Cationic diamine complexes of cyclopentadienylruthenium(II)

Rajendra Prasad, Lalit Mishra† & U C Agarwala∗
Department of Chemistry, Indian Institute of Technology, Kanpur 208 016
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Purely σ donor bidentate chelate diamine complexes of the type \([\text{RuCp(EPh}_3\text{h(N-N})]_{\text{Y}}\) and \([\text{RuCp(EPh}_3\text{h(N-N})]_{\text{Y}}\), where \(\text{Cp} = (\eta^5-C_5H_5)^{-}\); \(E = \text{P, As, Sb}\); \(N-N = \text{ethylenediamine, 1,2-diaminopropane, 1,6-diaminohexane, 1,2-phenylenediamine, and dimethylglyoxime; Y = BF}_3\), PF₆⁻, BPh₄⁻ have been synthesised. These complexes have been characterised, using microanalytical data, conductance measurements and spectral (IR, NMR, and UV-Visible) methods.

The half sandwich complexes of the type \([\text{RuCp(EPh}_3\text{hCl}\text{]}\) (where \(\text{Cp} = (\eta^5-C_5H_5)^{-}\), and \(E = \text{P, As, Sb}\)) are common precursors to synthesise their various substituted products. Thus these complexes undergo a variety of interesting reactions, but most of the previous work includes the stabilization of the low oxidation state of ruthenium(II) by strong π-acid ligands.

The published literature lacks substitution reactions using bidentate chelating strong σ donor ligands having no π-acid capabilities. This observation has led us to probe into the substitution reactions of these complexes using α,ω-diamines as substituents. As a follow up of our previous work, we report herein the reactions of \([\text{RuCp(EPh}_3\text{hCl}\text{]}\) with ethylenediamine (en), 1,2-diaminopropane(1,2-dap), 1,3-diaminopropane (1,3-dap), 1,6-diaminohexane (1,6-dah), ortho-phenylenediamine (1,2 dab) and dimethylglyoxime (dmg H₂).

Materials and Methods

Literature methods¹⁰–¹² were used to synthesise the complexes of the type \([\text{RuCp(EPh}_3\text{hCl}\text{]}\). Liquid diamines were distilled before use. 1,6-Diaminohexane, 1,2-diaminopropane and dimethylglyoxime were chemically pure. Various solvents were of AR grade and used as received.

The physicochemical measurements on the complexes (melting points, IR, electronic and PMR spectra were carried out as described elsewhere¹³.

The typical procedures to isolate the complexes are as follows:

(A) Preparation of chloride salts of \([\text{RuCp(EPh}_3\text{h}}_{\text{diamine}]^+\) cations

Diamine (0.4 to 0.8 mmole) was refluxed with a suspension of \([\text{RuCp(EPh}_3\text{hCl}\text{]}\) (0.2 mmole) in methanol (25 ml) for one and a half hr. A yellow solution resulted which was concentrated to 2-3 ml under reduced pressure, filtered through neutral alumina (deactivated by methanol) column (1 cm in length). The eluate was collected, which was subsequently used to isolate the complexes (vide supra).

(B) Preparation of chloride salts of \([\text{RuCp(EPh}_3\text{h}}_{\text{diamine}]^+\) cations

Diamine (0.4-0.8 mmole) was stirred with \([\text{RuCp(EPh}_3\text{hCl}\text{]}\) (0.2 mmole) in methanol (25 ml) for 6-8 hr. Solvent was removed under suction from the reaction mixture and the reduced volume was filtered through neutral alumina (deactivated by methanol) column (1 cm in length). The salts of the complex were obtained from the filtrate.

The tetraphenylborate salts of the complexes were obtained by adding concentrated methanolic solution of NaBPh₄ to the concentrated solution of chloride complexes obtained from procedures A and B. Yellow precipitate was formed immediately which was separated by filtration, washed with methanol followed by ether and dried under reduced pressure over CaCl₂. It was recrystallized from CH₂Cl₂/petroleum ether.

PF₆⁻ and BF₄⁻ salts do not separate out easily. They were obtained by adding a few drops of methanolic solutions of their sodium salts to the solutions of cationic complexes and removing the solvent under reduced pressure to obtain dry residue. It was extracted with dichloromethane and recrystallized by adding excess of petroleum ether. Precipitate was filtered and dried in vacuo over CaCl₂.

¹Filtration through methanol deactivated neutral alumina was necessary to remove certain suspended white particles from the complex solution.
Preparation of \([\text{RuCp(EPh)}_2\text{Cl}]\) complexes

\([\text{RuCp(EPh)}_2\text{Cl}]\) (0.1 mmole) and dimethylglyoxime (0.02 g; 0.2 mmole) in methanol (25 ml) was refluxed in the presence of sodium acetate (0.2 g). The reaction mixture was concentrated, cooled, the yellow solid filtered off, washed with methanol, followed by ether and dried in vacuo over CaCl₂.

Results and Discussion

Treatment of chlorocomplexes \([\text{RuCp(EPh)}_2\text{Cl}]\) with a very large excess of diamines in methanol, both at room temperature and under refluxing conditions resulted in the formation of yellow diamine cationic complexes by rapid displacement of one of the bulky EPh groups and the chloride ion in more than 50% yield. Their microanalytical data, melting points and the empirical formulae are listed in Table 1. All the complexes are stable in air at room temperature in solid state and are highly soluble in organic polar solvents like CH₂Cl₂, CHCl₃, acetone, DMF, etc. However, the tetraphenyl borate salts are only sparingly soluble in methanol and ethanol.

The molar conductivities (\(\Delta M\)) of their hexafluorophosphate salts \((1 \times 10^{-4} \text{ molar solutions})\) were found to be in the range of \(145 \pm 5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}\). This is well within the range for 1:1 electrolytes. The complexes 55-57 shown in Table 1 have molar conductances of around \(6 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}\) under identical conditions, indicating their nonelectrolytic nature.

The reaction of ethylenediamine, 1,2-diaminopropane and 1,2-phenylenediamine were smooth. These behaved as bidentate chelating ligands replacing Cl and one EPh, from \([\text{RuCp(EPh)}_2\text{Cl}]\) in methanol by both the methods (A) and (B). 1,3-Diaminopropane behaved as a bidentate ligand under method (A) but under method (B) it gave a mixture of mono- and bidentate products. With the increase in stirring period, the monodentate products got gradually converted into bidentate ones. Thus their monodentate cations have not been isolated.

The products of the reactions of 1,6-diaminohexane under refluxing condition (method A) yielded a mixture of monodentate and bidentate diamine complexes. But seemingly the amino groups and the six-carbon alkyl chain underwent some sort of rearrangement under the reaction conditions (method A), because no proper PMR signals for \(-\text{NH}_2\) and \(-\text{CH}_2-\) protons were observed in the PMR spectra of the products (vide supra). Variation in the reaction period has no effect on the nature of the mixture-product. In case only one molar excess of 1,6-diaminohexane was stirred with \([\text{RuCp(EPh)}_2\text{Cl}]\) in methanol, the cation complex \([\text{RuCp(EPh)}_2\text{Cl}]^{\text{I,6-dah}}\) was formed as a result of the facile ionization of chloride ion with subsequent attachment of diamine molecule. 1,6-Diaminohexane did not serve as a bidentate ligand in its reactions with \([\text{RuCp(EPh)}_2\text{Cl}]\) even after stirring upto 16 hr (method B).

Formation of hydrido derivative, \([\text{RuCp(EPh)}_2\text{Cl}];\text{H}\) has been frequently encountered as a parallel side reaction when the diamines and precursor complex are taken in 1:1 molar ratio. It is well documented that when alcohols which contain \(\alpha\)-hydrogen are used as reaction medium for \([\text{RuCp(EPh)}_2\text{Cl}];\text{Cl}\), bases catalyse formation of hydrido complexes. However, this side reaction is completely suppressed when the diamine is taken in excess amount, yielding exclusively diamine substitution products. Under these conditions amines directly displaces solvent (alcohol) molecule from the solvated cation of the precursor complex rather than abstracting proton and facilitating-hydrogen migration to give hydrides. Since the corresponding hydride complexes do not undergo substitution reaction by diamine, under similar conditions the possibility of the derivative as the intermediate is ruled out.

IR spectra

The IR and the PMR spectral data of the representative complexes are listed in Table 2. In their IR spectra all the complexes exhibited two absorption bands in the \(\nu \text{NH} - \text{H}\), viz. \(\nu_{\text{as}}\text{NH}\) and \(\nu_{\text{s}}\text{NH}\) in the region of 3250-3350 cm\(^{-1}\). The absorption bands characteristic of cyclopentadienyl, EPh, and counter anions dominate the rest of the IR spectrum.

\(^1\text{H NMR spectra}\)

As expected, all complexes contained only one signal corresponding to cyclopentadienyl protons. Coordinated \(\text{NH}_{2}\) protons appeared deshielded by nearly 1 ppm. The cyclopentadienyl proton signals in bidentate chelate complexes is invariably shifted low field than that in the corresponding monodentate cations (complexes 28-36). This downfield shift could tentatively be assigned to increased electron density on Ru atom.

Visible spectra

The lowest energy band in the diamine complexes assigned to Ru–Cp charge transfer (MLCT) appeared at 355-360 nm which is only little blue shifted compared to that in \([\text{RuCp(Ph)}_2\text{Cl}]\) (365 nm).

Complexes \([\text{RuCp(EPh)}_2\text{Cl}]\) where L is a non \(\pi\)-bonding ligand are well known to undergo solvo-
Table 1—Microanalytical data

<table>
<thead>
<tr>
<th>Complex</th>
<th>m.p. °C</th>
<th>C (%)</th>
<th>Found (%)</th>
<th>calc. (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
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<tbody>
<tr>
<td>1. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>160</td>
<td>52.41(52.17)</td>
<td>5.01(4.87)</td>
<td>5.10(4.87)</td>
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</tr>
<tr>
<td>2. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>165</td>
<td>47.70(47.39)</td>
<td>4.66(4.42)</td>
<td>4.72(4.42)</td>
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<td></td>
</tr>
<tr>
<td>3. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>168</td>
<td>52.90(52.57)</td>
<td>5.01(4.87)</td>
<td>5.10(4.87)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>160</td>
<td>48.73(48.47)</td>
<td>4.71(4.52)</td>
<td>4.43(4.52)</td>
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</tr>
<tr>
<td>5. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>165</td>
<td>46.60(46.31)</td>
<td>4.08(4.14)</td>
<td>4.08(4.14)</td>
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<tr>
<td>6. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>167</td>
<td>49.11(49.29)</td>
<td>4.87(4.74)</td>
<td>4.56(4.42)</td>
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</tr>
<tr>
<td>7. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>160</td>
<td>48.37(48.22)</td>
<td>4.54(4.64)</td>
<td>4.52(4.33)</td>
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<tr>
<td>8. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>165</td>
<td>45.33(45.15)</td>
<td>4.47(4.34)</td>
<td>4.20(4.05)</td>
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<tr>
<td>9. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>160</td>
<td>48.75(48.58)</td>
<td>4.70(4.42)</td>
<td>4.44(4.33)</td>
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<tr>
<td>10. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>169</td>
<td>52.57(52.24)</td>
<td>5.01(4.87)</td>
<td>5.10(4.87)</td>
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<tr>
<td>11. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>168</td>
<td>49.11(49.29)</td>
<td>4.87(4.74)</td>
<td>4.56(4.42)</td>
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<tr>
<td>12. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>165</td>
<td>45.33(45.15)</td>
<td>4.47(4.34)</td>
<td>4.20(4.05)</td>
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<tr>
<td>13. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>167</td>
<td>45.33(45.15)</td>
<td>4.47(4.34)</td>
<td>4.20(4.05)</td>
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<tr>
<td>14. [Ru Cp(PPh₃)(en)(PF₆)]</td>
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<td>48.37(48.22)</td>
<td>4.54(4.64)</td>
<td>4.52(4.33)</td>
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<tr>
<td>15. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>165</td>
<td>45.33(45.15)</td>
<td>4.47(4.34)</td>
<td>4.20(4.05)</td>
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<tr>
<td>16. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>168</td>
<td>42.43(42.28)</td>
<td>3.98(4.07)</td>
<td>3.82(3.79)</td>
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<tr>
<td>17. [Ru Cp(PPh₃)(en)(PF₆)]</td>
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<td>45.97(45.88)</td>
<td>4.26(4.41)</td>
<td>4.02(4.12)</td>
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<tr>
<td>18. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>170</td>
<td>52.37(52.17)</td>
<td>4.14(4.20)</td>
<td>4.29(4.20)</td>
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<td></td>
</tr>
<tr>
<td>19. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>171</td>
<td>49.89(49.69)</td>
<td>4.37(4.49)</td>
<td>4.53(4.42)</td>
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<tr>
<td>20. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>172</td>
<td>47.19(47.02)</td>
<td>4.04(4.06)</td>
<td>4.15(4.06)</td>
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<tr>
<td>21. [Ru Cp(PPh₃)(en)(PF₆)]</td>
<td>173</td>
<td>44.33(44.20)</td>
<td>3.74(3.82)</td>
<td>3.90(3.82)</td>
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</table>
Acknowledgement

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References

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