Synthesis and characterization of some cationic ruthenium(II) complexes based on polypyridyl ligand

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The cationic mononuclear complexes \([\text{Ru}(\eta^2\text{-arene})(\kappa^2\text{-dpp})(\text{EPH}_3)]^+\) (\(\eta^2\text{-arene} = \text{C}_9\text{H}_7\) (1), \(\text{C}_9\text{Me}_7\) (2), \(\text{CsH}_8\) (3); \(E=P\) (1a, 2, 3). As (1b); dpp = 2,3-bis(2-pyridyl) pyrazine) resulting from the reactions of \([\text{Ru}(\eta^2\text{-arene})(\kappa^2\text{-dpp})(\text{EPH}_3)]^+\) with dpp in equimolar ratio in methanol under refluxing conditions, containing both group 15 donor and a planar \(\pi\)-polypyridyl ligand are reported here. These complexes have been isolated as their hexafluorophosphate salts and fully characterized by elemental analyses and spectral techniques, viz. IR, \(^1\text{H}\) and \(^{31}\text{P}\) NMR, FAB-MS and electronic spectral studies.

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There is enormous attention recently in the synthesis and characterization of ruthenium(II) polypyridyl complexes because of their ability to behave as light harvesting antenna system, in the study of electron transfer reactions, elaboration at molecular level, self-assembly and as probes for DNA. Many luminescent and redox active compounds using polypyridyl bridging ligands containing delocalized \(\pi\) electron system have been synthesized and extensively studied. In this regard, 2,3-bis(2-pyridyl) pyrazine (dpp), a bis-chelating ligand which also acts as a good \(\pi\)-acceptor has drawn special attention. Further, extensive studies have been made on reactivity of readily available precursors, viz., \([\text{Ru}(\eta^2\text{-C}_9\text{H}_7\text{H})(\text{EPH}_3)]\) with \(E=P\) with various bases and polypyridyl ligands. In sharp contrast, reactivity of the analogous indenyl derivative \([\text{Ru}(\eta^2\text{-C}_9\text{H}_7\text{H})(\text{EPH}_3)]\) with \(E=P\) with N-bases and polypyridyl ligands has yet to be explored. Because of our interests in this area, we have examined reactivity of the above precursor complexes with dpp and isolated a new series of stable mononuclear cationic complexes \([\text{Ru}(\eta^2\text{-arene})(\kappa^2\text{-dpp})(\text{EPH}_3)]^+\). Due to the presence of the uncoordinated donor sites on dpp the cationic complexes, \([\text{Ru}(\eta^2\text{-arene})(\kappa^2\text{-dpp})(\text{EPH}_3)]^+\) offers an unique opportunity of behaving as \(\text{metallog-ligands}\) and could find applications in the synthesis of homo/hetero binuclear systems. As a prelude to our detailed studies in this direction, we describe herein reproducible synthesis and spectral characterization of highly stable cationic mononuclear complexes with the general formulation \([\text{Ru}(\eta^2\text{-arene})(\kappa^2\text{-dpp})(\text{EPH}_3)]PF_6\).

Materials and Methods

Analytical or chemically pure grade reagents were always used. All the reactions were performed under nitrogen atmosphere. The solvents were dried and distilled by standard procedure before use. Triphenylphosphine, triphenylarsine, hydrated ruthenium(III) chloride, 2,3-bis(2-pyridyl) pyrazine (dpp) and ammonium hexafluorophosphate (all Aldrich) were used as received. The precursor complexes \([\text{Ru}(\eta^2\text{-C}_9\text{H}_7\text{H})(\text{PPH}_3)]\), \([\text{Ru}(\eta^2\text{-C}_9\text{Me}_7\text{H})(\text{AsPPh}_3)]\), \([\text{Ru}(\eta^2\text{-C}_9\text{Me}_7\text{H})(\text{PPh}_3)]\) and \([\text{Ru}(\eta^2\text{-C}_9\text{H}_7\text{H})(\text{PPh}_3)]\) were prepared and purified following the reported procedures.

Microanalyses of the complexes were performed by micro-analytical division of SAIF, Central Drug Research Institute, Lucknow. Infrared and Electronic spectra of the complexes were recorded on a Perkin Elmer-577 and Shimadzu UV-1601 spectrophotometer, respectively. The \(^1\text{H}\) and \(^{31}\text{P}\) NMR spectra were recorded on a Bruker-DRX-300 NMR instrument in CDCl\(_3\) with tetramethylsilane as the internal standard. FAB mass spectra were obtained on a JEOL SX 102/DA 6000 mass spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature with m-nitrobenzyl alcohol as the matrix.
elemental analyses and spectral studies, viz. IR, $^1$H and $^{31}$P NMR, FAB-MS, and electronic spectroscopy.

Analytical data of the complexes (Table 1) are in good agreement with the respective formulations. Further information about composition of the complexes was obtained from FAB-MS of the complexes, as given in Table 2. The position of various peaks and overall fragmentation pattern of the complexes correspond to their respective formulations. Fragmentation pattern and the assignment of different peaks for the representative complexes 1a and 2 are shown in Fig. 1.

IR spectra of the complexes in nujol displayed bands in the region of 1670-1510 cm$^{-1}$, which can be assigned to $\nu$(C-N) and $\nu$(C=C) stretching vibrations of the dpp ligand. Precise assignment of different vibrations for all the complexes is not possible as vibrations are often coupled. All the complexes display broad bands due to presence of counter anion PF$_6$ at $\sim$830 cm$^{-1}$.

The $^1$H NMR spectral data and the numbering scheme used for the assignment of protons in the complexes 1a, 1b, 2, and 3 are recorded in Table 2. Spectra of all the complexes show analogous pattern and display signals associated with the coordinated dpp, cyclopentadienyl, pentamethylcyclopentadienyl, indenyl group and aromatic protons of EPh$_3$ in the respective complexes. Salient spectral features of the representative complex [Ru($\eta^5$-C$_5$H$_5$)(K$_2$-dpp)(PPh$_3$)]PF$_6$ (1a) is described here. The $^1$H NMR spectrum of the uncoordinated ligand dpp, displays doublets assignable to the proton at 1/2, 6/6' and 3/3' position and triplet corresponding to the proton at 5/5' and 4/4' position. The $^1$H NMR spectrum of the complex 1a displays resonance at $\delta$ 9.39 (d, 1H, J(HH) 2.7 Hz, H$_1$), 9.24 (d, 1H, J(HH) 5.4 Hz, H$_2$), 8.62 (d, 1H, J(HH) 4.5 Hz, H$_3$), 8.26 (d, 1H, J(HH) 3.3 Hz, H$_4$), 8.01 (dt, 2H, J(HH) 6.6 Hz, H$_{5r}$), 7.51 (dt, 2H, J (HH) 6.9 Hz, H$_{5s}$), 7.63 (d, 2H, J (HH) 6.4 Hz, H$_{12}$) ppm corresponding to dpp ligand. These protons exhibit a downfield shift as compared to that in the free ligand. Upon coordination with ruthenium, the dpp ligand loses its symmetry, results in different chemical shifts for pyrazine ring protons H$_1$ and H$_2$ a similar effect is visualized for the H$_{5r}$ and H$_{5s}$ of the uncoordinated and coordinated pyridyl ring protons of the dpp ligand. It clearly indicates that the ligand 2,3-bis(2-pyridyl) pyrazine (dpp) interacts with the metal centre in $\kappa^2$ manner. The aromatic protons of the PPh$_3$ resonate as a broad multiplet at $\delta$ 7.53-6.96 ppm, and the Cp

**Synthesis of the complexes**

All the cationic complexes (1a, 1b, 2, 3) were obtained by a general procedure. Detailed method for the synthesis of the complex 1a is given below:

**Synthesis of [Ru($\eta^5$-C$_5$H$_5$)(r$_2$-dpp)(PPh$_3$)]PF$_6$ (1a)**

To a suspension of the complex [Ru($\eta^5$-C$_5$H$_5$)(PPh$_3$)]Cl (0.728 g, 1.0 mmol) in 25 mL of methanol, dpp (0.234 g, 1.0 mmol) was added, and the contents of the flask were heated under reflux for 4 h. Slowly, the complex [Ru($\eta^5$-C$_5$H$_5$)(PPh$_3$)]Cl dissolved and gave a black-brown solution. After cooling to room temperature it was filtered to remove any solid residue. Then, the filtrate was concentrated under reduced pressure to one fourth of its volume and a saturated solution of ammonium hexafluorophosphate dissolved in methanol was added to it and left for slow crystallization in a refrigerator ($\sim$4°C). Slowly, a brown crystalline product was obtained, which was separated by filtration and washed with diethyl ether and dried in vacuo.

**Results and Discussion**

Reactions of the precursor complex [Ru($\eta^5$-arene)(EPh$_3$)-Cl] with 2,3-bis(2-pyridyl)pyrazine (dpp) in 1:1 molar ratio in methanol afforded new cationic complexes in excellent yield according to Scheme 1.

The complexes 1a, 1b, 2, and 3, were isolated as their hexafluorophosphate salts. The air stable, non-hygroscopic solids are soluble in common organic solvents, viz. dichloromethane, chloroform, dimethyl sulfoxide, dimethyl formamide, acetonitrile and sparingly soluble in methanol, ethanol, and insoluble in benzene, diethyl ether, and petroleum ether. Information about the composition and mode of bonding in the complexes has been derived from
### Table 1 — Analytical data of complexes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complexes</th>
<th>Found (Calcd.) %</th>
<th>Absorption (νC=O, cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>1a</td>
<td>[Ru(η⁵-C₅H₅)(κ²-dpp)(PPh₃)]PF₆</td>
<td>55.05</td>
<td>3.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(55.01)</td>
<td>(3.71)</td>
</tr>
<tr>
<td>Yield: 78% (0.629 g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>[Ru(η⁵-C₅H₅)(κ²-dpp)(AsPh₃)]PF₆</td>
<td>52.40</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(52.17)</td>
<td>(3.53)</td>
</tr>
<tr>
<td>Yield: 80% (0.680 g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>[Ru(η⁵-C₅Me₅)(κ²-dpp)(PPh₃)]PF₆</td>
<td>57.18</td>
<td>4.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(57.47)</td>
<td>(4.56)</td>
</tr>
<tr>
<td>Yield: 84% (0.737 g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[Ru(η⁵-C₅Me₅)(κ²-dpp)(PPh₃)]PF₆</td>
<td>57.07</td>
<td>3.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(57.41)</td>
<td>(3.73)</td>
</tr>
<tr>
<td>Yield: 77% (0.660 g)</td>
<td></td>
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</tbody>
</table>

### Table 2 — 'H NMR, '¹³C NMR and FAB mass spectral data of the complexes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complexes</th>
<th>'H NMR, ppm</th>
<th>'¹³C NMR, ppm</th>
<th>FAB-MS (m/z obs.(calcd.), rel.int., assignments)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>[Ru(η⁵-C₅H₅)(κ²-dpp)(PPh₃)]PF₆</td>
<td>9.39 (d, 1H, J(H,H) 2.7 Hz, H₁), 9.24 (d, 1H, J(H,H) 5.4 Hz, H₂), 8.62 (d, 1H, J(H,H) 4.5 Hz, H₃), 8.26 (d, 1H, J(H,H) 3.3 Hz, H₄), 8.01 (dt, 2H, J(H,H) 4.5 Hz, H₅+₆), 7.65 (d, 2H, J(H,H) 6.4 Hz, H₇+₈), 7.35 (d, 2H, J(H,H) 6.4 Hz, H₉+₁⁰), 7.53 (d, 2H, J(H,H) 6.4 Hz, H₁¹+₁²), 7.23-7.03 (br.m., 15H of PPh₃), 4.78 (s, 5H)</td>
<td>48.32, -144.1 (Septet, P₃Ph)</td>
<td>662 (662), 70 (Ru(η⁵-C₅H₅)(κ²-dpp)(PPh₃))²⁺, 400 (400), 100 (Ru(η⁵-C₅H₅)(κ²-dpp)P₃Ph₃)²⁺</td>
</tr>
<tr>
<td>1b</td>
<td>[Ru(η⁵-C₅Me₅)(κ²-dpp)(PPh₃)]PF₆</td>
<td>9.34 (d, 1H, J(H,H) 2.6 Hz, H₁), 9.20 (d, 1H, J(H,H) 5.5 Hz, H₂), 8.60 (d, 1H, J(H,H) 4.5 Hz, H₃), 8.24 (d, 1H, J(H,H) 3.0 Hz, H₄), 8.07 (dt, 2H, J(H,H) 6.4 Hz, H₅+₆), 7.62 (d, 2H, J(H,H) 5.4 Hz, H₇+₈), 7.54 (dt, 2H, J(H,H) 6.5 Hz, H₉+₁⁰), 7.23-7.03 (br.m., 15H of PPh₃), 4.75 (s, 5H)</td>
<td>143.7, -144.1 (Septet, P₃Ph₃)</td>
<td>705(706), 65 (Ru(η⁵-C₅Me₅)(κ²-dpp)(PPh₃))²⁺, 400 (400), 90 (Ru(η⁵-C₅Me₅)(κ²-dpp)P₃Ph₃)²⁺</td>
</tr>
<tr>
<td>2</td>
<td>[Ru(η⁵-C₅Me₅)(κ²-dpp)(PPh₃)]PF₆</td>
<td>9.16 (d, 1H, J(H,H) 3.0 Hz, H₁), 8.98 (d, 1H, J(H,H) 2.7 Hz, H₂), 8.78 (d, 1H, J(H,H) 5.7 Hz, H₃), 8.67 (d, 1H, J(H,H) 3.0 Hz, H₄), 8.50 (d, 1H, J(H,H) 3.0 Hz, H₅+₆), 8.00 (d, 2H, J(H,H) 8.5 Hz, H₇+₈), 7.81 (d, 2H, J(H,H) 6.6 Hz, H₉+₁⁰), 7.39-7.19 (br.m., 15H of PPh₃), 4.43 (s, 5H)</td>
<td>44.47, -144.2 (Septet, P₃Ph₃)</td>
<td>732 (732), 25 (Ru(η⁵-C₅Me₅)(κ²-dpp)(PPh₃))²⁺, 470(470), 60 (Ru(η⁵-C₅Me₅)(κ²-dpp)P₃Ph₃)²⁺</td>
</tr>
</tbody>
</table>

(Contd.)
protons resonate as a singlet at $\delta$ 4.78 ppm. The presence of a sharp resonance assignable to Cp protons suggests coordination of the Cp ligand with the metal centre in $\eta^5$-manner. The position and integrated intensity of various signals in the $^1$H NMR spectra of the complex 1 and other complexes have been found to be consistent with their respective formulations. In the $^{31}$P NMR spectrum of the complex 1a, the signal associated with $^{31}$P nuclei of the coordinated PPh$_3$ resonates as a singlet at $\delta$ 48.32 ppm, while the signal due to counter ion PF$_6$ appears at $\delta$ -144.1 ppm in its characteristic septet pattern. A similar trend of resonance is observed for the analogous ruthenium complexes 2 and 3.

The low spin $d^6$ configuration of new series of complexes provides filled orbital of proper symmetry on Ru(II), which can interact with the low lying $\pi$ orbital of the 2,3-bis(2-pyridyl) pyrazine (dpp). One should, therefore, expect a band attributed to metal to ligand charge transfer MLCT ($t_{2g} \rightarrow \pi$) transition in the electronic spectra of these complexes. Electronic spectra of these complexes 1a, 1b, 2, and 3 displayed medium intensity bands in the visible region at ~516 nm an intense band at ~309 nm and at ~234 nm. The
low intensity band centred at 516 nm has been assigned to metal-to-ligand charge transfer transition Ru(t$_2$)→π (dpp) bands. The intense band at 309 nm has been assigned to metal perturbed LC transition [Ru(e$^<$π$>$)→π (dpp)] by its analogy with the band in the free ligand. The high-energy band at 234 nm has been assigned to intra-ligand π→π transitions.

**Conclusions**

The new series of cationic complexes [Ru($\eta^5$-arene)(κ-dpp)(EPPh$_3$)]$^+$ (where, $\eta^5$-arene = C$_6$H$_5$, C$_6$Me$_5$, C$_6$H$_4$; EPPh = PPh$_3$, AsPh$_3$) have the potential to exhibit rich substitution chemistry. Due to presence of uncoordinated N-donor sites on the dpp ligand, the complexes have the potential to behave as ‘metallos' and could find wide applications in the development of binuclear complexes. At this stage, it has not been possible to confirm structure of any of the complexes by single crystal X-ray diffraction studies. More detailed investigations towards reactivity of the complexes and their use as ‘metallos' for the formation of binuclear complexes are in progress in our laboratory.

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**References**


