Synthesis and characterization of some homo/hetero binuclear hydrido carbonyl ruthenium(II) polypyridyl complexes

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Mononuclear hydrido carbonyl complex \([\text{RuHCO}(\text{PPh}_3)_2(\eta^2\text{tpz})]\)BF_4 (tpz = 2,4,6-tris(2'-pyridyl)-1,3,5-triazine) has been used as a building block in the synthesis of homo/hetero binuclear complexes. The complex \([\text{RuHCO}(\text{PPh}_3)_{(2\text{tpz})}]\)BF_4 behaves as a potential metallo-ligand. Its reaction with different molecules ranging from \(\text{K}_2\text{PtCl}_4, [\text{PdCl}_2(\text{PhCN})]_2\), chloro-bridged dimeric arene ruthenium complexes \([\text{Ru}(\text{PPh}_3)(\eta^2\text{arene})(\mu-\text{Cl})\text{Cl}_2]\) (arene = p-cymene or benzene), \([\text{Rh}(\text{COD})(\mu-\text{Cl})\text{Cl}_2]\) (COD = 1,5-cyclooctadiene) leads to the formation of binuclear complexes. The homo and hetero binuclear tptz bridged complexes \([\text{RuHCO}(\text{PPh}_3)(\mu-\text{tpz})\text{Cl}(\text{PhCN})]_2\), \([\text{RuHCO}(\text{PPh}_3)_2(\mu-\text{tpz})\text{Cl}(\text{PhCN})_2]\), \([\text{RuHCO}(\text{PPh}_3)_2(\mu-\text{tpz})(\eta^2\text{C}_6\text{H}_6)\text{RuCl}]_2\), \([\text{RuHCO}(\text{PPh}_3)_2(\mu-\text{tpz})(\eta^2\text{C}_6\text{H}_6)\text{RuCl}]_2\) have been synthesized and characterized using IR, NMR, ESMS and FAB mass spectra.

During recent past, there has been an increasing interest in the synthesis and characterization of binuclear organometallic complexes and such species have been used to model fundamental properties of multi- and polymeric organometallic materials that have potential optical and/or electronic applications. In binuclear complexes, each metal unit can impart specific properties to the resulting supramolecular structure such as the capacity to absorb or emit visible light and to reversibly exchange electrons. These compounds could find wide application as components in molecular electronics and as photochemical molecular devices for solar energy conversion and information storage. Since past few years we have been engaged in the synthesis of metallo-ligand, which might be used as a ligand or a small unit for building supramolecular systems. Only recently, we have synthesized and structurally characterized the complex \([\text{RuHCO}(\text{PPh}_3)_2(\eta^2\text{tpz})]\)BF_4 (Structure I) which contains uncoordinated nitrogen donor sites and can be employed as a metallo-ligand in the synthesis of homo/hetero binuclear systems.

The current interests in the poly-pyridyl ligands and in continuation of our studies towards synthesis of metallo-ligands/synths on based on organometallic systems, which could be employed in the synthesis of homo/hetero bi- or polynuclear complexes, have lead to study the reactivity of the complex \([\text{RuHCO}(\text{PPh}_3)_2(\eta^2\text{tpz})]\)BF_4. It is seen that the reaction of \(\text{K}_2\text{PtCl}_4, [\text{PdCl}_2(\text{PhCN})_2]\), chloro-bridged dimeric arene ruthenium complexes \([\text{Ru}(\text{PPh}_3)(\eta^2\text{arene})(\mu-\text{Cl})\text{Cl}_2]\) (arene = p-cymene or benzene), \([\text{Rh}(\text{COD})(\mu-\text{Cl})\text{Cl}_2]\) and \([\text{Rh}(\text{COD})(\mu-\text{Cl})\text{Cl}_2]\) (COD = 1,5-cyclooctadiene) leads to the formation of binuclear complexes \([\text{RuHCO}(\text{PPh}_3)_2(\mu-\text{tpz})\text{Cl}(\text{PhCN})]_2\)BF_4, \([\text{RuHCO}(\text{PPh}_3)_2(\mu-\text{tpz})\text{Cl}(\text{PhCN})_2]\)BF_4, \([\text{RuHCO}(\text{PPh}_3)_2(\mu-\text{tpz})(\eta^2\text{C}_6\text{H}_6)\text{RuCl}]_2\)BF_4, \([\text{RuHCO}(\text{PPh}_3)_2(\mu-\text{tpz})(\eta^2\text{C}_6\text{H}_6)\text{RuCl}]_2\)BF_4 and \([\text{RuHCO}(\text{PPh}_3)_2(\mu-\text{tpz})\text{Cl}(\text{PhCN})]_2\)BF_4, \([\text{RuHCO}(\text{PPh}_3)_2(\mu-\text{tpz})(\eta^2\text{C}_6\text{H}_6)\text{RuCl}]_2\)BF_4 and \([\text{RuHCO}(\text{PPh}_3)_2(\mu-\text{tpz})\text{Cl}(\text{PhCN})]_2\)BF_4 have been synthesized and characterized using IR, NMR, ESMS and FAB mass spectra.

Experimental

All the reactions were carried out under nitrogen atmosphere and with deaerated solvents. The solvents were of AR grade and were purified by standard procedures prior to their use. 2,4,6-tris(2'-pyridyl)-1,3,5-triazine, ammonium tetrafluoroborate, ammonium hexafluorophosphate, ruthenium(III) chloride hydrate (all Aldrich) and tetrabutyl ammonium perchlorate (Fluka) were used as received without further purification. The complex \([\text{RuHCO}(\text{Cl}(\text{PPh}_3))_2]^{11}, [\text{RuHCO}(\text{PPh}_3)_2(\eta^2\text{tpz})]-\)
Preparation of complexes

**Preparation of [RuH(CO)(PPh₃)_2(μ-μ₉-tptz)]BF₄⁻₁**

Methanolic solution (20 mL) of [RuH(CO)(PPh₃)_2(μ-μ₉-tptz)]BF₄ (527 mg, 0.5 mmol) was refluxed with K₂PtCl₆ (208 mg, 0.5 mmol) solution in methanol for 24 h. It was cooled to room temperature and filtered. Red brown solution thus obtained, was treated with a solution of NH₄BF₄ (163 mg, 1 mmol) dissolved in methanol (10 mL). It was evaporated to 10 mL under reduced pressure and left overnight. Light yellow coloured microcrystalline complex appeared. It was filtered, washed with methanol, diethyl ether and dried under vacuo. Yield: 70%; Anal. Caled. for BrCl,C₈H₁₄N₂O₂P₂Ru: C, 50.03; H, 3.26; N, 6.36; Found: C, 50.91; H, 3.48; N, 5.94; FAB MS [m/z]: 1232 (calcd.) for [RuH(CO)(PPh₃)_2(μ-μ₉-tptz)]BF₄⁻₁, 1234 (calcld.); IR (cm⁻¹, nujol): 2006 ν(Ru-H), 1955 ν(CO), 1585, 1575, 1550, 1540, 1520, 1440, 1365, 1312, 1250, 1160, 1035, 986, 845, 735, 690 (bands due to tptz, PPh₃ and counter anion BF₄⁻₁); ¹H NMR (δ ppm, Acetone-d₆, 300 MHz, 25°C): 9.21 (d, 4.5 Hz), 8.82 (d, 4.2 Hz), 8.32 (t, 7.5 Hz), 7.92 (t, 7.1 Hz), 7.72 (t, 5.2 Hz), 7.34 (br. m), -11.70 (t, 21 Hz); ³¹P[¹H]: 41.44 (s); UV-vis (λmax nm): 510, 391, 336.

**Preparation of [RuH(CO)(PPh₃)_2(μ-μ₉-tptz)]PtCl₄⁻₂**

This complex was prepared by the above procedure except that the complex [PtCl₄Cl(CN)₄] was used in place of K₂PtCl₆. It separated as brown crystalline product. Yield: 52%; Anal. Caled. for BrCl,C₈H₁₄N₂O₂P₂Ru: C, 53.65; H, 3.49; N, 6.82; Found: C, 54.51; H, 3.93; N, 6.26; FAB MS [m/z]: 1143 (calcld.) for [RuH(CO)(PPh₃)_2(μ-μ₉-tptz)]BF₄⁻₁, 1144; ¹H NMR (δ ppm, Acetone-d₆, 300 MHz, 25°C): 9.32 (d, 6.1 Hz), 8.92 (d, 4.2 Hz), 8.46 (t, 4.6 Hz), 7.92 (m), 7.52 (t, 3.6 Hz), 7.21 (br. m), -11.93 (t, 19 Hz); ³¹P[¹H]: 45.44 (s); UV-vis (λmax nm): 516, 362, 310.

**Preparation of [RuH(CO)(PPh₃)_2(μ-μ₉-tptz)](μ-C₆H₆)RuCl⁺₂**

Complex 3 was prepared by reaction of [RuH(CO)(PPh₃)_2(μ-μ₉-tptz)]BF₄ (527 mg, 0.5 mmol) in methanol (20 mL) with [Ru(η⁶-C₆H₆)(μ-μ₉-tptz)]BF₄ (306 mg, 0.5 mmol) following the above procedure. It was filtered and treated with methanolic solution of NH₄BF₄ (163 mg, 1 mmol). It appeared in the form of dark green crystalline solid. Yield: 51%; Anal. Caled. for BrCl,C₈H₁₄N₂O₂P₂Ru: C, 55.27; H, 4.03; N, 5.95; Found: C, 53.99; H, 4.06; N, 5.18; FAB MS [m/z]: 1240, (calcld.) for [RuH(CO)(PPh₃)_2(μ-μ₉-tptz)(μ-C₆H₆)]BF₄⁻₂, 1237; ¹H NMR (δ ppm, CDCl₃, 300 MHz, 25°C): 9.55 (d, 5.7 Hz), 9.14 (d, 4.8 Hz), 8.63 (d, 5.6 Hz), 8.09 (t, 4.6 Hz), 7.62 (m), 7.25 (br. m), 6.74 (s), 6.05-5.87 (dd), 2.56 (sep, 7.1 Hz), 2.21 (s), 0.98 (dd), -10.50 (t, 16 Hz); ³¹P[¹H]: 46.52 ppm (s); UV-vis (λmax nm): 495, 380, 290.

**Preparation of [RuH(CO)(PPh₃)_2(μ-μ₉-tptz)](μ-C₆H₆)PtCl⁺₂**

It was prepared by reaction of [RuH(CO)(PPh₃)_2(μ-μ₉-tptz)]BF₄ (527 mg, 0.5 mmol) complex in methanol (20 mL) with [Ru(η⁶-C₆H₆)(μ-μ₉-tptz)]BF₄ (306 mg, 0.5 mmol) following the above procedure. After filtration methanolic solution of NH₄BF₄ (163 mg, 1 mmol) was added. It separated as intense green micro-crystals. Yield: 70%; Anal. Caled. for BrCl,C₈H₁₄N₂O₂P₂Ru: C, 54.02; H, 3.61; N, 6.19; Found: C, 54.32; H, 3.58; N, 5.70; FAB MS [m/z]: 1177, (calcld.) for [RuH(CO)(PPh₃)_2(μ-μ₉-tptz)(μ-C₆H₆)]Cl⁻₂, 1181; ¹H NMR (δ ppm, CDCl₃, 300 MHz, 25°C): 9.26 (d, 5.2 Hz), 8.84 (d, 4.7 Hz), 8.48 (m), 8.17-7.88 (m), 7.84-7.36 (m), 7.40-6.92 (br. m), 5.41 (s), -12.9 (t, 1.7 Hz); ³¹P[¹H]: 50.82 ppm (s); UV-vis (λmax nm): 532, 437, 315.
Preparation of $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{tpz})(\text{COD})][\text{BF}_4]$₂, 5

Complex 5 was prepared following the above procedure from $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{tpz})][\text{BF}_4]$ (527 mg, 0.5 mmol) and $[\text{Rh}(\text{COD})(\text{μ-Cl})]_2$ (246.5 mg, 0.5 mmol). It was treated with methanolic solution of NH₄BF₄ (163 mg, 1 mmol), and separated as yellow brown microcrystalline solid. Yield: 43%; Anal. Calcd. for B₂C₅F₈H₂₃N₂OP₂Rh: C, 55.95; H, 4.07; N, 6.21; Found: C 56.7; H, 4.12; N, 6.87; 'H NMR (δ ppm, Acetone-d₆, 300 MHz, 25°C): 9.25(d, 7.6 Hz), 8.78(d, 5.4 Hz), 8.38(t, 5.7 Hz), 7.90(t, 5.5 Hz), 7.62(t, 5.4 Hz), 7.38(br.m), 1.65, -11.70(t, 18 Hz); ³¹P{₁H}: 44.41(s)UV-vis (λₘₐₓ nm): 567, 432, 283.

Preparation of $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{μ-tpz})\text{Rh}(\text{η}^2\text{-C}_5\text{Me}_5\text{Cl})][\text{BF}_4]$₂, 6

The complex 6 was prepared according to the above described method with $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{tpz})][\text{BF}_4]$ (527 mg, 0.5 mmol) and $[\text{Rh}(\text{COD})(\text{μ-tpz})\text{Cl}]_2$ (306 mg, 0.5 mmol) dissolved in methanol (20 mL). It was cooled to room temperature and filtered. The red brown solution thus obtained, was treated with methanolic solution of NH₄BF₄ (163 mg, 1 mmol). It was rotaraported to 10 mL and left overnight. Light yellow colored microcrystalline complex appeared. These were filtered, washed with methanol, diethyl ether and dried under vacuo. Yield 41% Anal. Calcd. for B₂C₅F₈H₂₃N₂OP₂Rh: C, 55.16; H, 4.10; N, 5.94; Found: C 55.31; H, 4.18; N, 5.28; FAB MS (m/z): 1325, (calcd. for $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{μ-tpz})\text{Rh}(\text{η}^2\text{-C}_5\text{Me}_5\text{Cl})][\text{BF}_4]$): 1327); 'H NMR (δ ppm, Acetone-d₆, 300 MHz, 25°C): 9.23(d, 5.4 Hz), 8.76(d, 7.6 Hz), 8.38(t, 5.7 Hz), 7.90(t, 6.0 Hz), 7.62(t, 5.4 Hz), 7.38(br.m), 1.65, -11.73(t, 22 Hz), ³¹P{₁H}: 44.35(s), UV-vis (λₘₐₓ nm): 517, 440, 335.

Results and discussion

Synthetic interest in hetero bimetallic complexes have increased during past few years, due to the fact that the reactivity and properties of metal may be strongly modified by the presence of another metallic centre in close proximity. One of the main reasons of such interest might be cooperative influence of neighbouring metal centres on catalytic reactions. The design of these complexes involves multidentate polypyrrolidyl ligand tpz as a bridging ligand between Ru-Rh containing complexes, specially systems incorporating Ru polypyrrolidyl moiety is well known photosensitizer⁷. Precursor complex $[\text{RuH}(\text{CO})(\text{PPh}_3)(\text{η}^2\text{-tpz})][\text{BF}_4]$ has been synthesized by our previously reported method⁸. The complexes 1-6 have been obtained following general Scheme 1.

Here ligand tpz is used as a bridging ligand between two metal centres. Schematic representation of the synthesized complexes have shown in Scheme 2.

The binuclear complexes $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{μ-tpz})\text{PdCl}]_2$ 1, $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{μ-tpz})][\text{PdCl}]_2$ 2, $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{μ-tpz})\text{Rh}(\text{η}^2\text{-COD})\text{Cl}]_2$ 3, $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{μ-tpz})\text{Rh}(\text{η}^2\text{-COD})\text{Cl}]_2$ 4, $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{μ-tpz})\text{Rh}(\text{η}^2\text{-COD})\text{Rh}]_2$ 5, $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{μ-tpz})\text{Rh}(\text{η}^2\text{-COD})\text{Rh}]_2$ 6 are yellowish brown to green, air-stable, non-hygroscopic shiny crystalline solids. These are sparingly soluble in dichloromethane, chloroform, methanol and ethanol, highly soluble in acetone, acetonitrile, dimethylsulphoxide, dimethylformamide and insoluble in benzene, petroleum ether, and diethyl ether. These exhibit 1:1 conductance behaviour in nitromethane. Carbon, hydrogen and nitrogen analyses of all the complexes conformed well to our formulations (Table 1). FAB MS spectra of the complex 1 and 2 show prominent peaks at m/z 1234.
Scheme 2

$[\text{Ru}(\text{CO})(\text{Ph})_3]_2(\mu-\text{tpz})[\eta^6-C_{10}H_{14}]\text{RuCl}]^{2+}$
$m/z$ 1240 (calcd. 1237)

$[\text{Ru}(\text{CO})(\text{Ph})_3]_2(\mu-\text{tpz})[\text{RuCl}]^{2+}$
$m/z$ 1102 (calcd. 1103)

Scheme 3

$[\text{Ru}(\text{CO})(\text{Ph})_3](\mu-\text{tpz})]^{2+}$
$m/z$ 675 (calcd. 675)

$[\text{Ru}(\text{tpz})]^{2+}$
$m/z$ 414 (calcd. 414)
Table 1—Analytical data of the complexes

<table>
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<tr>
<th>Sl. No.</th>
<th>Complexes</th>
<th>Colour</th>
<th>Found (%)</th>
<th>Calcd (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{RuH(CO)(PPh}_3\text{H}_2\text{tptz)}\text{PtCl}_2\text{BF}_4])</td>
<td>Light yellow</td>
<td>50.91</td>
<td>5.94</td>
</tr>
<tr>
<td>2</td>
<td>([\text{RuH(CO)(PPh}_3\text{H}_2\text{tptz)}\text{PdCl}_2\text{BF}_4])</td>
<td>Brown</td>
<td>50.03</td>
<td>6.36</td>
</tr>
<tr>
<td>3</td>
<td>([\text{RuH(CO)(PPh}<em>3\text{H}<em>2\text{tptz)}\text{C}</em>{11}\text{H}</em>{14}\text{RuCl}]\text{BF}_4)</td>
<td>Dark green</td>
<td>53.99</td>
<td>5.18</td>
</tr>
<tr>
<td>4</td>
<td>([\text{RuH(CO)(PPh}_3\text{H}_2\text{tptz)}\text{Rh(COD)}\text{BF}_4])</td>
<td>Green</td>
<td>53.22</td>
<td>5.70</td>
</tr>
<tr>
<td>5</td>
<td>([\text{RuH(CO)(PPh}_3\text{H}_2\text{tptz)}\text{Rh(CCOD)}\text{BF}_4])</td>
<td>Yellow Brown</td>
<td>54.02</td>
<td>6.82</td>
</tr>
<tr>
<td>6</td>
<td>([\text{RuH(CO)(PPh}_3\text{H}_2\text{tptz)}\text{Rh(CCOD)}\text{BF}_4])</td>
<td>Red Brown</td>
<td>55.31</td>
<td>5.28</td>
</tr>
</tbody>
</table>

and 1143 respectively, corresponding to complexes \([\text{RuH(CO)(PPh}_3\text{H}_2\text{tptz)}\text{PtCl}_2\text{BF}_4]\) and \([\text{RuH(CO)(PPh}_3\text{H}_2\text{tptz)}\text{PdCl}_2\text{BF}_4]\) which are consistent with our formulations. In the FAB mass spectrometry of 3, the molecular ion peak corresponding to \([\text{RuH(CO)(PPh}_3\text{H}_2\text{tptz)}\text{C}_{11}\text{H}_{14}\text{RuCl}]\text{BF}_4\) appears at m/z 1240 (calcd. 1237). Fragmentation pattern of the complex is according to Scheme 3.

The FAB mass spectra of complex 4 exhibit peaks at m/z 1177, 1144 (calcd., 1146), 1108 (calcd. 1108), 1068 (calcd. 1068), 967 (calcd. 967) corresponding to \([\text{RuH(CO)(PPh}_3\text{H}_2\text{tptz)}\text{C}_{11}\text{H}_{14}\text{RuCl}]\text{BF}_4\) respectively. Overall fragmentation patterns of the other complexes are also consistent with the formulation of the binuclear complexes.

Infra red spectra of the complexes exhibit characteristic bands due to coordinated ligands tptz, PPh3, CO and hydride group in the respective complexes. Interestingly, the position of \(\nu(\text{C}=\text{O})\) and \(\nu(\text{Ru-H})\) in the IR spectra of the complexes shifts toward higher and lower frequency. It indicates a decrease in the metal to carbonyl carbon interaction and an increase in the Ru-H bond order.

To facilitate assignment of different resonance, \(^1\text{H}-\) \(^1\text{H}\) COSY experiment for the complex 3 has been carried out. \(^1\text{H}\) NMR spectrum of complex 1 exhibits distinct resonances in the region \(\delta 9.21(\text{d}, 4.5 \text{ Hz}), 8.82(\text{d}, 4.2 \text{ Hz}), 8.32(\text{t}, 7.5 \text{ Hz}), 7.92(\text{t}, 7.1 \text{ Hz}), 7.72(\text{t}, 5.2 \text{ Hz}), 7.34(\text{br.m}), -11.70(\text{t}, 21 \text{ Hz}) \text{ ppm}\). It falls in the same range as that observed in the \(^1\text{H}\) NMR of the precursor complex \([\text{RuH(CO)(PPh}_3\text{H}_2\text{tptz)}\text{BF}_4]\).

The signals associated with tptz, PPh3 and hydride group displayed a downfield shift in complex 1 as compared to that in the precursor complex, clearly indicates that the ligand tptz is interacting with another metal centre through its uncoordinated nitrogen donor atoms. The \(^1\text{H}\) NMR spectra of complexes 2, 3, 4, 5 and 6 display additional signals due to coordinated arenes and dienes. The position and integrated intensity of different signals corroborated well to formulation of the complexes.

In the \(^1\text{H}\) NMR spectra of the 1, 2, 3, 4, 5 and 6 complexes, the hydride proton resonates in the high field side at \(\delta -11.70(\text{t}, 21 \text{ Hz}), -11.93(\text{t}, 19 \text{ Hz}), -10.50(\text{t}, 16 \text{ Hz}), -12.9(\text{t}, 17 \text{ Hz}), -11.70(\text{t}, 18 \text{ Hz})\) and \(-11.73(\text{t}, 22 \text{ Hz}) \text{ ppm}\) respectively. Presence of a triplet associated to metal bound hydride proton in the \(^1\text{H}\) NMR spectra of these complexes suggests that the hydride group be coupled with two equivalent \(^3\text{P}\) nuclei.

The \(^3\text{P}\{^1\text{H}\}\) NMR spectra of these complexes 1-6 display sharp singlets at \(\delta 41.44, 45.44, 46.52, 50.82, 41.44\) and 45.37 ppm respectively. It indicates that both the triphenylphosphine ligands in these complexes are equivalent and are mutually trans disposed.

Electronic spectra

Interaction of the filled orbitals of proper symmetry on d\(^6\) Ru(II), with the low lying \(\pi^*\) orbital of the ligand tptz should provide MLCT transition (\(\tau_2 \rightarrow \pi^*\)) in the electronic spectra of these complexes, with the transition energy varying with nature of the ligands acting as a \(\pi\) acceptor. In the electronic spectra of the precursor complex \([\text{RuH(CO)(PPh}_3\text{H}_2\text{tptz)}\text{BF}_4]\), three strong absorptions were observed at about 441, 389, and 335 nm. On the basis of the intensity and position
of the lowest energy absorption, it has been assigned to MLCT transition\textsuperscript{18}, while the one at \textasciitilde 389 nm may be of MLCT character, but the possibility of \( \sigma \) bond to ligand charge transfer SBLCT cannot be ruled out\textsuperscript{19}. The high-energy band has been assigned to intra-ligand \( \pi \rightarrow \pi^* \) transition or \( \pi_{(pheno)} \) to \( \pi^*_{(pheno)} \) transition\textsuperscript{20}. Electronic spectra of the bimetallic complexes in acetonitrile (recorded in the experimental section) at room temperature display intense peaks throughout the ultra-violet and visible region of the spectrum. It was found that Ru\textendash tptz CT transition of the precursor complex [RuH(CO)(PPh\(_3\))(η\(^2\)-tptz)]BF\(_4\) upon interaction with another metal centre through bridge formation on the tptz ligand, exhibits significant red shifts [complex I, 510; 2, 516; 3, 495; 4, 532 and 5, 567 nm] as compared to that in the precursor complex. The red shift in the position of Ru \textrightarrow tptzCT transition towards lower energy in these complexes, may result from stabilization of the tptz \( \pi^* \) orbital upon coordination of the second metal centre. Generally coordination of another metal ion at the remote uncoordinated site, results in stabilization of the \( \pi^* \) level of the bridging ligand leading to enhanced \( \pi \rightarrow \pi^* \) overlap\textsuperscript{21}. This effect lowers the HOMO-LUMO gap, which results in a lower energy shift of the MLCT bands in the binuclear complexes. The stabilization of the tptz \( \pi^* \) also leads to a red shift of the ligand based \( \pi \rightarrow \pi^* \) transitions. These observations strongly support the formation of the binuclear complexes and are consistent with other reports\textsuperscript{22}.

The above analytical and spectral data clearly indicate formation of tptz bridged homo/hetero binuclear complexes. We have proposed the above structures tentatively. At this stage, it has not been possible for us to confirm structure of any of these complexes by single crystal X-ray diffraction studies. We are trying to grow single crystals of a couple of these and hope that we will be able to confirm the structure in future.

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