



Study of complexes of platinum group metals containing nitrogen bases derived from pyridine aldehydes: Interesting molecular structures with unpredicted bonding modes of the ligands

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ABSTRACT

A series of mono-cationic dinuclear half sandwich ruthenium, rhodium and iridium metal complexes have been synthesized using ((pyridin-2-yl)methylimino)nicotinamide (**L1**) and ((picolinamido)phenyl)picolinamide (**L2**) ligands: $[(\eta^6\text{-arene})_2\text{Ru}_2(\mu\text{-L1})\text{Cl}_3]^+$ (arene = C₆H₆, **1**; *p*-PrC₆H₄Me, **2**; C₆Me₆, **3**), $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{M}_2(\mu\text{-L1})\text{Cl}_3]^+$ (M = Rh, **4**; Ir, **5**), and $[(\eta^6\text{-arene})_2\text{Ru}_2(\mu\text{-L2})(\mu\text{-Cl})]^+$ (arene = C₆H₆, **6**; *p*-PrC₆H₄Me, **7**; C₆Me₆, **8**), $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{M}_2(\mu\text{-L2})\text{Cl}_2]^+$ (M = Rh, **9**; Ir, **10**). All the complexes have been isolated as their hexafluorophosphate salts and fully characterized by use of a combination of NMR and IR spectroscopy. The solid state structure of three representatives **4**, **6** and **9** has been determined by X-ray crystallographic studies. Interestingly, in the molecular structure of **4**, the first metal is bonded to two nitrogen atoms whereas the second metal center is coordinated to only one nitrogen atom with two terminal chloride ligands. Fascinatingly in the case of the complexes with the symmetrical ligand **L2**, both ruthenium centers having $\eta^6\text{-arene}$ groups are bonded to nitrogen atoms with a bridging chloride atom between the two metal centers, whereas the metals with $\eta^5\text{-Cp}^*$ groups are bonded to the ligand *N,O* and *N,N* fashion.

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1. Introduction

The synthesis of metal complexes with multiple coordination domains is an area of significant current interest in organometallic chemistry. Such complexes have been prepared as part of studies in diverse areas such as inter-metallic communication [1], bioinorganic enzyme active site modeling [2], supramolecular approaches to chiral materials [3] and functional devices [4]. The organometallic chemistry of half sandwich complexes have been broadly developed in the past few decades, due to their wide range of potential applications as catalyst precursors for hydrogen transfer [5,6], ring opening metathesis polymerization [7,8] and olefin oxidation [9]. Arene ruthenium compounds have also been extensively investigated for their persuasive antibacterial and anticancer activity [10,11]. The arene confers great stability to ruthenium in the +2 oxidation state and the characteristic “piano-stool” structure offers the possibility to vary the additional donors *via* substitution of halide(s) with a variety of

σ -donors ranging from tertiary phosphines [12] to β -diketones [13] to aliphatic as well as aromatic amines [14–16]. In recent years, we have been carrying out reactions of arene ruthenium, rhodium and iridium dimers with a variety of nitrogen-based ligands [17–25] including pyridyl-pyridazine and pyrazolyl-pyridazine ligands. Arene metal complexes of these types of nitrogen-based ligands have the capacity to function as catalysts for the oxidation of water to dioxygen [26,27].

Herein, we describe the syntheses of interesting mono-cationic dinuclear complexes of arene metals having *N,O* and *N,N* type donor ligands. Although extensive studies have been carried out in the preparation of ruthenium, silver, nickel and copper metal complexes [28–30], mono-cationic dinuclear complexes of arene ruthenium, rhodium and iridium complexes with this type of bases have not been investigated. The mode of binding of these ligands especially **L2** with these dimers (arene ruthenium and Cp* rhodium and iridium) is found to be very interesting. The dinuclear ruthenium complexes are found to be *N,N* coordinated with a terminal chloride bridged between both the metal centers whereas for rhodium and iridium, the first metal is coordinated through *N,O* while the second metal is *N,N* coordinated. The two ligands used in this study are shown below (Chart 1):

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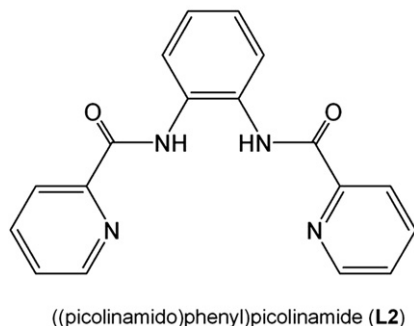
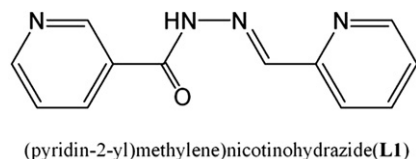


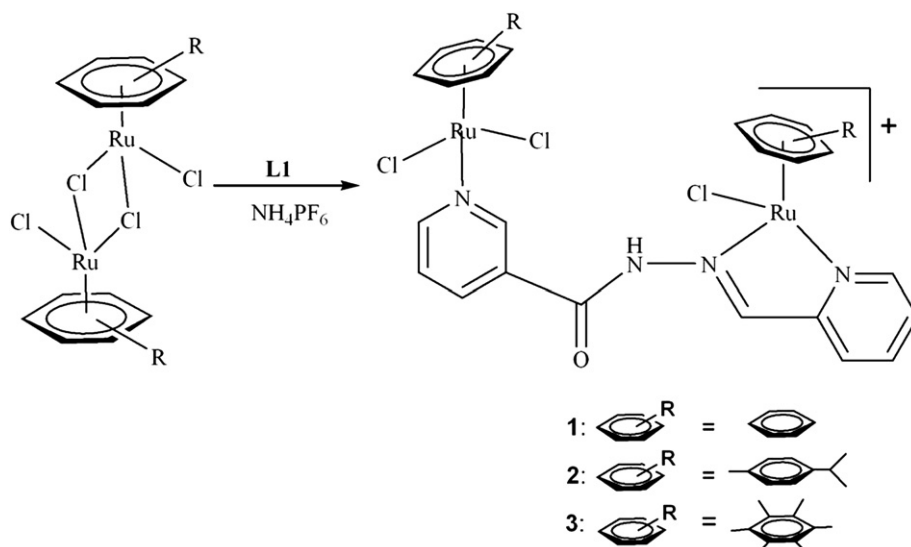
Chart 1. Ligands used in this study.

2. Results and discussion

The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ react with the multidentate $\text{N}\cap\text{O}$ and $\text{N}\cap\text{N}$ type nitrogen bases **L1** and **L2** in methanol to afford the mono-cationic dinuclear complexes $[(\eta^6\text{-arene})_2\text{Ru}_2(\mu\text{-L1})\text{Cl}_3]^+$ (arene = C_6H_6 , **1**; $p\text{-}^i\text{PrC}_6\text{H}_4\text{Me}$, **2**; C_6Me_6 , **3**), and $[(\eta^6\text{-arene})_2\text{Ru}_2(\mu\text{-L2})(\mu\text{-Cl})]^+$ (arene = C_6H_6 , **6**; $p\text{-}^i\text{PrC}_6\text{H}_4\text{Me}$, **7**; C_6Me_6 , **8**), isolated as their hexafluorophosphate salts (Scheme 1 and 2). Cations **2**, **3**, **7** and **8** are yellow in color, while **1** and **6** are brown. These salts are non-hygroscopic and stable in air as well as in solution. They are sparingly soluble in polar solvents like dichloromethane, chloroform, acetone and acetonitrile but are insoluble in non-polar solvents like hexane, diethyl ether and petroleum ether. The analytical data of these compounds are consistent with the formulations. All compounds are characterized by ^1H NMR and IR spectroscopy. The IR spectra of these complexes exhibit sharp bands due to chelated multidentate ligands between 1637 and 1437 cm^{-1} corresponding to the different stretching frequencies of $\text{C}=\text{O}$, $\text{C}=\text{C}$ and $\text{C}=\text{N}$ bond

after coordination to the metal centers (see experimental section). In addition, the infrared spectra contain a strong band between 843 and 849 cm^{-1} due to the stretching frequency of the $\text{P}-\text{F}$ bonds of PF_6^- counter ions for these complexes. Comparing the IR spectra of the free ligands to that of the metal complexes, we find that the IR spectra of the free ligands show a sharp band at around 1672 cm^{-1} assigned to the stretching frequencies of $\text{C}=\text{O}$ group of the ligands, but in the case of the metal complexes the stretching frequencies of $\text{C}=\text{O}$ group appears in the lower frequency around 1637 and 1615 cm^{-1} . The decrease in the stretching frequencies and the presence of only one band shows that the metal has coordinated in only one fashion *i.e.*, either $\text{N}\cap\text{N}$ coordination or $\text{N}\cap\text{O}$ coordination which has been finally confirmed by the single crystal X-ray structure analysis of **6** and found that the mode of coordination is through $\text{N}\cap\text{N}$ and not $\text{N}\cap\text{O}$ coordination.

The proton NMR spectra of all these complexes show the ligand resonances downfield shifted as compared to that of the free ligands. For the complexes with ligand **L1**, only eight signals are apparently observed due to overlapping on two occasions, whereas with that of ligand **L2** it shows set of six signals, corresponding to the different protons of these ligands as mentioned in the experimental section. Beside these signals, complexes **1** and **6** shows two singlets each between 5.72 and 5.33 ppm respectively which arises due to the six protons of the benzene rings, complex **2** and **7** shows four doublets at *ca.* $5.73\text{--}5.49\text{ ppm}$ corresponding to the aromatic protons of the *p*-cymene ligand, two septets at around 2.67 and 2.59 ppm which is assigned to the isopropyl protons, two singlets between 2.38 and 2.15 ppm for the methyl protons and another two doublets at *ca.* $1.13\text{--}0.87\text{ ppm}$ due to the methyl protons of the isopropyl groups of this complex. In addition to the ligand peaks, complexes **3** and **8** show a pair of singlets each between 2.18 and 2.02 ppm respectively corresponding to the eighteen protons of the hexamethylbenzene group of these complexes. It is difficult to assign the exact structure of these complexes on the basis of spectral data, so we have carried out single crystal X-ray study of few representative compounds. We are unable to isolate single crystals of complexes **1** to **3**, so we extended the proposed structure on the basis of complex **4**. In the case of complexes **6**, **7** and **8**, the molecular structure of complex **6** was solved and presented in Fig. 1. The molecular structure of complex **6** uncovered the two metal centers are bonded by a bridging chloride. In the case of complexes



Scheme 1. Preparation of complexes $1(\text{PF}_6)\text{-}3(\text{PF}_6)$.

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