Study of novel $\eta^5$-cyclopentadienyl and $\eta^6$-arene platinum group metal complexes containing a $\eta_4$-type ligand and their structural characterization

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Abstract

The mononuclear $\eta^5$-cyclopentadienyl complexes [($\eta^5$-C$_5$H$_5$)Ru(PPh$_3$)$_2$Cl]$_2$ and [($\eta^5$-C$_5$H$_5$)Os(PPh$_3$)$_2$Br]$_2$ and pentamethylcyclopentadienyl complex [($\eta^5$-C$_5$Me$_5$)Ru(PPh$_3$)$_2$Cl] react in the presence of 1 eq. of the tetradeutate N,N'-chelating ligand 3,5-bis(2-pyridyl)pyrazole (bpp-H) and 1 eq. of NH$_4$PF$_6$ in methanol to afford the mononuclear complexes [($\eta^5$-C$_5$H$_5$)Ru(PPh$_3$)$_2$(bpp-H)]PF$_6$ ([8]PF$_6$) and [($\eta^5$-C$_5$Me$_5$)Ru(PPh$_3$)$_2$(bpp-H)]PF$_6$ ([3]PF$_6$), respectively. The dinuclear $\eta^6$-pentamethylcyclopentadienyl complexes [($\eta^6$-C$_5$Me$_5$)Rh(bpp-H)]PF$_6$ and [($\eta^6$-C$_5$Me$_5$)Ir(bpp-H)]PF$_6$ as well as the dinuclear $\eta^6$-arene ruthenium complexes [($\eta^6$-C$_5$H$_5$)Ru(\mu-Cl)]PF$_6$ and [($\eta^6$-C$_5$H$_5$)Ir(\mu-Cl)]PF$_6$ react with 2 eq. of bpp-H in the presence of NH$_4$PF$_6$ or NH$_4$BF$_4$ to afford the corresponding mononuclear complexes [($\eta^6$-C$_5$H$_5$)Rh(bpp-H)]PF$_6$ ([4]PF$_6$) and [($\eta^6$-C$_5$Me$_5$)Ir(bpp-H)]PF$_6$ ([5]PF$_6$) and [($\eta^6$-C$_5$H$_5$)Ir(bpp-H)]PF$_6$ ([3]PF$_6$). However, in the presence of 1 eq. of bpp-H and NH$_4$BF$_4$ the reaction with the same $\eta^6$-arene ruthenium complexes affords the dinuclear salts [($\eta^6$-C$_5$H$_5$)Ru$_2$(\mu-Cl)]PF$_6$ ([6]PF$_6$) and [($\eta^6$-C$_5$Me$_5$)Ir$_2$(\mu-Cl)]PF$_6$ ([7]PF$_6$), respectively. These compounds have been characterized by IR, NMR and mass spectrometry, as well as by elemental analysis. The molecular structures of [1]PF$_6$, [5]PF$_6$ and [8]PF$_6$ have been established by single crystal X-ray diffraction studies and some representative complexes have been studied by UV-vis spectroscopy.

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1. Introduction

Within the large family of $\eta^5$- and $\eta^6$-cycloalkadienyl metal complexes, piano-stool complexes of ruthenium are undeniably the most studied class of complexes. They have found applications in catalysis, supramolecular assemblies and molecular devices, and have shown antiviral, antibiotic and anticancer activities. These three-legged piano-stool complexes possess a pseudo-octahedral geometry at the metal center, the arene ligand occupying three coordinating sites (the seat) with three other ligands (the legs). Therefore, the octahedral geometry can be viewed as pseudo-tetrahedral, thus limiting the number of possible isomers.

Transition metal complexes containing polypyridyl ligands are associated with interesting photochemical and electrochemical properties [1-8], and they are used as catalysts [9,10], multi-electron storage systems [11-13], in the design of new materials [14-17] and as molecular devices [18-22]. Complexes with these ligands are also potential DNA intercalators with an ability to inhibit nucleic acid synthesis [23]. Recently, metal polypyridyl complexes have been widely used as building blocks [24-27]. The occurrence of isomers by the synthetic assembly of mononuclear building blocks is a major problem in the design of supramolecular systems.

Half-sandwich complexes have proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses, and therefore, have attracted lot of attention [28-31]. In addition, the four coordinated, pseudo-tetrahedral geometry makes them particularly suitable for investigation of the stereochemistry of reactions at the metal center [32]. Many studies of pentamethylcyclopentadienyl and arene ruthenium(II) complexes with bidentate ligands have shown that substitution reactions occur predominantly with retention of the configuration at the metal center [33]. A few studies have been carried out on pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with poly(pyridyl) ligands [34]. The reactivity of ruthenium(II), osmium(II), rhodium(III) and iridium(III) with various poly(pyridyl) ligands has been reported [35-37].

In this paper, we report a series of $\eta^5$-cyclopentadienyl ruthenium, osmium, $\eta^6$-pentamethylcyclopentadienyl ruthenium, rhodium and iridium and $\eta^6$-arene ruthenium complexes with a tetradeutate N,N'-donor ligand, viz. 3,5-bis(2-pyridyl)pyrazole (bpp-H) (see below). The 3,5-bis(2-pyridyl)pyrazole (bpp-H) ruthenium metal complexes are associated with being an extremely interesting water oxidation catalyst [38,39]. This ligand can act as...
Mononuclear Complexes of Platinum Group Metals Containing $\eta^6$ and $\eta^5$-Cyclic $\Pi$-Perimeter Hydrocarbon and Pyridylpyrazolyl Derivatives: Syntheses and Structural Studies


Keywords: Phenylpyrazolylpyridines; Ruthenium; Rhodium; Iridium; Osmium; versatile intermediates in organic synthesis; they contain three nitrogen-based ligands received considerable attention in the recent years. In particular, $\eta^6$-arene metal complexes emerged as versatile intermediates in organic synthesis; they contain three labile coordination sites, whereas another three coordination sites are occupied by a rigid arene ring [34, 35]. They haveorage application in catalysis, supramolecular assemblies, and in molecular devices. Additionally, $\eta^6$-arene metal complexes showed antiviral, antibiotic, and anticancer activities. Half-sandwich complexes attracted attention because they proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses [36-39]. The tetracoordinate, pseudo-tetrahedral arrangement makes them particularly suitable for investigation of the stereochemistry of reactions at the metal atom [40]. In recent years, we carried out reactions of $\eta^5$- and $\eta^6$-cyclic $\Pi$-perimeter hydrocarbon metal complexes with a variety of nitrogen-based ligands [41-48] including various polypyridyl ligands. Ruthenium compounds with these types of ligands have the capacity to function as catalysts for the oxidation of water to dioxygen [49, 50]. Although extensive studies were carried out on $\eta^2$- and $\eta^6$-transition metal complexes; compounds containing phenylpyrazolylpyridine ligands of the type shown below have not been investigated yet.

Herein we describe the syntheses of nine mononuclear $\eta^5$- and $\eta^6$-cyclic $\Pi$-perimeter hydrocarbon platinum group metal compounds bearing the ligand phenylpyrazolylpyridine. Our main goal in choosing this phenyl-substituted ligand was to synthesize a series of mononuclear and dinuclear compounds by activating the carbon atom of the phenyl ring. But attempts to prepare a dimetallic derivative through the addition of a second organometallic anion by activation of the carbon atom were unsuccessful and we ended up with a series of mononuclear compounds only with metal bound to two nitrogen atoms (N1 and N11) of the ligand. All these compounds were fully characterized by IR and NMR spectroscopy, and mass spectrometry. Molecular structures of the two representative compounds are also presented in this paper.

2. Experimental Section

All solvents were dried and distilled prior to use. The ligand L was synthesized by following a literature method [51]. The precursor complexes $[(\eta^6$-arene)Ru(µ-C5)]PF6 (arene = C5H4, C4H10, and C6Me6), $[(\eta^6$-C5Me5)M(µ-Cl)]PF6 (M = Rh, Ir) [52-55], $[(\eta^4$-C6H6)Ru(PPh3)L]PF6, $[(\eta^4$-C6H6)Os(PPh3)L]PF6, and $[(\eta^4$-C6H6)Ru(PPh3)L]PF6 were prepared by following the literature methods [56-61].

NMR spectra were recorded with a Bruker AMX 400 MHz spectrometer.
Ruthenium half-sandwich complexes with tautomerized pyrazolyl-pyridazine ligands: Synthesis, spectroscopic and molecular structural studies

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Condensation of 1,4-dichloropyridazine with pyrazole, 3,5-dimethylpyrazole and 3-methylpyrazole yielded two types of pyrazolyl-pyridazine ligands, viz., (i) products of substitution on one side of the pyridazine as 3-chloro-6-(pyrazolyl)pyridazine (CI-L1), 3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine (CI-L2) and 3-chloro-6-(3-methylpyrazolyl)pyridazine (CI-L3), and (ii) products of substitution on both sides such as 3,6-bis(pyrazolyl)pyridazine (L1), 3,6-bis(3,5-dimethylpyrazolyl)pyridazine (L2) and tautomers of 3,6-bis(3-methylpyrazolyl)pyridazine (L3). The reactions of narene-ruthenium complexes in methanol with the above mentioned pyrazolyl-pyridazine ligands form mononuclear complexes of the type [nareneRuCl-L3]+ and [nareneRuCl-Cl]+; (arene = benzene and p-cymene; Cl-L = CI-L1, CI-L2, CI-L3; L = L1, L2, L3). All these complexes are characterized by IR, NMR, mass spectrometry and UV-vis spectroscopy. The structures of some representative complexes are established by single crystal X-ray diffraction studies.

1. Introduction

Arene metal complexes have been extensively investigated by organometallic and organic chemists for over 40 years. In particular, narene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized [1,2]. Coordination of a metal fragment to an arene ring dramatically facilitates electrophilic aromatic addition and substitution, arene deprotonation, and benzylic deprotonation. Arene metal complexes have been utilized as homogeneous catalysts or catalyst precursors in numerous transformations such as hydrogenation, esterification, olefin metathesis and Diels–Alder cycloaddition [3–6]. In recent years, we have been carrying out reactions of arene ruthenium dimers with a variety of nitrogen-based ligands [7–12] including pyridyl-pyridazine and pyrazolyl-pyridazine ligands. Ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to oxygen [13,14]. Although extensive studies have been made on ruthenium complexes containing poly-pyridyl ligands, complexes containing annular tautomerized pyrazolyl-pyridazine ligands have not yet been investigated.

Herein, we describe the synthesis of pyrazole-based ligands in which the starting 3-methylpyrazole moiety tautomerizes to 5-methylpyrazole moiety [15]; the existence of both tautomers in a single compound is reported here. The synthesis of 12 mononuclear arene ruthenium complexes incorporating these as well as some other pyrazolyl-pyridazine ligands are also reported. Given below are the structures of the ligands used in this study. All these complexes are characterized by IR, NMR, mass spectrometry and UV-vis spectroscopy. The molecular structures of the ligand (L3) and four representative complexes are also presented in this paper.

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**Half sandwich platinum group metal complexes containing tetradentate N-donor ligand bearing two pyrazolyl-pyridine units linked by an aromatic spacer**

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**ABSTRACT**

Reaction of the bis-bidentate ligand, 1,3-bis(3-(pyridin-2-yl)-1H-pyrazol-1-yl)methyl)benzene (NNnNN), containing two chelating pyrazolyl-pyridine units connected by an aromatic spacer with platinum group metal complexes results in a series of cationic binuclear complexes, [(η^6-arene)Ru(μ-Cl)Cl]_2(NNnNN)Cl_2 (arene = C6H6; 1; η^6-PCy3C6H2Me; 2; C6Me6; 3; [(η^5-PCy3C6H2)2M2(NNnNN)Cl]_2 (M = Rh; 4; Ir. 5). [(η^5-C5H5)Ru(μ-NNnNN)Ph3]_2^2+ (M = Ru; 6; Os; 7). [(η^5-C5H5)Ir(μ-NNnNN)Ph3]_2^2+ (8) and [(η^5-C5H5)Ir(μ-NNnNN)Ph2Cl]_2^2+ (9). These complexes have been isolated as their hexafluorophosphate salts and fully characterized by use of a combination of NMR spectroscopy, IR spectroscopy and mass spectrometry. The solid state structures of three complexes, [(η^5-PCy3C6H2)2Rh2(μ-NNnNN)Cl]_2 (2), [(η^5-PCy3C6H2)2Ir2(μ-NNnNN)Cl]_2 (4) and [(η^5-C5H5)Ir2(μ-NNnNN)2(μ-Cl)]_2 (6), have been determined by X-ray crystallographic studies.

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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 N-donors ranging from tertiary phosphines [12] to β-diketones [13] to aliphatic as well as aromatic amines [14-16].

We describe in this paper the coordination chemistry of the tetradentate nitrogen donor ligand, 1,3-bis(3-(pyridin-2-yl)-1H-pyrazol-1-yl)methyl)benzene (NNnNN), in which the two pyrazolyl-pyridine units are connected by an aromatic spacer. Although extensive studies have been carried out in the preparation of polyhedral cages of Cu, Ag, Ni and other metal complexes of pyrazolyl-pyridine ligands by varying the spacer units, dinuclear complexes of platinum group metals with NNnNN have not yet been investigated. This ligand has the ability to form both mono and dinuclear complexes with metals like Cu [17,18] and Ag [18], but surprisingly in the case of arene ruthenium and Cp*rhodium and Cp*iridium systems, it only forms dinuclear complexes. Herein, we describe the syntheses of nine dinuclear η^5 and η^6-cyclic π-perimeter hydrocarbon platinum group metal complexes bearing the ligand NNnNN. The complexes are characterized by a combination of NMR spectroscopy, IR spectroscopy, mass spectrometry and UV–Vis spectroscopy. The solid state structures of three complexes are determined by single crystal X-ray crystallographic studies. The ligand used in this study is in Scheme 1.

2. Results and discussion

2.1. Dinuclear arene ruthenium, rhodium and iridium complexes 1-5

The dinuclear arene ruthenium complexes [(η^5-arene)Ru(μ-Cl)]_2 react with the NNnNN tetradentate pyrazolyl-pyridine ligand in
Study of half-sandwich platinum group metal complexes bearing dpt-NH$_2$ ligand

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**ABSTRACT**

A quite general approach for the preparation of $\eta^5$-and $\eta^6$-cyclichydrocarbon platinum group metal complexes is reported. The dinuclear arene ruthenium complexes $[\eta^6$-arene]Ru(µ-Cl)Cl$_2$ (arene $=$ C$_6$H$_6$, C$_{10}$H$_{14}$ and C$_6$Me$_6$) and $\eta^5$-pentamethylcyclopentadienyl rhodium and iridium complexes $[\eta^6$-C$_5$Me$_5$]M(µ-Cl)Cl$_2$ (M $=$ Rh, Ir) react with 2 equiv. of 4-amino-3,5-di-pyridyltriazole (dpt-NH$_2$) in presence of NH$_4$PF$_6$ to afford the corresponding mononuclear complexes of the type $[\eta^6$-arene]Ru(dpt-NH$_2$)Cl]PF$_5$ (arene $=$ C$_{10}$H$_{14}$ (1), C$_6$H$_6$ (2) and C$_6$Me$_6$ (3)) and $[\eta^6$-C$_5$Me$_5$]M(dpt-NH$_2$)Cl]PF$_5$ (M $=$ Rh (4), Ir (5)). However, the mononuclear $\eta^5$-cyclopentadienyl analogues such as $[\eta^5$-C$_5$H$_5$]Os(PPh$_3$)$_2$Br]$_2$ and $[\eta^5$-C$_5$Me$_5$]Ru(PPh$_3$)$_2$Cl] and $[\eta^5$-C$_5$H$_5$]Ru(PPh$_3$)$_2$Cl] complexes react in presence of 1 equiv. of dpt-NH$_2$ and 1 equiv. of NH$_4$PF$_6$ in methanol yielded mononuclear complexes $[\eta^5$-C$_5$H$_5$]Ru(PPh$_3$)(dpt-NH$_2$)]PF$_6$ (6), $[\eta^5$-C$_5$H$_5$]Os(PPh$_3$)(dpt-NH$_2$)]PF$_6$ (7), $[\eta^5$-C$_5$Me$_5$]Ru(PPh$_3$)(dpt-NH$_2$)]PF$_6$ (8) and $[\eta^5$-C$_5$H$_5$]Ru(PPh$_3$)(dpt-NH$_2$)]PF$_6$ (9), respectively. These compounds have been totally characterized by IR, NMR and mass spectrometry. The molecular structures of 4 and 6 have been established by single crystal X-ray diffraction and some of the representative complexes have also been studied by UV-Vis spectroscopy.

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1. Introduction

Within the large family of $\eta^5$- and $\eta^6$-cyclichydrocarbon metal complexes, piano-stool complexes of ruthenium are undeniably the most studied class of complexes. Arene metal complexes have been extensively investigated by organometallic and organic chemists for over 50 years. In particular, $\eta^6$-arene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized [1,2]. 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 [3-6]. In addition, the four coordinated, pseudo-tetrahedral geometry makes them particularly suitable for investigation of the stereochemistry of reactions at the metal center [7]. In recent years we have been carrying out reactions of $\eta^5$- and $\eta^6$-cyclichydrocarbon metal complexes with a variety of nitrogen-based ligands [8-15] including various poly-pyridyl ligands. Ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to dioxygen [16,17]. Although comprehensive studies have been made on $\eta^5$- and $\eta^6$-transition metal complexes, complexes containing NH$_2$ substituted poly-pyridyl ligand of this type shown below have not yet been reported.

Herein we describe the syntheses of nine mononuclear $\eta^5$- and $\eta^6$-cyclichydrocarbon platinum group metal complexes bearing dpt-NH$_2$ ligand. Attempts to prepare dimetallic derivatives by addition of a second organometallic anion were unsuccessful. All these complexes have been fully characterized by IR, NMR, mass spectrometry and UV-Vis spectroscopy. Molecular structures of the two representative complexes are also presented in this paper.
Spectral, structural and DFT studies of platinum group metal 3,6-bis(2-pyridyl)-4-phenylpyridazine complexes and their ligand bonding modes

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ABSTRACT

Reactions of 3,6-bis(2-pyridyl)-4-phenylpyridazine (LPh) with [(η5-arene)Ru(µ-Cl)Cl]2 (arene = C6H6, p-PC6H4Me and C6Me6), [(η5-C6Me6)M(µ-Cl)Cl]2, (M = Rh and Ir) and [(η5-Cp)Ru(PPh3)L] (Cp = C5H5, C6Me6, and C6H5) afford mononuclear complexes of the type [(η5-C6H6)LPh]PF6, [(η5-C6Me6)LPh]PF6 and [(η5-C6Me6)µ-Cl]PF6 with different structural motifs depending on the π-acidity of the ligand, electronic properties of the central metal atom and nature of the co-ligands. Complexes [(η5-C6H6)LPh]PF6 1, [(η5-p-PC6H4Me)Ru(µ-Cl)Cl]PF6 2, [(η5-C6Me6)LPh]PF6 3 and [(η5-C6Me6)µ-Cl]PF6 4 show the type-A binding mode (see text), while complexes [(η5-C6Me6)LPh]PF6 5 and [(η5-C6Me6)µ-Cl]PF6 6 show the type-8 binding mode (see text). These differences reflect the more electron-rich character of the [(η5-C6H6)LPh]PF6 and [(η5-C6Me6)LPh]PF6 complexes compared to the other starting precursor complexes. Binding modes of the ligand LPh are determined by 1H NMR spectroscopy, single-crystal X-ray analysis as well as evidence obtained from the solid-state structures and corroborated by density functional theory calculations. From the systems studied here, it is concluded that the electron density on the central metal atom of these complexes plays an important role in deciding the ligand binding sites.

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1. Introduction

Polypyridyl complexes of platinum group metals are being continuously investigated because of their multiple applications in fields of science including photophysics and photochemistry [1-6], supramolecular chemistry [7], catalysis [8-13] and bioinorganic chemistry [14-19]. The organometallic complexes of η6-arene ruthenium [20,21] and η5-half-sandwich complexes of rhodium and iridium have attracted considerable current interest as potential anticancer agents (Dyson et al.) [14-19,22,23]. Another important aspect, especially from the catalytic prospective, is the design of Ru=O functional groups and analogues capable of reversibly accepting multiple electrons and protons within a relatively small potential range [24-26]. This capacity to modify the environment in order to induce electronic as well as steric effects gives scope for the design and fabrication of tailored catalysts for specific reactions.

The properties of metal complexes largely depend on how the nature of the bridging ligand mediates metal-metal interactions. This role of bridging ligands is strongly influenced by factors such as the acceptor and donor properties of coordination sites, the length and rigidity of the spacers, the presence or absence of conjugated bonds, the orientation of substituents and the scope for manipulating ligand charge. In this regard, bridging poly(pyridyl) ligands (viz., 2,2'-bipyrimidine (bpybi), 2,3-bis(2-pyridyl)pyrazine (bptz), 3,5-bis(2-pyridyl)-1,2,4,5-tetrazine (bppz), 3,6-bis(2-pyridyl)pyridazine (bppn), and 2,4,6-tris(2-pyridyl)-1,3,5-triazine ligands) have received much attention [27-33]. The wider family of such ligands with 4- or 4,5-substituted pyridazine moieties (viz., 3,6-bis(2-pyridyl)-4-phenylpyridazine (LPh) (Fig. 1) has been relatively less studied. More recently, Constable and co-workers published a few reports on silver(I) complexes [34-37] incorporating such ligands.

Symmetrical 3,5-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) and to a lesser extent 3,6-bis(2-pyridyl)pyridazine (bppn) frequently bind via any of the four nitrogen atoms present (N1 and N2 or N3 and N4) on the pyridine and tetrazine/pyridazine moieties, employing a bidentate k2 bonding mode to coordinate with d6 metal centers [38,39]. A phenyl substituent introduces a element of asymmetry in the 3,6-bis (2-pyridyl)pyridazine (LPh) ligand. This can bind to a metal via atoms N1 and N2 (type-A) or atoms N3 and N4 (type-B) (see Fig. 2) in a bidentate k2 bonding mode. The ligand is a four electron donor since the phenyl substituent creates differences in the electronic environment on the two available binding sites. Apart from the above two possibilities (type-A or type-B) (Fig. 2), a combination of the two types...
New series of platinum group metal complexes bearing \( \eta^5 \)- and \( \eta^6 \)-cyclichydrocarbons and Schiff base derived from 2-acetylthiazole: Syntheses and structural studies

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1. Introduction

Recent interest in half-sandwich platinum group metal complexes with symmetrical Schiff bases come from the fact they can serve as synthetic models related to biological systems [1-7], as homogeneous catalysts in systems like [8-17], and supported chemical processes [18,19], and very recently as non-linear optical (NLO) materials [20,21]. Their attractiveness also does come from their preparative accessibility, their structural variability in addition to many of these novel ruthenium complexes combine an appropriate balance between the electronic and steric environment around the metal core.

Moreover, some of the nitrogen-donor ligands impart to the catalyst for good tolerance towards various organic functionalities, air, and moisture, thus widening the scope and limit’s of their application. Of the above mentioned ligands, Schiff bases are of a great interest for creating new active and selective ruthenium catalytic systems [22,23]. There are few reports of half-sandwich Ru(II), Ru(III) and Ir (III) complexes with N,N-donor polypyridyl azine Schiff base ligands [24,25], but there are no reports with thiazole azine ligand in the literature. Complexes imparting other than pyridyl azine ligands are yet to be explored, in view of the fact that ring size and the substituents in the heterocyclic ring system significantly modifies the acidity and regulate the physical and chemical properties of the complexes [26,27]. The arene and cyclopentadienyl platinum group metal complexes containing thiazole azine ligand is being reported for the first time.

In the present communication we focus on the synthetic methodology applied for the development of homogeneous and immobilized half-sandwich ruthenium, rhodium and iridium complexes bearing Schiff base (ata) as a specific N,N-bidentate bridging ligand.