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Pyridyl azine Schiff-base ligands exhibiting unexpected bonding modes towards ruthenium, rhodium and iridium half-sandwich complexes: Synthesis and structural studies

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ABSTRACT

The reaction of multidentate azine Schiff-base ligands was investigated towards *p*-cymene ruthenium, Cp*Rh and Cp*Ir complexes. The reaction of $[(arene)MCl_2]_2$ (arene = *p*-cymene, Cp*; M = Ru, Rh and Ir) with azine Schiff-base ligands (L1-L3) in 1:2 M ratio led to the formation of mononuclear complexes of the type $[(arene)M(L)Cl]^+$ whereas the reaction of $[Cp^*MCl_2]_2$ (M = Rh/Ir) with azine Schiff-base ligands (L1-L3) in 1:1 M ratio afforded dinuclear rhodium and iridium complexes bearing formula $[\{Cp^*MCl\}_2(\mu\text{-}L)]^+$ (M = Rh/Ir). The ligands in dinuclear complexes exhibited interesting coordination modes towards the metal atom. The reaction of ligand L3 with $[Cp^*IrCl_2]_2$ dimer yielded two coordination isomers whereas with $[Cp^*RhCl_2]_2$ yielded exclusively one isomer. The molecular structure of both the isomers of the iridium complex has been established. In rhodium and iridium complexes the ligand L3 acted as uninegative pentadentate bridging ligand coordinating one metal center in a tridentate fashion and the other metal in a bidentate fashion. In the other isomer the ligand L3 behaved as uninegative tetradentate bridging ligand coordinating both iridium centers in a bidentate fashion. In the mononuclear complexes, the ligands are coordinated to the metal atom in a bidentate N∩N fashion through pyridine nitrogen and azine nitrogen. The ligand (L1 and L2) acted as tetradentate bridging ligand in dinuclear complexes. All these complexes were isolated and characterized by spectroscopic and analytical techniques.

1. Introduction

Increasing interest in the chemistry of half-sandwich arene metal complexes arises from their wide applications in various areas [1–3]. These complexes having the general formula [(arene)M(LL')Cl] (arene = *p*-cymene and its derivatives, M = Ru, Rh and Ir) have been extensively studied and found to be promising candidates as anti-cancer agents [4–7]. Arene ruthenium complexes with various bidentate donor ligands have also been widely employed as catalysts for various transformation reactions [8,9]. Pentamethylcyclopentadienyl rhodium and iridium complexes have also been extensively investigated for their antiproliferative properties [10,11]. Ruthenium complexes incorporating polypyridyl ligands have also displayed interesting photophysical, photochemical, and electrochemical properties their potential use as molecular devices and photosensitizers in redox reactions [12,13]. It is also seen that the cytotoxicity and DNA binding of rhodium complexes bearing polypyridyl ligand increases with increase in size of the polypyridyl ligand [14,15].

Among the various polypyridyl ligands, the diazine ligands linked by a single N–N bond have drawn much attention because of their coordinative flexibility about the N–N bond. The N–N linkage offers several mono- and di-nucleating coordinating sites [16,17]. These N–N bridging ligand have been incorporated into Mn(II) and Cd(II) azido systems to form 1D, 2D and 3D polymers with interesting structures and magnetic properties [18,19]. Transition metal complexes of various Schiff-bases have been reported which have found wide applications in biological fields [20]. Diazine ligands have also been employed as potential ligands to synthesize mononuclear, dinuclear and polynuclear complexes exhibiting interesting magnetic properties [21].

Over the years we have synthesized a number of half-sandwich arene ruthenium, rhodium and iridium complexes with a variety of nitrogen donor polypyridyl azine ligands [22]. As part of our

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investigations with polypyridyl azine ligands herein, we report the synthesis and structural characterization of mononuclear and dinuclear half-sandwich metal complexes containing multidentate pyridyl azine Schiff-base ligands. Based on the reactivity and coordinative flexibility of the N–N bond in azine ligand we anticipated that these ligands could give rise to complexes with interesting coordination modes and we therefore explored this possibility in the present work. As expected these ligands exhibited very interesting bonding modes, which are presented in this work. Ligands used in the present study are presented in Chart 1.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were purchased commercially and used as received. $RuCl_3.xH_2O$, $RhCl_3.xH_2O$ and $IrCl_3.xH_2O$ were purchased from Arora Matthey Limited. α-phellandrene, pentamethylcyclopentadiene, 2-cyano pyridine, 2-acetyl pyridine and 2-acetyl thiazole were purchased from Sigma Aldrich. Hydrazine hydrate and 2-pyridine aldehyde were obtained from Qualigens and Alfa Aesar. The solvents were dried and distilled before use according to standard procedures [23]. The starting metal precursors $[(p\text{-cymene})RuCl_2]_2$ and $[Cp^*MCl_2]_2$ (M = Rh/Ir) were prepared according to the literature methods [24,25]. The azine Schiff-base ligands {1-(pyridine-2-yl)ethylidene}picolinohydrazonamide (L1), pyridine-2-yl methylene)picolinohydrazonamide (L2) and {1-(thiazol-2-yl)ethylidene}picolinohydrazonamide (L3) were prepared according to published procedures [17,18]. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer by using KBr pellets in the range of 400–4000 cm^{-1}. ^1H NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer using DMSO-d_6 and $CDCl_3$ as solvents. Absorption spectra were recorded on a Perkin-Elmer Lambda 25 UV/visible spectrophotometer in the range of 200–800 nm at room temperature in acetonitrile.

2.2. Single crystal X-ray diffraction

Crystal's suitable for X-ray analyses for complexes (**1**), (**2**), (**5**), (**7**), (**8**), (**10**), (**11**), (**12**), (**14**), (**15a**) and (**15b**) were obtained by slow diffusion of hexane into acetone or DCM solution. The single crystals of complexes were attached to a glass fiber and placed into the Oxford Diffraction Xcalibur Eos Gemini diffractometer. Single crystal X-ray diffraction data for the complexes were collected on an Oxford Diffraction Xcalibur Eos Gemini diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The strategy for the data collection was evaluated using the CrysAlisPro CCD software. Crystal data were collected by standard "phi–omega scan" techniques and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares with SHELXL-97 refining on F^2 [26,27]. The metal atoms in the complex were located from the E-maps and non-hydrogen atoms were refined anisotropically. The hydrogen atoms bound to the carbon were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 U_{eq} of their parent atoms. The crystallographic and structure refinement parameters for the complexes are listed in Table 1, Table 2 and Table S1 and selected bond lengths and bond angles are presented in Tables S2 and S3. Figs. (1-4), Figs. (S9 and S10) were drawn with ORTEP3 program whereas Figs. (S11-S13) were drawn using MERCURY 3.6 program [28].

Crystal structure of complexes (**1**, **12** and **15 a**) has disorder in their PF_6 counter anion species. Crystal structure of complexes (**10**, **11** and **14** and **15 a**) contains solvent molecule in their solved structures.

2.3. General procedure for preparation of mononuclear ruthenium complexes

A mixture of metal precursor $[(p\text{-cymene})RuCl_2]_2$ (0.1 mmol), ligands (L1-L3) (0.2 mmol) and 2.5 equivalents of NH_4PF_6 were dissolved in dry methanol (10 mL) and stirred at room temperature for 8 h. A yellow compound precipitated out from the reaction mixture. The precipitate was filtered washed with cold methanol (2 × 5 mL) and diethyl ether (3 × 10 mL) and air-dried.

2.3.1. [(p-cymene)Ru(L1)Cl]PF_6 (1)

Yield 95 mg (73%); IR (KBr, cm^{-1}): 3436(m), 3163(w), 2969(m), 1632(m), 1600(m), 1472(w), 844(s); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.42$ (d, 1H, $J = 8$ Hz), 8.67 (d, 1H, $J = 4$ Hz), 8.41 (d, 1H, $J = 4$ Hz), 8.02 (t, 1H, $J = 8$ Hz), 7.95 (t, 1H, $J = 8$ Hz), 7.83 (d, 1H, $J = 8$ Hz), 7.69 (t, 1H, $J = 4$ Hz), 7.53 (t, 1H, $J = 4$ Hz), 7.24, (s, 1H, NH), 7.18(s, 1H, NH), 2.52 (s, 3H, CH_3) 5.89 (d, 1H, $J = 4$ Hz, $CH_{(p\text{-cym})}$), 5.65 (d, 1H, $J = 4$ Hz, $CH_{(p\text{-cym})}$), 5.57 (d, 1H, $J = 8$ Hz, $CH_{(p\text{-cym})}$), 5.46 (d, 1H, $J = 4$ Hz, $CH_{(p\text{-cym})}$), 2.80 (sept, 1H, $CH_{(p\text{-cym})}$), 2.26 (s, 3H, $CH_{(p\text{-cym})}$), 1.17(d, 1H, $J = 8$, $CH_{(p\text{-cym})}$), 1.11 (d, 1H, $J = 4$, $CH_{(p\text{-cym})}$); UV–Vis {Acetonitrile, λ_{max}, nm ($\varepsilon/10^{-4}$ M^{-1} cm^{-1})}: 287 (1.41), 347 (0.73).

2.3.2. [(p-cymene)Ru(L2)Cl]PF_6 (2)

Yield 102 mg (79%); IR (KBr, cm^{-1}): 3428(s), 3280(m), 2972(m), 1640(m), 1611(m), 1403(m), 839(s); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.41$ (d, 1H, $J = 8$ Hz), 8.70 (d, 1H, $J = 4$ Hz), 8.43 (s, 1H, $CH_{(imine)}$), 8.36 (d, 1H, $J = 8$ Hz), 8.07 (t, 1H, $J = 8$ Hz), 7.89–7.99 (m, 2H), 7.70 (t, 1H, $J = 4$ Hz), 7.57 (m, 2H), 7.37, (s, 1H, NH), 5.94 (d, 1H, $J = 8$ Hz, $CH_{(p\text{-cym})}$), 5.71 (d, 1H, $J = 8$ Hz, $CH_{(p\text{-cym})}$), 5.65 (d, 1H, $J = 8$ Hz, $CH_{(p\text{-cym})}$), 5.51 (d, 1H, $J = 8$ Hz, $CH_{(p\text{-cym})}$), 2.80 (sept, 1H, $CH_{(p\text{-cym})}$), 2.31 (s, 3H, $CH_{(p\text{-cym})}$), 1.20 (dd, 1H, $J = 8$ and 8 Hz, $CH_{(p\text{-cym})}$); UV–Vis {Acetonitrile, λ_{max}, nm ($\varepsilon/10^{-4}$ M^{-1} cm^{-1})}: 287 (0.79), 354 (0.54).

2.3.3. [(p-cymene)Ru(L3)Cl]PF_6 (3)

Yield 104 mg (75%); IR (KBr, cm^{-1}): 3320(s), 3129(m), 2969(m), 1635(m), 1600(m), 1471(m), 843(s); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.39$ (d, 1H, $J = 8$ Hz), 8.73 (d, 1H, $J = 4$ Hz), 8.46 (d, 1H, $J = 4$ Hz), 8.36 (t, 1H, $J = 8$ Hz), 8.07 (d, 2H), 7.75 (s, 1H, NH), 7.60 (s, 1H, NH), 2.53 (s, 3H, CH_3), 5.92 (d, 1H, $J = 8$ Hz, $CH_{(p\text{-cym})}$), 5.78 (d, 1H, $J = 4$ Hz, $CH_{(p\text{-cym})}$), 5.66 (d, 1H, $J = 8$ Hz, $CH_{(p\text{-cym})}$), 5.49 (d, 1H, $J = 4$ Hz, $CH_{(p\text{-cym})}$), 2.82 (sept, 1H, $CH_{(p\text{-cym})}$), 2.33 (s, 3H, $CH_{(p\text{-cym})}$), 1.15 (d, 1H, $J = 8$ Hz, $CH_{(p\text{-cym})}$), 1.10 (d, 1H, $J = 8$ Hz, $CH_{(p\text{-cym})}$); UV–Vis {Acetonitrile, λ_{max}, nm ($\varepsilon/10^{-4}$ M^{-1} cm^{-1})}: 268 (0.45), 334 (0.56).

2.4. General procedure for preparation of mononuclear Cp*Rh and Cp*Ir complexes

A mixture of starting metal precursor $[Cp^*MCl_2]_2$ (M = Rh/Ir) (0.1 mmol), ligands (L1-L3) (0.2 mmol) and 2.5 equivalents of NH_4PF_6 were dissolved in dry methanol (10 mL) and stirred at room temperature for 8 h. A yellow/orange compound precipitated out from the reaction mixture. The precipitate was filtered washed with cold methanol (2 × 5 mL) and diethyl ether (3 × 10 mL) and air-dried.

2.4.1. [Cp*Rh(L1)Cl]PF_6 (4)

Yield 108 mg (82%); IR (KBr, cm^{-1}): 3381(m), 3232(m), 2923(w), 1636(m), 1602(m), 1476(m), 843(s); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.80$ (d, 1H, $J = 4$ Hz), 8.64 (d, 1H, $J = 4$ Hz), 8.41 (d, 1H, $J = 8$ Hz), 8.12 (t, 1H, $J = 8$ Hz), 7.93 (m, 2H), 7.80 (t, 1H, $J = 8$ Hz), 7.49 (t, 1H, $J = 8$ Hz), 7.28 (s, 1H, NH), 7.14 (s, 1H, NH), 2.58 (s, 3H, CH_3), 1.64 (s, 15H, $CH_{(Cp^*)}$); UV–Vis {Acetonitrile, λ_{max}, nm ($\varepsilon/10^{-4}$ M^{-1} cm^{-1})}: