF}_6$ (**15**), $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{PPh}_3)(\text{L}_2)]\text{PF}_6$ (**16**), $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)(\text{L}_2)]\text{PF}_6$ (**17**) and $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)(\text{L}_2)]\text{PF}_6$ (**18**) respectively. These compounds have been systematically characterized by IR, NMR and mass spectrometry. The molecular structures of **2**, **4** and **15** have been established by single crystal X-ray diffraction study and some of the representative complexes have also been studied by UV–visible spectroscopy. The crystal packing diagram of complex **4** reveals that the cation $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{L}_2)\text{Cl}]^+$ is engaged in non-covalent interaction. This compound gives rise to a 1D helical architecture along the 'a' axis via intermolecular N–H...Cl hydrogen bonds.

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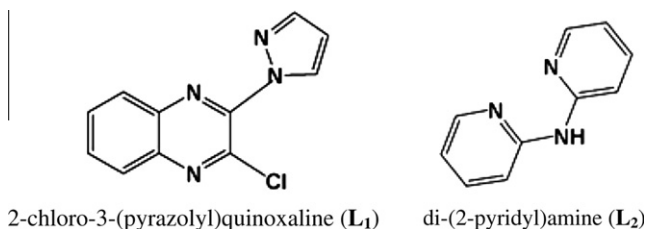
1. Introduction

Mononuclear compounds of platinum group metals containing nitrogen-based ligands have received considerable attention owing to their photochemical properties [1–5], catalytic activities [6–12], electrochemical behavior [13–16], as well as in the development of new biological active agents [17–21]. In particular, η^6 -arene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the availability of three labile coordinate sites and rigid arene ring occupying another three coordinate sites [22,23]. They have found applications in catalysis, supramolecular assemblies, molecular devices, and have shown antiviral, antibiotic, and anticancer

activities. Half-sandwich complexes have proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses and therefore attracted more attention [11,24–26]. In addition, the four-coordinated, pseudo-tetrahedral geometry makes them particularly suitable for investigation of the stereochemistry of reactions at the metal center [27]. In recent years we have been carrying out reactions of η^5 - and η^6 -cyclic Π -perimeter hydrocarbons metal complexes with a variety of nitrogen-based ligands [28–35] including various poly-pyridyl ligands. Ruthenium compounds of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to dioxygen [36,37]. Recently, we have reported a number of compounds of ruthenium containing tetra-dentate nitrogen bases as a model compounds for water oxidation studies [38–40]. However till now there is no investigations have been made on η^5 - and η^6 -ruthenium compounds containing quinoxaline and pyridine derivatives of the type shown below:

* Corresponding author.

E-mail address: mohanrao59@gmail.com (K.M. Rao).



Herein we describe the syntheses of eighteen mononuclear η^5 - and η^6 -cyclic 11-perimeter hydrocarbons platinum group metal compounds bearing quinoxaline and pyridine derivative ligands. All these compounds are completely characterized by IR, NMR and mass spectrometry. Molecular structures of the three representative compounds are also presented in this paper. Notably complex **4** considered here generate helical structures via N–H...Cl interactions.

2. Experimental

2.1. Physical measurements

Infrared spectra were recorded on a Perkin–Elmer Model 983 spectrophotometer with the sample prepared as KBr pellets. The NMR spectra were obtained using Bruker Avance II 400 spectrometer in CD₃CN, CDCl₃ and Acetone-*d*₆ respectively for complexes using TMS as an internal standard. Mass spectra were obtained from a Waters ZQ – 4000 mass spectrometer by the ESI method. All chemicals used were of reagent grade. Elemental analyses of the complexes were performed on a Perkin–Elmer 2400 CHN/S analyzer. All reactions were carried out in distilled and dried solvents. The precursor complexes [(η^6 -arene)Ru(μ -Cl)Cl]₂ (arene = C₆H₆, C₁₀H₁₄ and C₆Me₆), [(η^5 -C₅Me₅)M(μ -Cl)Cl]₂ (M = Rh and Ir) [41–45], [(η^5 -C₅H₅)Ru(PPh₃)₂Cl], [(η^5 -C₅H₅)Os(PPh₃)₂Br], [(η^5 -C₅Me₅)Ru(PPh₃)₂Cl] and [(η^5 -C₉H₇)Ru(PPh₃)₂Cl] were prepared by following the literature methods [46–50].

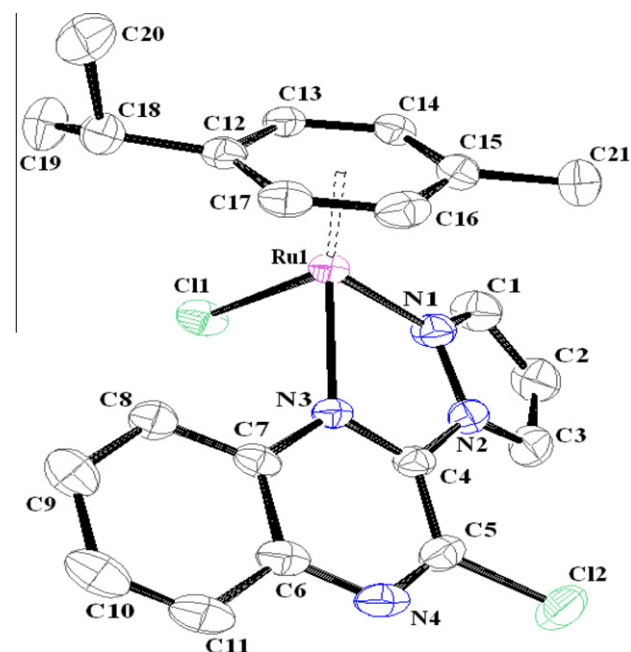


Fig. 1. Molecular structure of a complex **2** with 35% probability thermal ellipsoids. Hydrogen atoms, CH₂Cl₂ and PF₆[−] are omitted for clarity.

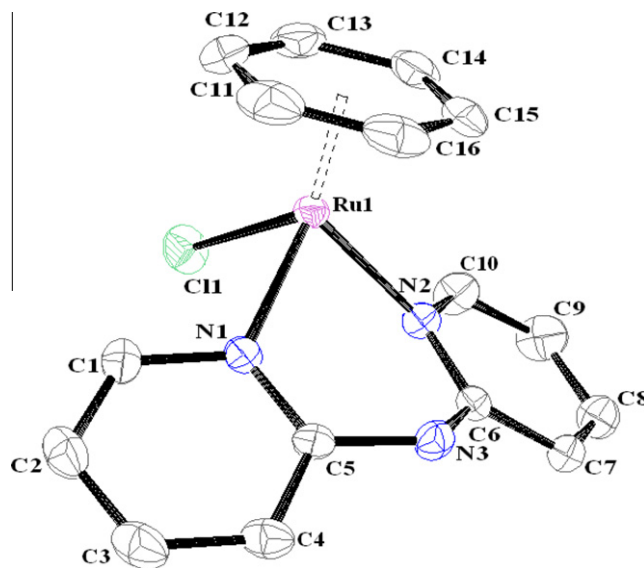


Fig. 2. Molecular structure of a complex **4** with 35% probability thermal ellipsoids. Hydrogen atoms and PF₆[−] are omitted for clarity.

2.2. Single-crystal X-ray structure analyses

Crystals of **2** and **15** were grown from dichloromethane/petroleum ether as small red plates. Crystals of **4** were grown by slow diffusion of petroleum ether into a mixture of acetonitrile and dichloromethane solution of the respective complex as deep brown blocks. The crystallizations were done at room temperature. The intensity data of **2**, **4** and **15** were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo K α radiation (α = 0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART [51] software was used for data acquisition. Data integration and reduction were undertaken with the SAINT [51] software. Structures were solved by direct methods using SHELXS-97 [52] and refined with full-matrix least squares on F₂ using SHELXL-97 [53]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 [54] for Windows. The ORTEP presentations of the representative complexes are shown in Figs. 1–3, respectively. The data collection parameters and bond lengths and angles are presented in Tables 2 and 3.

2.3. Preparation of [(η^6 -arene)M(L₁)Cl](PF₆) {M = Ru, arene = C₆H₆, [**1**](PF₆); C₁₀H₁₄, [**2**](PF₆); C₆Me₆, [**3**](PF₆), M = Rh, arene = C₅Me₅, [**7**](PF₆) and M = Ir, arene = C₅Me₅, [**8**](PF₆) and [(η^6 -arene)M(L₂)Cl](PF₆) {M = Ru, arene = C₆H₆, [**4**](PF₆); C₁₀H₁₄, [**5**](PF₆); C₆Me₆, [**6**](PF₆); M = Rh, arene = C₅Me₅, [**9**](PF₆) and M = Ir, arene = C₅Me₅, [**10**](PF₆)}

A mixture of [(η^6 -arene)Ru(μ -Cl)Cl]₂ or [(η^5 -Cp*)M(μ -Cl)Cl]₂ (M = Rh and Ir) (0.17 mmol or 0.23 mmol), 2-chloro-3-(pyrazolyl)quinoxaline (**L**₁) (40 mg, 0.17 mmol) or di-(2-pyridyl)amine (**L**₂) (40 mg, 0.23 mmol) and two equivalents of NH₄PF₆ was stirred in dry methanol (30 ml) for 4 h at room temperature. The yellow compound which formed was filtered, washed with ethanol, diethyl ether and dried under vacuum.

Compound 1(PF₆): Yield: 75 mg, 63.3%. Elemental Anal. (%) Calc. for C₁₇H₁₃Cl₂F₆N₄PRu: C 34.61; H 2.23; N 9.48; found: C 34.79; H 2.41; N 9.17; IR (KBr pellets, cm^{−1}): 1616 (m), 1445 (s), 844 (s), 773 (s), 558 (s); ¹H NMR (400 MHz, CD₃CN): δ = 9.43 (d, *J* = 2.8 Hz, 1H), 8.76 (d, *J* = 7.6 Hz, 1H), 8.22–8.09 (m, 2H), 7.50

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