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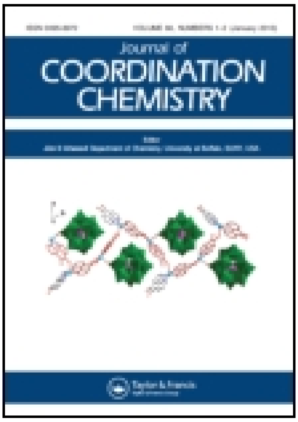

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Hydroxylation of azomethine carbon: isolation of complexes of η^5 and η^6-cyclic hydrocarbon platinum group metals with a new Schiff-base ligand

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Published online: 18 Nov 2011.

To cite this article: Sairem Gloria, Gajendra Gupta, Venkateswara Rao Anna, Babulal Das & Kollipara Mohan Rao (2011) Hydroxylation of azomethine carbon: isolation of complexes of η^5 and η^6-cyclic hydrocarbon platinum group metals with a new Schiff-base ligand, Journal of Coordination Chemistry, 64:23, 4168-4181, DOI: 10.1080/00958972.2011.636427

To link to this article: http://dx.doi.org/10.1080/00958972.2011.636427

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Journal of Coordination Chemistry
Vol. 64, No. 23, 10 December 2011, 4168–4181

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Hydroxylation of azomethine carbon: isolation of complexes of η^5 and η^6-cyclic hydrocarbon platinum group metals with a new Schiff-base ligand

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(*Received 5 August 2011; in final form 14 October 2011*)

A new Schiff base, (pyridin-2-yl)-N-(3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-yl)methanimine, (**L**), was synthesized. Reaction of $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ and $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Rh and Ir) with one equivalent of **L** in the presence of NH_4PF_6 in methanol yielded dinuclear complexes, $[(\eta^6\text{-arene})_2Ru_2(\mathbf{L}\text{-OH})Cl](PF_6)_2$ {arene = C_6H_6 (**1**), $p\text{-}^iPrC_6H_4Me$ (*p*-cymene) (**2**) and C_6Me_6 (**3**)}, and $[Cp^*{}_2M_2(\mathbf{L}\text{-OH})Cl](PF_6)_2$ [M = Rh (**4**) and Ir (**5**)], respectively, leading to the formation of five new chiral complexes with –OH on the azomethine carbon. **L** is a pentadentate ligand where one of the metal centers is coordinated to two nitrogen atoms in a bidentate chelating fashion while the other metal is bonded tridentate to three nitrogen atoms. Although the ligand is neutral before coordination, after complexation it is anionic (uninegative) with negative charge on the azo nitrogen {see the structures: N(5) in $\mathbf{2}[PF_6]_2$ and N(3) for $\mathbf{4}[PF_6]_2$}. The complexes have been characterized by various spectroscopic methods including infrared and ^{1}H NMR and the molecular structures of the representative complexes are established by single-crystal X-ray diffraction studies.

Keywords: Arene; Cyclopentadienyl; Ruthenium; Rhodium; Iridium; Schiff base

1. Introduction

The chemistry of η^5- and η^6-cyclic hydrocarbons of platinum group metal complexes has been explored for decades, particularly η^6-arene metal complexes owing to their biological and catalytic properties [1–6]. Catalytic activities of these complexes range from hydrogen transfer [7] to ring-closing metathesis [8]. Moreover, antitumor [5, 6, 9], antiviral [10], and catalytic activities [11, 12] exhibited by some water-soluble η^6-(arene) ruthenium(II) complexes have evoked interest in recent years. Platinum group metal complexes bearing nitrogen bases have been widely studied as these complexes function as catalyst for the oxidation of water to dioxygen [13, 14]. Complexes of platinum group metals with η^5- and η^6-cyclic hydrocarbons having 3,5-bis(2-pyridyl) pyrazole (H-bpp),

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2011.636427

the analogous type 4-amino-3,5-di-pyridyltriazole (dpt-NH_2), and other nitrogen bases have already been reported by our group [15–23]. During the last decade, new interest has arisen in pharmacological applications of Schiff bases and their transition metal complexes, which are antibacterial agents, used in radiopharmaceuticals for treating cancer, anticancer agents, model systems for bio macromolecules, and are dioxygen carriers [24]. Ruthenium complexes have opened up enormous possibilities for catalytic organic processes [25, 26] as a result of the advancement in the design and synthesis of efficient and selective catalysts based on the design of new ligands such as N-heterocyclic carbenes [27, 28], Schiff bases [29–31], etc.

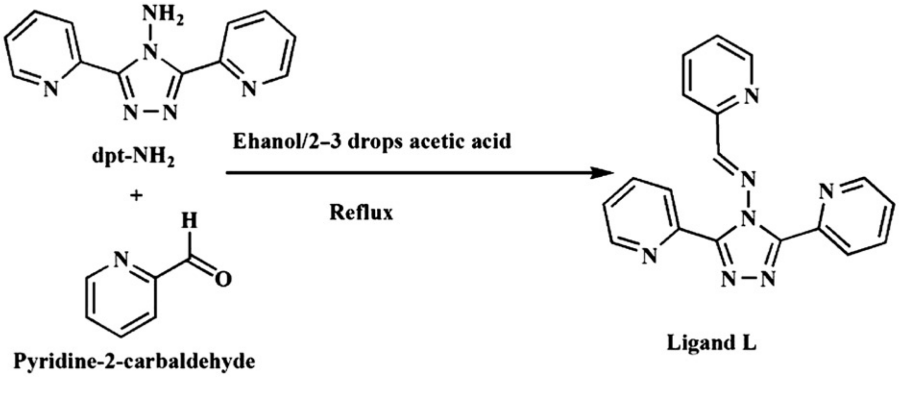
In this manuscript, we report a new Schiff base derived from dpt-NH_2 and pyridine-2-carbaldehyde and its reactions with complexes of platinum group metals. The ligand used in this study is shown in scheme 1.

Here, the ligand binds bidentate with one metal and tridentate with the other yielding hydroxylated products forming a negative charge center on the azomethine nitrogen to form the dicationic complexes. Although there have been reports of the hydrolysis of Schiff-base complexes [32], leading to the isolation of stable aqua adducts and formation of amide from aldimine [33] as well, the complexes which have been isolated and discussed in this communication are quite different from the earlier reported one owing to the ability of the azomethine nitrogen to bind to the metal ion in anionic form.

2. Experimental

2.1. *Physical measurements*

Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer with the sample prepared as KBr pellets. NMR spectra were obtained using a Bruker Avance II 400 spectrometer in $CDCl_3$ and acetone-d_6 using TMS as an internal standard. All chemicals used were of reagent grade. Elemental analyses of the complexes were performed on a Perkin-Elmer 2400 CHN/S analyzer. Absorption spectra were obtained at room temperature using a Perkin Elmer Lambda 25 UV-Vis Spectrophotometer. (Pyridin-2-yl)-N-(3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-yl)methanimine **(L)** was prepared



Scheme 1. Synthesis of **L**.

by refluxing the amine and aldehyde by the method described below. The precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, $p\text{-}^iPrC_6H_4Me$ and C_6Me_6) and $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) were synthesized by the literature procedures.

2.2. *Single-crystal X-ray structure analyses*

Crystals of **L** were grown from acetone/petroleum ether as white needles, while crystals of **2**$[PF_6]_2$ and **4**$[PF_6]_2$ were grown by slow diffusion of hexane into acetone solutions of the complexes, isolated as light red blocks and yellow plates, respectively. The crystallizations were done at room temperature. The intensity data of **L**, **2**$[PF_6]_2$, and **4**$[PF_6]_2$ were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with fine focus 1.75 kW sealed tube Mo-Kα radiation ($\alpha = 0.71073$ Å) at 296(2) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s per frame. SMART [34] software was used for data acquisition. Data integration and reduction were undertaken with SAINT [34] software. Structures were solved by direct methods using SHELXS-97 and refined with full-matrix least squares on F^2 using SHELXL-97 [35]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 [36] for Windows. ORTEP presentations of the representative complexes are shown in figures 2 and 3, respectively. The data collection parameters are presented in table 1.

2.3. *Preparation of the ligand (L)*

A mixture of 4-amino-3,5-di-2-pyridyl-4H-1,2,4-triazole (dpt-NH_2) [15] (600 mg, 2.51 mmol) and pyridine-2-carbaldehyde (0.213 mL, 2.51 mmol) was dissolved in 25 mL of dry ethanol. Two–three drops of glacial acetic acid was added to the solution and it was then refluxed for 12–15 h during which TLC were taken after every 2 h interval. Then, the solution was removed on a rotary evaporator and the residue was extracted, washed with diethyl ether and dried in vacuum to yield a dull white crystalline compound. It was recrystallized in ethanol to yield a pale white crystalline compound.

Yield: 500 mg, 60%; m.p.: 161–163°C. Elemental Anal. Calcd for $C_{18}H_{13}N_7$ (%): C, 66.06; H, 4.02; N, 29.94. Found (%): C, 66.38; H, 4.23; N, 30.21; IR (KBr pellets, cm^{-1}): 1583 (s); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.82$ (s, 1H–C$\underline{H}$=N); 8.72 (d, $J = 4$ Hz, 1H); 8.59 (d, $J = 4$ Hz, 2H); 8.23 (t, $J = 8$ Hz, 2H), 7.85 (dt, $J = 7.6$ and 1.6 Hz, 4H); 7.45 (dt, $J = 4.8$ Hz, 1H); 7.35 (qt, $J = 4.4$ Hz, 2H). $^{13}C\ \{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 121.734$, 123.183, 124.318, 127.894, 137.099, 137.585, 147.406, 148.256 (pyridyl carbons); 150.224 (triazole carbons); 193.464 (azomethine carbon).

2.4. *Preparation of $[(\eta^6\text{-arene})_2Ru_2(L\text{-}OH)Cl](PF_6)_2$ {arene = C_6H_6, 1$[PF_6]_2$; $p\text{-}^iPrC_6H_4Me$, 2$[PF_6]_2$; C_6Me_6, 3$[PF_6]_2$}*

A mixture of $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (0.10 mmol), **L** (0.10 mmol), and two equivalents of NH_4PF_6 was stirred in dry methanol (30 mL) for 4 h at room temperature, resulting in the formation of a precipitate. The precipitate was then filtered, washed with diethyl ether, and dried in vacuum.

1[PF$_6$]$_2$: Yield: 65 mg (63%). Color: Brownish precipitate. Elemental Anal. Calcd for $C_{30}H_{26}ClF_{12}N_7OP_2Ru_2$ (%): C, 35.04; H, 2.54; N, 9.53. Found (%): C, 34.97; H, 2.65; N, 9.33. IR (KBr pellets, cm^{-1}): 3429 (w), 1629 (s); 1450 (s); 841 (s); ^{1}H NMR (400 MHz, acetone-d$_6$): $\delta = 9.90$ (d, $J = 8$ Hz, H$_1$); 9.77 (d, $J = 8$ Hz, H$_{13}$); 9.71 (d, $J = 8$ Hz, H$_{18}$); 9.60 (d, $J = 8$ Hz, H$_{15}$); 9.55 (d, $J = 8$ Hz, H$_{10}$); 8.55 (d, $J = 8$ Hz, H$_4$), 8.39 (m, $J = 8$ Hz, H$_{17}$ and H$_{16}$); 8.21 (m, $J = 8$ Hz, H$_{12}$ and H$_{11}$); 7.80 (m, $J = 8$ Hz, H$_2$ and H$_3$); 6.32 (s, 6H); 6.25 (s, 6H, C_6H_6); 5.93 (s,1H, $\underline{H}$C–N); 2.80 (s, 1H, OH). UV-Vis. [CH_3CN, λ_{max} nm), ϵ ((mol L^{-1})$^{-1}$cm^{-1})]: 299 (9.83×10^4).

2[PF$_6$]$_2$: Yield: 70 mg (75%). Color: orange precipitate. Elemental Anal. Calcd for $C_{38}H_{42}ClF_{12}N_7OP_2Ru_2$ (%): C, 40.02; H, 3.71; N, 8.60. Found (%): C, 39.91; H, 3.65; N, 8.52. IR (KBr pellets, cm^{-1}): 3454 (w),1629 (s); 1455 (s); 842 (s); ^{1}H NMR (400 MHz, acetone-d$_6$): $\delta = 9.80$ (dd, $J = 11.6$ and 9.2 Hz, H$_{18}$ and H$_{13}$); 9.65 (d, $J = 8$ Hz, H$_1$); 9.37 (d, $J = 8$ Hz, H$_{15}$); 8.63 (d, $J = 8$ Hz, H$_{10}$); 8.54 (t, $J = 8$ Hz, H$_{17}$), 8.44 (t, $J = 8$ Hz, H$_{16}$); 8.25 (t, $J = 8$ Hz, H$_{12}$); 8.01 (t, $J = 8$ Hz, H$_{11}$); 7.85 (m, H$_2$ and H$_3$); 7.51 (d, $J = 8$ Hz, H$_4$); 6.36 (d, $J = 8$ Hz, 1H$_{\text{Ar-cym}}$); 6.26 (d, $J = 8$ Hz, 1H$_{\text{Ar-cym}}$); 6.16 (d, $J = 8$ Hz, 1H$_{\text{Ar-cym}}$), 6.10 (d, $J = 8$ Hz, 1H$_{\text{Ar-cym}}$); 5.98 (dd, $J = 8$ Hz, 2H$_{\text{Ar-cym}}$); 5.73 (d, $J = 8$ Hz, 1H$_{\text{Ar-cym}}$); 5.53(s, 1H, –$\underline{H}$C–N); 5.15 (d, $J = 8$ Hz, 1H$_{\text{Ar-cym}}$); 3.36 (s, 1H, OH); 3.00 (sept, $J = 8$ Hz, cym-C$\underline{H}$(CH$_3$)$_2$); 2.54 (sept, $J = 8$ Hz, cym-C$\underline{H}$(CH$_3$)$_2$); 2.40 (s, 3H, cym-CH$_3$); 1.72 (s, 3H, cym-CH$_3$); 1.29 (d, $J = 8$ Hz, 3H, CH(C$\underline{H}_3$)$_2$); 1.20 (d, $J = 8$ Hz, 3H, CH(C$\underline{H}_3$)$_2$); 1.00 (d, $J = 8$ Hz, 3H, CH(C$\underline{H}_3$)$_2$); 0.93 (d, $J = 8$ Hz, 3H, CH(C$\underline{H}_3$)$_2$). UV-Vis. [CH_3CN, λ_{max} (nm), ϵ ((mol L^{-1})$^{-1}$cm^{-1})]: 296 (6.74×10^4).

3[PF$_6$]$_2$: Yield: 55 mg (61%); Color: Yellow precipitate. Elemental Anal. Calcd for $C_{42}H_{50}ClF_{12}N_7OP_2Ru_2$ (%): C, 42.16; H, 4.21; N, 8.20. Found (%): C, 42.00; H, 4.08; N, 8.13. IR (KBr pellets, cm^{-1}): 3446 (w); 1636 (s); 1474 (s); 842 (s); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 9.75$ (d, $J = 8$ Hz, H$_{18}$ and H$_{13}$); 9.34 (d, $J = 8$ Hz, H$_1$); 9.10 (d, $J = 4$ Hz, H$_{15}$); 8.75 (d, $J = 8$ Hz, H$_{10}$); 8.53 (t, $J = 8$ Hz, H$_{17}$); 8.36 (q, $J = 8$ Hz, H$_{12}$), 8.22 (t, $J = 8$ Hz, H$_2$); 8.06 (t, $J = 8$ Hz, H$_{16}$); 7.93 (t, $J = 8$ Hz, H$_{11}$); 7.84 (t, $J = 8$ Hz, H$_3$); 7.46 (d, $J = 8$ Hz, H$_4$); 5.51 (s, 1H, –$\underline{H}$C–N); 3.30 (s, 1H, OH); 2.35 (s, 18H, C_6Me_6); 1.85 (s, 18H, C_6Me_6). UV-Vis. [CH_3CN, λ_{max} (nm), ϵ ((mol L^{-1})$^{-1}$cm^{-1})]: 302 (1.08×10^5).

2.5. *Preparation of [(Cp*)$_2$M$_2$(L-OH)Cl](PF$_6$)$_2$, M = Rh, 4[PF$_6$]$_2$; M = Ir, 5[PF$_6$]$_2$*

A mixture of [(η^5-C$_5$Me$_5$)M(μ-Cl)Cl]$_2$ (0.08 mmol), **L** (0.08 mmol), and two equivalents of NH_4PF_6 was stirred in dry methanol (30 mL) for 4 h at room temperature, resulting in the formation of a yellow precipitate. The precipitate was then filtered, washed with diethyl ether, and dried in vacuum.

4[PF$_6$]$_2$: Yield: 63 mg (68%); Elemental Anal. Calcd for $C_{38}H_{44}ClF_{12}N_7OP_2Rh_2$ (%): C, 39.83; H, 3.87; N, 8.55. Found (%): C, 40.05; H, 4.02; N, 8.32; IR (KBr pellets, cm^{-1}): 3429 (w); 1604 (s); 1451 (s); 841 (s); ^{1}H NMR (400 MHz, acetone-d$_6$): $\delta = 9.69$ (d, $J = 8$ Hz, H$_1$); 9.21 (t, $J = 4$ Hz, H$_2$); 9.08 (d, $J = 8$ Hz, H$_{13}$); 8.71 (d, $J = 8$ Hz, H$_{18}$); 8.35 (m, $J = 4$ Hz, 4H$_{(17,16,12,11)}$), 8.17 (t, $J = 8$ Hz, H$_3$); 7.94 (d, $J = 8$ Hz, H$_{15}$);

7.82 (d, $J = 8$ Hz, H_{10}); 7.49 (d, $J = 8$ Hz, H_4); 5.51 (s, 1H, –$\underline{H}$C–N); 3.22 (s, 1H, OH); 1.84 (s, 15H, Cp*), 1.37 (s, 15H, Cp*).

5[PF₆]₂: Yield: 68 mg (71%); Elemental Anal. Calcd for $C_{38}H_{44}ClF_{12}N_7OP_2Ir_2$ (%): C, 34.45; H, 3.35; N, 7.40. Found (%): C, 35.06; H, 3.30; N, 7.32; IR (KBr pellets, cm^{-1}): 3423(w); 1639(s); 1460(s); 844(s); ^{1}H NMR (400 MHz, acetone-d_6): $\delta = 9.53$ (d, $J = 8$ Hz, H_{18} and H_{13}); 9.22 (d, $J = 4$ Hz, H_1); 9.07 (d, $J = 8$ Hz, H_{15}); 8.69 (d, $J = 8$ Hz, H_{10}); 8.43 (t, $J = 8$ Hz, H_{17}), 8.30 (t, $J = 8$ Hz, H_{12}); 8.22 (t, $J = 8$ Hz, H_{16}); 7.94 (t, $J = 8$ Hz, H_{11}); 7.81(m, $J = 8$ Hz, H_2 and H_3); 7.53 (d, $J = 8$ Hz, H_4); 6.11 (s, 1H, –$\underline{H}$C–N); 3.24 (s, 1H, OH); 1.77 (s, 15H, Cp*), 1.37 (s, 15H, Cp*). UV-Vis. [CH_3CN, λ_{max} (nm), $\epsilon((mol\ L^{-1})^{-1}cm^{-1})$]: 300 ($9.03 \times 10^4$).

3. Results and discussion

3.1. *Ligand, (pyridin-2-yl)-N-(3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-yl) methanimine (L)*

In continuation of the previous work [15], a new hexadentate Schiff base, (pyridin-2-yl)-N-(3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-yl)methanimine having the formula $C_{18}H_{13}N_7$, has been synthesized in moderate yield by simple Schiff-base condensation of dpt-NH_2 and pyridine 2-carbaldehyde in ethanol in the presence of 2–3 drops of glacial acetic acid. This ligand has been characterized by IR and ^{1}H NMR and ^{13}C NMR spectroscopy, and its structure has been confirmed by single-crystal X-ray diffraction. The ORTEP structure is not presented in this communication due to the lack of presentable data. However, mercury drawing of the ligand is presented in figure 1 with the available data set. The IR spectrum of this ligand shows sharp bands at

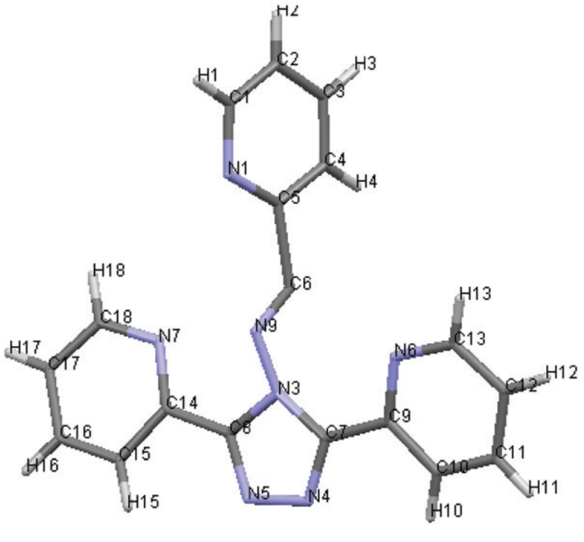


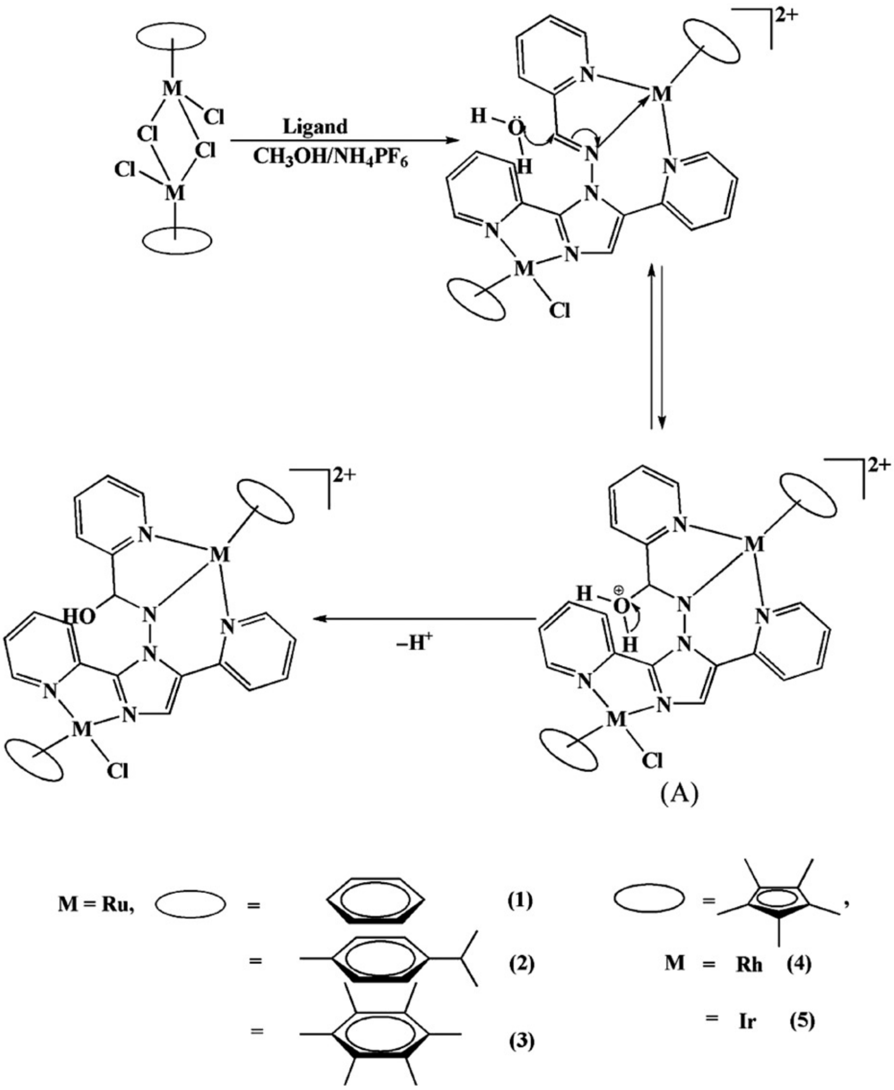
Figure 1. Mercury drawing of **L**.

1583 cm^{-1} for the azomethine C=N bond, and from 1568 to 1431 cm^{-1} for the C=N and C=C bonds of the pyridyl moieties. The presence of the sharp stretching band of the azomethine group shows that condensation of the amine and the aldehyde has taken place. The ^1H NMR spectrum of the ligand displays a singlet at δ 8.82 for the proton bonded to azomethine carbon, two doublets, one triplet, two doublets of triplets and one quintet at δ 8.72, 8.59, 8.23, 7.85, 7.45 and 7.35, respectively, for the protons of the pyridyl moieties. In the ^{13}C NMR of the ligand, the pyridyl carbons resonate at δ 121.734 to 148.256 while the resonance of the triazole carbons is at δ 150.224. Schiff-base formation has been confirmed from the resonance value at δ 193.64 assigned to the azomethine carbon.

3.2. *Dinuclear η^6-arene ruthenium complexes*

The dinuclear $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ complex (arene = C_6H_6, $p\text{-}^iPrC_6H_4Me$ and $C_6(CH_3)_6$) reacts with **L** in 1 : 1 molar ratio yielding the new dinuclear cationic complexes shown in scheme 2 which have been isolated as hexafluorophosphate salts. Complexes **2**$[PF_6]_2$ and **3**$[PF_6]_2$ are orange to yellow while **1**$[PF_6]_2$ is brownish.

All the complexes are non-hygroscopic, air-stable, and soluble in polar solvents like dichloromethane, chloroform, acetone, and acetonitrile, but are insoluble in low-boiling non-polar solvents like hexane, petroleum ether, and diethyl ether. IR spectra of these three complexes show broad bands at 3429–3454 cm^{-1} for OH bending; sharp to medium bands at 1629–1636 cm^{-1} for C=N; and 1450–1474 cm^{-1} for the C=C stretching of the ligand. Apart from these frequencies, a sharp band at 840 cm^{-1} for the $\nu_{P\text{–}F}$ stretch of the counter ion is also observed. The ^1H NMR spectra of these complexes show noticeable downfield shifts with the ligand peaks splitting into a number of peaks with more than the expected multiplicities owing to the unsymmetrical nature of the ligand when coordinated, i.e., one of the metals is bonded bidentate while the other metal is bonded tridentate showing 11–13 sets of signals for the ligand. The spectrum of **2**$[PF_6]_2$ displays four doublets, four triplets, one doublet of doublets, and one multiplet for the pyridyl groups of the ligand. All these resonances shift downfield compared to the free ligand signals. One singlet for the proton bonded to the carbon which was initially the azomethine carbon, and one singlet for the OH proton arise after hydroxylation δ 5.53 and δ 3.36, respectively. This hydroxylation on the azomethine carbon takes place in the process of complexation, resulting in a change of hybridization of the azomethine carbon from sp^2 to sp^3. As a result, the CH proton is shifted upfield compared to the free ligand signal after hydroxylation. This process is inferred by the presence of OH signal and the upfield shift of the proton bonded to what was initially the azomethine carbon. The appearance of OH signal in the ^1H NMR spectrum of the complexes prompted us to grow crystal of the ligand as no such signal is present in the spectrum of the ligand. The crystal structure confirmed that no OH group is present in the ligand and hydroxylation takes place only during complexation, which is evident from the crystal structure of the complex. Taking **2**$[PF_6]_2$ as an example, when N(5) of the Schiff base binds with the metal, it develops a partial positive charge thereby making C(13) electron deficient and more susceptible to nucleophilic attack [37]. Therefore, the minimal levels of moisture which may be present in methanol attack the electron-deficient carbon of the Schiff base to form **A** (scheme 2) that subsequently loses the proton to yield the dicationic complex rather than the tricationic complex (which



Scheme 2. Plausible mechanism for the formation of **1**$[PF_6]_2$–**5**$[PF_6]_2$.

would have been expected if the ligand was coordinated in its original neutral pentadentate fashion as predicted). After complexation it acts as an anionic ligand (uninegative) where the negative charge center is on N(5) azo nitrogen of **2**$[PF_6]_2$. This is supported by X-ray studies confirming the formation of a dicationic complex. In contrast to the observations reported by Paul *et al.* [37], free movement of the attached pyridyl ring does not play a role in our case.

For **1**$[PF_6]_2$, protons of the pyridyl moieties show six doublets and three multiplets in the range δ 9.90–7.80, while two singlets are displayed at δ 5.93 and 2.80 for CH and OH, respectively. The ^{1}H NMR spectrum of **3**$[PF_6]_2$ displays five doublets, five triplets, and one quartet at δ 9.75–7.46 for pyridyl protons while the CH and OH appear at

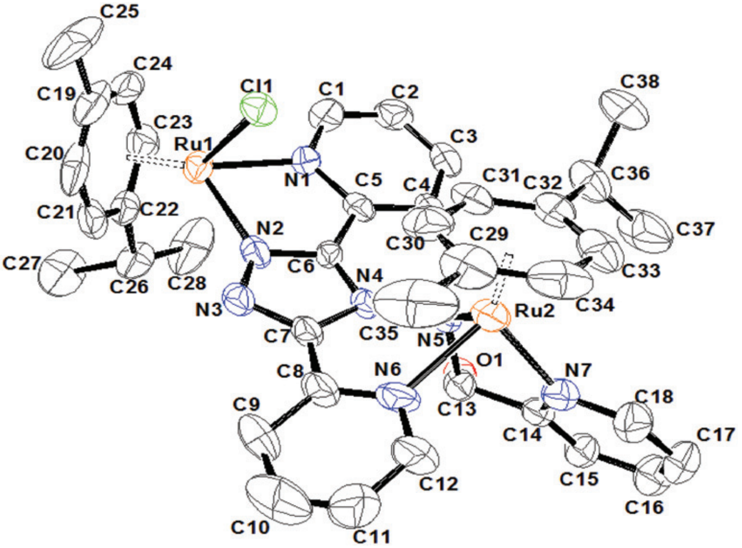


Figure 2. Molecular structure of **2**[PF$_6$]$_2$ at 25% probability level. Hydrogen atoms and hexafluorophosphate have been omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–Ru(1) 2.104(6), N(2)–Ru(1) 2.057(7), Cl(1)–Ru(1) 2.409(2), Ru(1)–centroid 1.692, N(5)–Ru(2) 2.062(6), N(6)–Ru(2) 2.139(7), N(7)–Ru(2) 2.081(7), Ru(2)–centroid 1.702, C(13)–O(1) 1.420(8), C(13)–N(5) 1.480(8), N(4)–N(5) 1.424(7), N(2)–Ru(1)–N(1) 75.9(3), N(1)–Ru(1)–Cl(1) 84.94(17), N(2)–Ru(1)–Cl(1) 83.48, N(5)–Ru(2)–N(7) 77.2(3), N(5)–Ru(2)–N(6) 84.2(3), N(7)–Ru(2)–N(6) 88.3(3), C(13)–O(1)–H(1A) 109.5.

δ 5.51 and 3.30, respectively. Apart from the ligand peaks, **2**[PF$_6$]$_2$ displays six doublets and one doublet of doublets at δ 6.36–5.15 for the aromatic protons of the cymene groups; two septets at δ 3.00 and 2.54; four doublets at δ 1.29–0.93 for the methyl protons of the isopropyl groups; and two singlets at δ 2.40 and 1.72 for the methyl groups. For **1**[PF$_6$]$_2$ and **3**[PF$_6$]$_2$, apart from the ligand peaks, two singlets at δ 6.32 and 6.25 appear for the benzene ring, while singlets are displayed at δ 2.35 and 1.85 for the hexamethylbenzene. The nature of the complex may be understood by the single-crystal X-ray diffraction structure of **2[**PF$_6$]$_2$, as shown in figure 2.

3.3. *Dinuclear η^5-pentamethylcyclopentadienyl metal complexes (Metal = Rh and Ir)*

The binuclear [(η^5-C$_5$Me$_5$)M(μ-Cl)Cl]$_2$ (M = Rh and Ir) reacts with **L** in 1 : 1 ratio, yielding the new binuclear cationic complexes shown in scheme 2 and isolated as their hexafluorophosphate salts.

Complexes **4**[PF$_6$]$_2$ and **5**[PF$_6$]$_2$ are yellow in color with similar physical properties with those of the above three complexes. The IR spectra of these complexes display a weak broad band at 3429 cm^{-1} and 3423 cm^{-1} for OH bending, sharp bands at 1604 and 1639 cm^{-1} for C=C stretching, and at 1451 and 1460 cm^{-1} for C=N stretching. A sharp band due to $\nu_{\mathrm{P-F}}$ stretched from the counter ion is also observed at 850 cm^{-1}. The ^{1}H NMR spectra of **4**[PF$_6$]$_2$ and **5**[PF$_6$]$_2$ display a set of 11 and 12 signals, respectively, for the ligand. The pyridyl moieties of **4**[PF$_6$]$_2$ show six doublets, two triplets, and one multiplet while **5**[PF$_6$]$_2$ show five doublets, four triplets, and one multiplet. The CH proton signals are singlets at δ 5.51 and 6.11, while the OH proton is

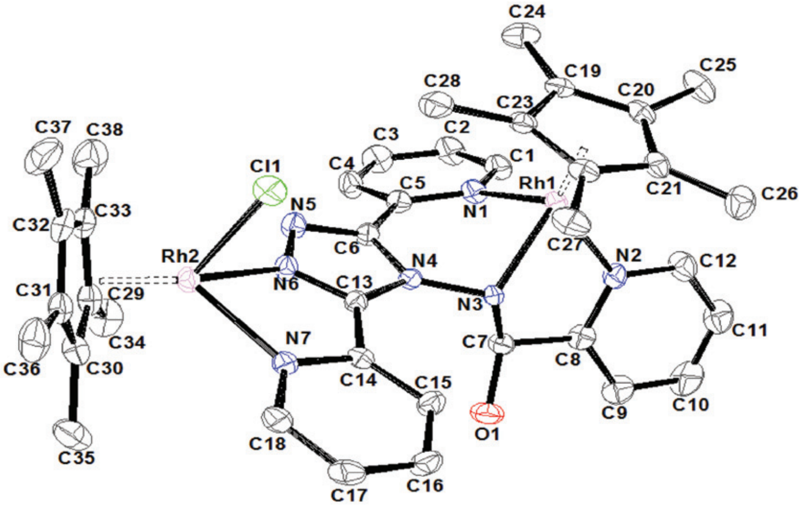


Figure 3. Molecular structure of $\mathbf{4}[PF_6]_2 \cdot H_2O \cdot CH_3COCH_3$ at 25% probability level. Hydrogen atoms, solvated molecules, and hexafluorophosphate have been omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–Rh(1) 2.118(4), N(2)–Rh(1) 2.110(4), N(3)–Rh(1) 2.098(3), Rh(1)–centroid 1.802, N(6)–Rh(2) 2.107(4), N(7)–Rh(2) 2.147(4), Cl(1)–Rh(2) 2.3932(15), Rh(2)–centroid 1.774, C(7)–O(1) 1.411(6), C(7)–N(3) 1.470(6), N(3)–N(4) 1.412(5), N(6)–Rh(2)–N(7) 75.23(14), N(6)–Rh(2)–Cl(1) 87.721, N(7)–Rh(2)–Cl(1) 85.16(11), N(3)–Rh(1)–N(1) 85.78(15), N(3)–Rh(1)–N(2) 78.34(15), N(2)–Rh(1)–N(1) 89.80(17), C(7)–O(1)–H(1A) 109.5.

a singlet at δ 3.22 and 3.24 for $\mathbf{4}[PF_6]_2$ and $\mathbf{5}[PF_6]_2$, respectively. Apart from these peaks, both complexes display two more singlets at δ 1.84 and 1.37 for $\mathbf{4}[PF_6]_2$ and at δ 1.77 and 1.37 for $\mathbf{5}[PF_6]_2$, representing the 15 protons of Cp*. Single-crystal X-ray diffraction structure of the $\mathbf{4}[PF_6]_2$ is shown in figure 3. From ^1H NMR data, hydroxylation takes place on the azomethine carbon similar to the ruthenium complexes. To evaluate the result unambiguously, the molecular structure (figure 3) was determined and proved that the hydroxyl assignment is correct.

Since the complexes bear four chiral centers, two at the metal centers, one at the carbon and nitrogen centers (initially the azomethine carbon and nitrogen, respectively), there is a possibility for the formation of diastereomers. But, all efforts to separate the diastereomers were unfruitful. However, the existence of diastereomers has been supported by the ill-resolved NMR data. Since the signals of the minor diastereomers are hidden or not well resolved, we are unable to make any precise interpretation. As a result, we have laid focus only on the major diastereomeric products in this communication.

3.4. *UV-visible studies*

The UV-visible spectra of $\mathbf{1}[PF_6]_2$, $\mathbf{2}[PF_6]_2$, $\mathbf{3}[PF_6]_2$, and $\mathbf{5}[PF_6]_2$ were acquired in acetonitrile at room temperature. The spectra of these complexes display an intense band *ca* 300 nm which is attributed to the ligand-centered $\pi \rightarrow \pi^*$ transition. Electronic spectra of representative complexes are depicted in figure 4. These complexes do not exhibit a MLCT band except for $\mathbf{2}[PF_6]_2$, with a band of medium intensity *ca* 425 nm

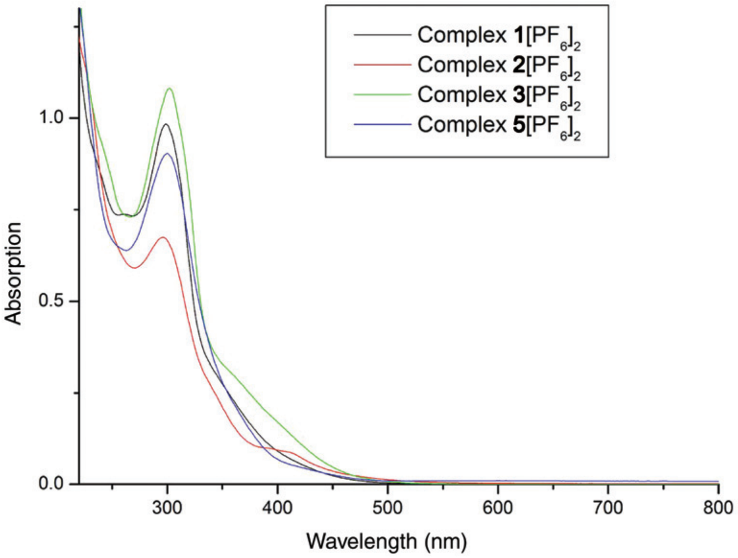


Figure 4. UV-Vis absorption spectra of **1**[PF$_6$]$_2$, **2**[PF$_6$]$_2$, **3**[PF$_6$]$_2$, and **5**[PF$_6$]$_2$ in acetonitrile at 298 K.

due to metal-to-ligand charge transfer (MLCT) $t_{2g} \rightarrow \pi^*$ transition in electronic spectrum [38].

3.5. *Molecular structures and interactions*

Molecular structures of **2**[PF$_6$]$_2$ and **4**[PF$_6$]$_2$ have been determined by single crystal X-ray diffraction studies. Details about data collection, refinement, and structure solution are recorded in table 1. Structures of **2**[PF$_6$]$_2$ and **4**[PF$_6$]$_2$ with atom-numbering schemes are shown in figures 2 and 3, respectively, along with some selected bond lengths and angles.

2[PF$_6$]$_2$ and **4**[PF$_6$]$_2$ crystallize in the monoclinic P2$_1$/c and triclinic P$\bar{1}$ space groups, respectively. The metals are bonded to nitrogen in two different bonding modes. For **2**[PF$_6$]$_2$, Ru(1) is bonded to N(1) and N(2) in κ^2 manner, while Ru(2) is bonded to N(5), N(6), and N(7) in κ^3 manner. Although the two metals have different binding modes, each maintains typical piano stool geometry. The Ru–N bond lengths are 2.057(7)–2.139(7) Å, while the Ru–Cl bond length is 2.409(2) Å, consistent with the reported values [15]. The distances of Ru(1) and Ru(2) from the centroid of the *p*-cymene moiety are 1.692 Å and 1.702 Å, respectively. The addition of a hydroxyl group onto the azomethine carbon is confirmed by the presence of an oxygen bonded to C(13). The carbon–oxygen C(13)–O(1) bond length in **2**[PF$_6$]$_2$ is 1.420(8) Å, within the range of the reported literature values. Furthermore, the lengths of C(13)–N(5) and N(4)–N(5) bonds are 1.480(8) and 1.424(7) Å, respectively, indicative of their single-bond character. **4**[PF$_6$]$_2$ crystallizes with a molecule of water and acetone, and the hydrogen atoms of water were unable to be located. One rhodium is bonded to nitrogen in κ^2 manner while the other rhodium is bonded in κ^3 manner, maintaining the piano-stool geometry. Addition of OH to the azomethine carbon is confirmed by bond lengths and

Table 1. Crystallographic and structure refinement parameters for **2**[PF$_6$]$_2$ and **4**[PF$_6$]$_2$ · H$_2$O · (CH$_3$)$_2$CO.

	2[PF$_6$]$_2$	**4**[PF$_6$]$_2$ · H$_2$O · acetone
Chemical formula	$C_{38}H_{42}Cl\ F_{12}N_7OP_2Ru_2$	$C_{41}H_{52}ClF_{12}N_7O_3P_2Rh_2$
Formula weight	1140.32	1222.11
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Crystal size (mm^3)	0.34 × 0.22 × 0.15	0.41 × 0.30 × 0.25
Unit cell dimensions (Å, °)		
a	14.3563(9)	12.5543(3)
b	13.4996(4)	13.460(3)
c	16.0167(5)	16.810(3)
α	90	66.014(10)
β	114.870(4)	82.868(2)
γ	90	84.998(2)
Volume (Å^3), Z	4533.3(5), 4	2458.86(12), 2
Temperature (K)	296(2)	296(2)
Calculated density (Mg m^{-3})	1.671	1.651
Absorption coefficient (mm^{-1})	0.885	0.881
θ range for data collection (°)	1.53–28.35	1.40–24.00
Reflections collected	54,230	29,214
Independent reflection	3721 [R(int) = 0.1123]	6357 [R(int) = 0.0459]
Final R indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.0767$, $wR_2 = 0.2067$	$R_1 = 0.0482$, $wR_2 = 0.1563$
R indices (all data)	$R_1 = 0.1112$, $wR_2 = 0.2414$	$R_1 = 0.0550$, $wR_2 = 0.1621$
Goodness-of-fit on F^2	0.834	1.071
Largest difference peak and hole (e Å^{-3})	1.103 and −0.924	1.052 and −0.837

[a] Structures were refined on F_o^2: $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

angles around C7. The carbon–oxygen C(7)–O(1) bond length is 1.411(6) Å. As for **2**[PF$_6$]$_2$, lengths of the C(7)–N(3) and N(3)–N(4) bonds are 1.470(6) and 1.412(5) Å, respectively, suggesting single bond character here. Rh–N, Rh–Cl distances and rhodium centers from the Cp* centroid are in the range 2.098(3)–2.147(4), 2.3932(15), and 1.774–1.802 Å, respectively, in agreement with such bond lengths in other rhodium polypyridyl complexes [15].

In **2**[PF$_6$]$_2$, the hydroxyl of one molecule shows hydrogen-bonding interactions Cl · · · H and O · · · Cl with a bond distance of 2.407 and 3.117 Å, respectively, with the chloride of another molecule. In these interactions, the hydroxyl oxygen and hydrogen of one molecule form hydrogen bonds simultaneously with the same chloride of another molecule. Apart from these, an intermolecular $\pi \cdots \pi$ interaction with a bond distance of 3.337 Å has also been observed between the pyridyl moieties of different molecules, as shown in figure 5.

In **4**[PF$_6$]$_2$, each molecule is associated with one molecule of acetone and one molecule of water as solvents of crystallization. The main centers of interactions in this complex are hydroxyl group, chloride, and solvents of crystallization, as shown in figure 6. The solvent molecules are bridges between the two complex molecules. Chloride of one molecule forms hydrogen bonds with the hydrogen of acetone (2.834 Å) and the oxygen of acetone forms hydrogen bonds with one hydrogen of water (2.797 Å). Hydrogen and oxygen of water form interactions with oxygen (2.620 Å) and hydrogen (1.838 Å) of the hydroxyl group. The oxygen of water also interacts with hydrogen on the azomethine carbon (C7) with a bond distance of 2.075 Å. Unfortunately, hydrogen atoms of water are not able to be located.

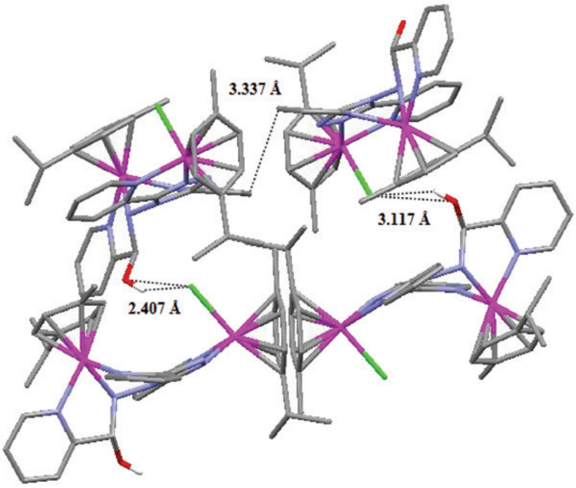


Figure 5. Hydrogen bonding network in **2**$[PF_6]_2$. Hydrogen atoms except for hydroxyl group have been removed for clarity.

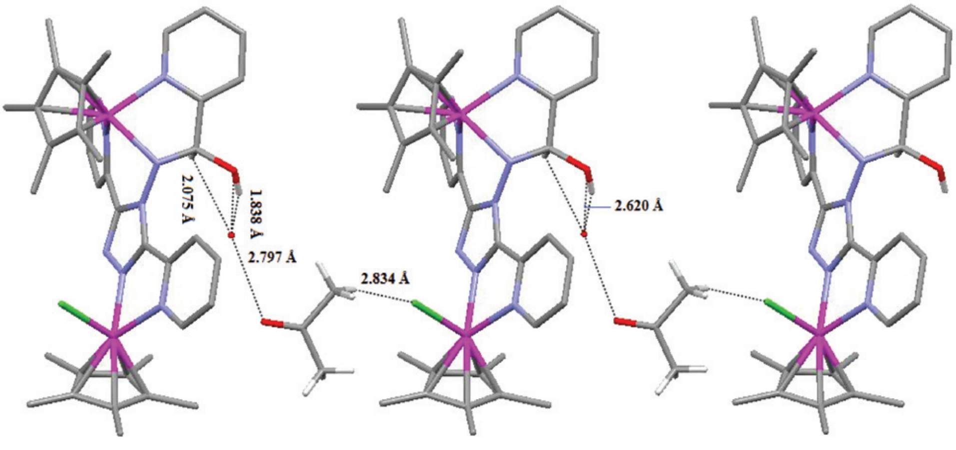


Figure 6. Hydrogen-bonding network in **4**$[PF_6]_2$. Hydrogen atoms except for hydroxyl group and acetone have been removed for clarity.

4. Conclusions

We have synthesized a new hexadentate Schiff base derived from dpt-NH_2 and pyridine 2-carbaldehyde in moderate yield. This ligand binds to metal centers in N,N and in N,N,N fashion and five new binuclear complexes have been synthesized. To the best of our knowledge, these are the first examples of hydroxylation which takes place on an azomethine carbon yielding stable hydroxylated products from the electrophilicity of the azomethine carbon. The ligand is uninegative, supported from crystal structure evidence pointing to the formation of dicationic complexes. Efforts to synthesize mononuclear and trinuclear complexes have not been successful, although we have carried out various attempts by varying the metal to ligand ratio as well as by varying the reaction conditions. The only products obtained are the dinuclear complexes, where a 1 : 1 ligand to metal ratio gives the highest yield of the complexes.

Supplementary material

CCDC-799974 [**2**]$(PF_6)_2$, 799975 [**4**]$(PF_6)_2 \cdot H_2O \cdot (CH_3)_2CO$ contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by e-mailing to data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

Acknowledgments

S. Gloria thanks UGC, New Delhi (F. 24-25/DSW/2009/187), for providing financial assistance in the form of fellowship. K.M. Rao gratefully acknowledges financial support from the UGC, New Delhi, through the Research grant No. F.No.39-793/2010 (SR). We thank Prof. R.H. Duncan Lyngdoh for his help in preparing this manuscript.

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