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Heteroleptic rhodium complexes containing both the dipyrrin/cyclooctadiene ligands and application of [(η^4-C_8H_{12})Rh(4-pyrdpm)] in the construction of homo-/hetero-bimetallic complexes

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ABSTRACT

Heteroleptic rhodium(I) complexes with the general formulations [(η^4-C_8H_{12})Rh(L)] [η^4-C_8H_{12} = 1,5-cyclooctadiene; L = 5-(4-cyanophenyl)dipyrromethene, cydpm; 5-(4-nitrophenyl)dipyrromethene, ndpm; and 5-(4-benzyloxyphenyl)dipyrromethene, bdpm; 5-(4-pyridyl)dipyrromethene, 4-pyrdpm; 5-(3-pyridyl)dipyrromethene, 3-pyrdpm] have been synthesized. The complex [(η^4-C_8H_{12})Rh(4-pyrdpm)] have been used as a synthon in the construction of homo-bimetallic complex [(η^4-C_8H_{12})Rh(μ-4-pyrdpm)Rh(η^5-C_5Me_5)Cl_2] and hetero-bimetallic complexes [(η^4-C_8H_{12})Rh(μ-4-pyrdpm)Ir(η^5-C_5Me_5)Cl_2], [(η^4-C_8H_{12})Rh(μ-4-pyrdpm)Ru(η^6-$C_{10}H_{14}$)Cl_2] and [(η^4-C_8H_{12})Rh(μ-4-pyrdpm)Ru(η^6-C_6H_6)Cl_2]. Resulting complexes have been characterized by elemental analyses and spectral studies. Molecular structures of the representative mononuclear complexes [(η^4-C_8H_{12})Rh(ndpm)] and [(η^4-C_8H_{12})Rh(4-pyrdpm)] have been authenticated crystallographically.

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1. Introduction

Immense current interest has arisen in the chemistry of dipyrrin compounds owing to their rich optical properties [1–3]. In this regard *meso*-substituted dipyrrins have drawn special attention [4]. Synthesis of the *meso*-substituted dipyrrins can be easily achieved by condensation of the aldehydes with pyrrole followed by oxidation using DDQ or *p*-chloranil [5]. Extensive π-skeleton of the substituted phenyl ring as the *meso*-substituent and two conjugated rigid pyrrole rings in dipyrrins represents a versatile and fascinating class of ligands. Although, there are a number of reports dealing with the dipyrrin complexes with boron, main group metals or first row transition metals and multimetallic complexes based on 5-(4-pyridyl)dipyrromethene [1–4,6–10], there are only a few reports dealing with the ruthenium, rhodium and iridium dipyrrin complexes [11–14].

Further, the dimeric chloro-bridged rhodium complex di-μ-chlorobis[(1,2,5,6-η^4)-1,5-cyclooctdiene] dirhodium [{(η^4-C_8H_{12})Rh(μ-Cl)}$_2$] have proved to be a good starting material in the organometallic chemistry [15,16]. The complex undergoes rich variety of chemistry *via* intermediacy of the chloro bridge cleavage reactions leading to the formation of a number of interesting neutral and cationic mononuclear complexes [17–19]. Because of their potential applications in many areas, η^4-cyclooctadienyl rhodium(I) complexes have been widely investigated by various research groups during recent past [20,21]. Furthermore, heteroleptic dipyrrin complexes based on Fe(II), Zn(II), Pd(II), Hg(II), Rh(I), Cr(III), Co(III), and Cu(II) metal centers are well documented in the literature [4,6–10,22,23]. However, rhodium(I) complexes containing both the dipyrrin and cyclooctadiene group have not yet been reported.

With an objective of expanding the chemistry of heteroleptic dipyrrin complexes we have synthesized cyclooctadiene rhodium(I) complexes imparting *meso*-substituted dipyrrins. These represent the first examples of rhodium(I) complexes containing both the dipyrrin and cyclooctadiene ligands. In this paper we report reproducible syntheses, spectral and structural characterization of some neutral heteroleptic rhodium(I) complexes based on *meso*-substituted dipyrrins with the general formulations [(η^4-C_8H_{12})Rh(L)] and L = cydpm, ndpm, bdpm, 3-pyrdpm or 4-pyrdpm). Also, we describe herein the syntheses and characterization of some homo- and hetero-bimetallic complexes employing the complex [(η^4-C_8H_{12})Rh(4-pyrdpm)] as a synthon.

2. Experimental

2.1. Materials and physical measurements

All the synthetic manipulations were performed under nitrogen atmosphere. The solvents were purified rigorously by standard procedures prior to their use [24]. Hydrated rhodium(III) chloride,

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cyclooctadiene, 2,3-dicloro-5,6-dicyano-1,4-benzoquinone (DDQ), 4-cyanobenzaldehyde, 4-benzyloxybenzaldehyde, 4-nitrobenzaldehyde, 4-pyridylcarboxaldehyde, 3-pyridylcarboxaldehyde and pyrrole (all Aldrich) were used as received without further purifications. The precursor complexes $[\{(\eta^4\text{-}C_8H_{12})Rh(\mu\text{-}Cl)\}_2]$ [25], $[\{(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl\}_2]$; [($\eta^6$-arene) = *p*-cymene, benzene] [26,27] and $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ [28–30] (M = Rh or Ir) and the ligands 5-(4-cyanophenyl)dipyrromethane [31], 5-(4-nitrophenyl)dipyrromethane [32], 5-(4-benzyloxyphenyl)dipyrromethane [33], 5-(4-pyridyl)dipyrromethane [34] and 5-(3-pyridyl)dipyrromethane [34] were prepared and purified by the literature procedures. Elemental analyses for C, H and N were performed on an Exeter Analytical Inc. Model CE-440 Elemental Analyzer. IR spectra in the region 4000–400 cm^{-1} in KBr discs were acquired on a Varian 3300 FT-IR spectrometer. Electronic and emission spectra were recorded on a Shimadzu UV-1700 series and LS-45 (Perkin–Elmer) luminescence spectrophotometers, respectively. ^{1}H NMR spectra were acquired on a JEOL AL 300 FT-NMR spectrometer at r.t. using $CDCl_3$ as a solvent and TMS as an internal reference. FAB mass spectra were recorded on a JEOL SX 102/Da-600 Mass Spectrometer.

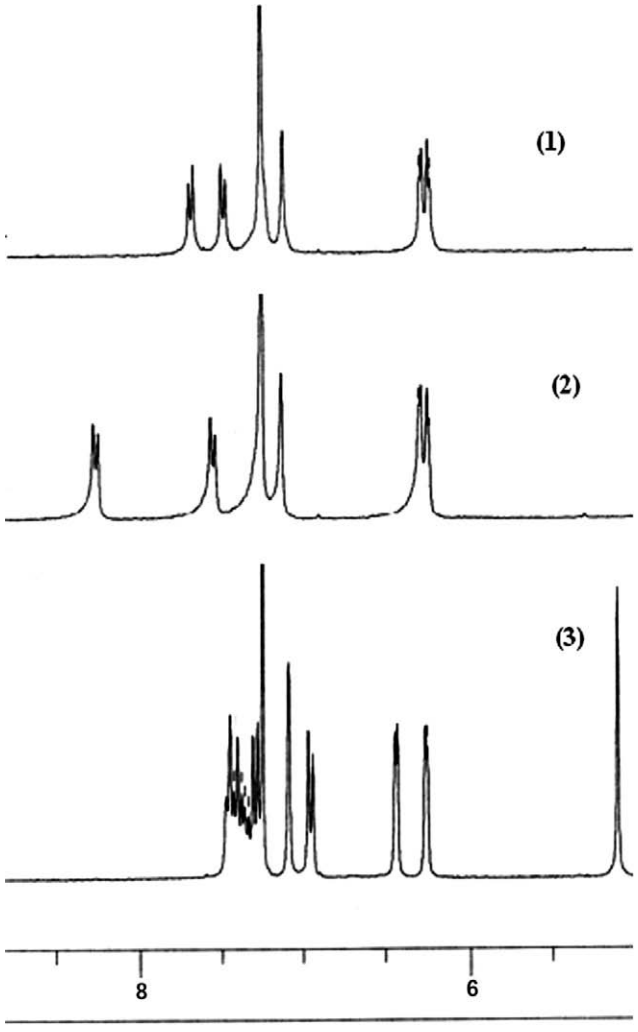
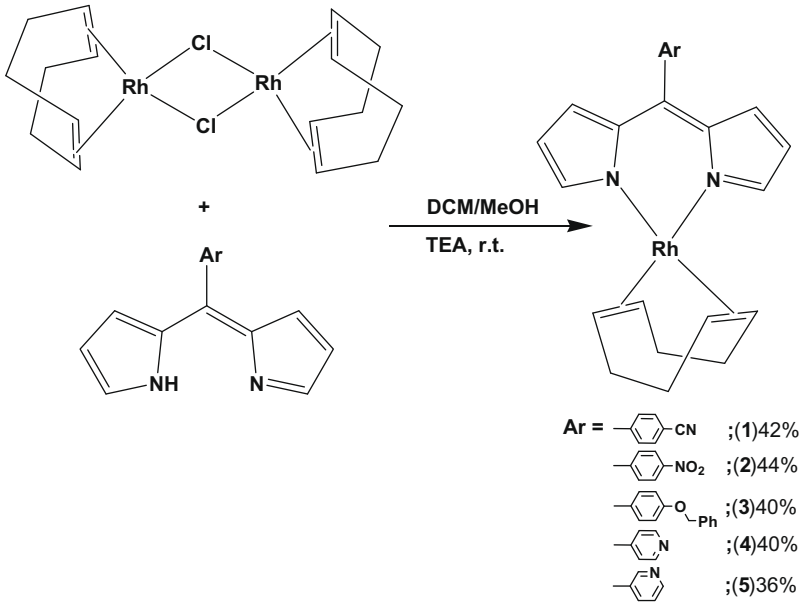


Fig. 1. The aromatic region of the ^{1}H NMR spectrums of complexes **1**–**3** in $CDCl_3$.

2.2. Syntheses

2.2.1. Synthesis of $[(\eta^4\text{-}C_8H_{12})Rh(cydpm)]$ ***1***

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.320 g, 1.40 mmol) dissolved in benzene (100 mL) was added dropwise to a stirred solution of 5-(4-cyanophenyl)dipyrromethane (0.346 g, 1.40 mmol) in 150 mL of $CHCl_3$ cooled in an ice bath (4 °C). After the completion of addition, the reaction mixture was concentrated to half of it's volume and rhodium complex $[\{(\eta^4\text{-}C_8H_{12})Rh(\mu\text{-}Cl)\}_2]$ (0.247 g, 0.50 mmol) dissolved in MeOH (50 mL) was added to this solution. The mixture was stirred for an additional 10 min. The dark red solution thus obtained was concentrated to dryness, and resulting product was purified by column chromatography (SiO_2; $CHCl_3$ with 10% hexane) to afford a dichroic red/green solid. Yield: 42%, (0.191 g). *Anal.* Calc. for $C_{24}H_{22}N_3Rh$: C, 63.30; H, 4.87; N, 9.23. Found: C, 63.61; H, 4.99: N, 9.03%. IR (KBr pellet, cm^{-1}): 2225, 1557, 1480, 1379, 1338, 1237, 1175, 1032, 989,



Scheme 1. Scheme showing the synthesis of mononuclear complexes **1**–**5**.

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