Reactions of [RuH(CO)Cl(PPh₃)₃] with imidazole, 2-methylimidazole, 2-ethylimidazole and pyrazole

D S Pandey*, K B Pandey & I P Tripathi
Department of Chemistry, APS University, Rewa 486 003, MP
and
U C Agarwala
Department of Chemistry, IIT, Kanpur 208 016

Received 20 July 1993; revised 15 November 1993. Accepted 27 December 1993.

Reactions of [RuH(CO)Cl(PPh₃)₃] have been carried out with imidazole, 2-methylimidazole, 2-ethylimidazole and pyrazole in the presence of suitable anions [BF₄⁻, BPh₄⁺, ClO₄⁻, & PF₆⁻]. The reaction products are found to be cationic and have been characterized by elemental analyses, IR, UV/vis and NMR spectral studies.

The complex [RuH(CO)Cl(PPh₃)₃] (I) and its related species have been a subject of continuing attention during the past several years¹⁷. Usually the complex (I) undergoes three types of reactions. (A) Substitution of a PPh₃ molecule by a neutral ligand yielding [RuH(CO)Cl(PPh₃)₂L] (where L = CO, RNC, etc.) where L in most cases goes trans to hydride ion; (B) substitution reactions involving chloride abstraction leading to the formation of cationic or neutral complexes⁶⁻⁸ of the type [RuH(CO)(PPh₃)₃-nL+n⁺]⁺ [where x = 1, L = P(OR)₃, n = 1; x = 1, L = PPh₃(OR), n = 3; x = 0, 1 = S₂CY⁻, Y = N(R₃), n = 1, 2]; and (C) insertion of arenediazonium salts, 2-vinylpyridine, methyl sorbate, dimethyl fumarate, acryonitrile, carbonbisulphide, dialkyl and diaryl carbodiimides, 1,3 diaryl triazines and acetylenes in Ru-H bond to yield the corresponding inserted complexes⁹⁻¹⁵. In a few cases both Cl⁻ ion and a PPh₃ molecule are substituted resulting in the formation of cationic complexes¹⁶⁻¹⁹. Our interest in such reaction mechanisms prompted us to investigate the substitution reactions of complex (I) with relatively less studied pyrazoles and imidazoles. In this note, we report the results of the reactions of pyrazole, imidazole and their derivatives with [RuH(CO)Cl(PPh₃)₃].

Experimental

All the chemicals used were of AR grade. The solvents were purified and dried using the literature procedures. The reactions were carried out under dry nitrogen atmosphere. The complex [RuH(CO)Cl(PPh₃)₃] was prepared as described elsewhere²⁰ and the ligands were used as such without further purification. The melting points of the complexes were determined on a Fischer John’s melting point apparatus. The IR spectra of the complexes in KBr discs were recorded on a Perkin-Elmer-580 spectrophotometer and ¹H, ³¹P NMR and electronic spectra on a Jeol FX-90 Q and Shimadzu UV-160 spectrophotometer respectively. The complexes were analyzed for C, H, N by the Micro analytical laboratory of the CDRI, Lucknow.

Procedure

In a typical reaction, a mixture of [RuH(CO)Cl(PPh₃)₃] (~ 1.0 mmol) and the ligand (2.0 mmol) in 30 ml of benzene was refluxed for ~ 5 h. In the case of methyl imidazole or ethyl imidazole refluxing was carried out for 8-9 h. After cooling the resulting solution at room temperature, the insoluble impurity present in the solution was removed by filtration and a solution of a suitable anion (BF₄⁻, BPh₄⁺, ClO₄⁻, & PF₆⁻) in 25 ml of methanol was added to the filtrate. The solution thus obtained was left for slow crystallization. After 12-14 h shiny, microcrystalline complexes were formed in the solution, which were separated by filtration, washed twice with methanol and finally twice with diethyl ether. The crystals were dried in vacuo.

Results and discussion

The analytical data of the reaction products along with the observed ¹H and ³¹P NMR signals and UV absorption bands are given in Table 1. The analytical data suggest that reactions of the ligands (pyrazole and imidazole) with [RuH(CO)Cl(PPh₃)₃] yield stable cationic complexes according to the following equation,

\[
{\text{[RuH(CO)Cl(PPh₃)₃]} + 2L \xrightarrow{\text{Reflux \ Benzene}} \text{[RuH(CO)(PPh₃)₂L]}}
\]

(where L = pyrazole or imidazole).

Evidently, the substitution reactions take place only when unsubstituted pyrazoles and imidazoles are used. Although the electron donating CH₃ or C₂H₅ group should make the ligands more basic, their non-reactivity reflects perhaps steric crowding in the complex [RuH(CO)Cl(PPh₃)₃L₁₋ₓ]⁺⁻ (where x = 0.1, L = CH₃ or C₂H₅).
Table 1—Analytical data of the complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found (Calc.), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>[RuH(CO)(PPh₃)₂(IZ)₂]BF₄</td>
<td>58.8</td>
</tr>
<tr>
<td>(Yellowish green, 178)</td>
<td>(58.9)</td>
</tr>
<tr>
<td>[RuH(CO)(PPh₃)₂(PZ)₂]BF₄</td>
<td>58.9</td>
</tr>
<tr>
<td>(White, 185)</td>
<td>(58.8)</td>
</tr>
<tr>
<td>[RuH(CO)(PPh₃)₂(IZ)₂]BF₄</td>
<td>71.9</td>
</tr>
<tr>
<td>(Yellowish green, 176)</td>
<td>(71.8)</td>
</tr>
<tr>
<td>[RuH(CO)(PPh₃)₂(PZ)₂]BF₄</td>
<td>72.4</td>
</tr>
<tr>
<td>(White, 190)</td>
<td>(72.5)</td>
</tr>
<tr>
<td>[RuH(CO)(PPh₃)₂(IZ)₂]ClO₄</td>
<td>58.3</td>
</tr>
<tr>
<td>(Yellowish green, 190)</td>
<td>(58.1)</td>
</tr>
<tr>
<td>[RuH(CO)(PPh₃)₂(PZ)₂]ClO₄</td>
<td>58.3</td>
</tr>
<tr>
<td>(White, 185)</td>
<td>(58.1)</td>
</tr>
<tr>
<td>[RuH(CO)(PPh₃)₂(IZ)₂]PF₆</td>
<td>56.4</td>
</tr>
<tr>
<td>(Yellowish green, 180)</td>
<td>(56.2)</td>
</tr>
<tr>
<td>[RuH(CO)(PPh₃)₂(PZ)₂]PF₆</td>
<td>56.9</td>
</tr>
<tr>
<td>(White, 179)</td>
<td>(56.2)</td>
</tr>
</tbody>
</table>

In addition, the earlier experiments have indicated that the substitution of two trans ligands in the complex - [RuH(CO)Cl(PPh₃)₂] is difficult. It implies lower possibility of incoming of two methyl or ethyl substituted molecules in the cis position.

The complexes are yellow to brown, shiny microcrystalline, non-hygroscopic solids, soluble in common organic solvents like DMF, DMSO, dichloromethane, chloroform, acetonitrile, slightly soluble in benzene and insoluble in methanol, ethanol, diethyl ether and pet. ether. Their cationic behaviour was confirmed by testing their dilute solution through cation exchanger (Dowex-50) whereby the cationic species are absorbed in the resin.

The bonding mode in these complexes and their tentative structures have been deduced from their spectral studies.

The ligands having two bonding sites may either coordinate through ring nitrogen or through imino nitrogen atom after deprotonation in which case the bands arising from the N-H groups are expected to be absent in the IR spectra of the complexes. In addition to this, substitution of Cl by the ligand molecule (trans to CO) ought to shift the position of ν(CO) and ν(Ru-H).

The presence of a broad medium intense band ~3200 cm⁻¹, assigned to νN-H in the spectra of all the complexes suggests the coordination of the ligand through ring nitrogen. This band exhibits splitting possibly owing to the cis geometry of two ligand molecules in the complex. The new band ~2990 and 800 cm⁻¹ assigned to νC-H and out-of-plane bending mode of CH respectively confirm the presence of ligand molecules in the complexes. Other ring stretching vibrations of the ligand are present in the region 1450 cm⁻¹. The characteristic bands due to PPh₃ and the corresponding anions were also present in the IR spectra of the complexes.

The shift in the position of νRu-H from 1995 cm⁻¹ in the parent complex to 2015-2030 cm⁻¹ and that of νCO from 1900-1920 cm⁻¹ to 1920-1940 cm⁻¹ in the resulting complexes suggest the linkage of the ligands in the complexes. A shift in the position of νRu-H and νCO towards higher frequency side is interesting. The shift in the position of νCO would possibly be attributed to the increased metal carbon π interaction as a result of lesser π delocalization from metal to ligands (pyrazole or imidazole) with respect to a good π acid viz. PPh₃. The effect is higher in imidazole than in the pyrazole complexes.

Because of the poor solubility of the complexes in deuterated benzene and their tendency to react with halogenated solvents, it was not possible to get good NMR spectra of these complexes. However, NMR spectra of these complexes were recorded in CDCl₃ using TMS as internal reference immediately after dissolving the samples.

The ¹H NMR spectra of imidazole complexes (Table 1) exhibited bands in the region δ 7.2-7.8 ppm (PPh₃ protons) δ 5.6 (C-4 protons of imidazole ring), δ 11.25 ppm (N-H protons) of the ligands imidazole. Interestingly, in the ¹H NMR spectra of both the series of complexes, we are not able to detect any band due to hydride proton (present in the parent hydride complex at δ -13 ppm). Presumably, this could be due to the substitutions of the hydride by chloro group in the halogenated solvents. This type of substitution was earlier reported in the literature for ruthenium hydride complexes.

A well-resolved ³¹P NMR spectra could be obtained only for pyrazole complexes. The ³¹P nuclei of PPh₃ group in these complexes were observed to resonate at δ 44.6 and δ 46.08 ppm. These signals exhibited a downfield shift as compared to that in the parent complexes (δ 37.8) (ref. 3). Possibly the deshielding of phosphorus may be due to relatively lesser donation of electron density from metal to phosphorus through back bonding.

The electronic spectra of the complexes were recorded in benzene. These exhibited broad to medium intensity bands in the region 300-350 nm. Their spectra did not exhibit any band in the visible region. The bands present in the region 300-350 nm
has been assigned to metal to ligand charge transfer bands (M$\rightarrow$CO). These cannot be assigned to M$\rightarrow$PPh$_3$ MLCT bands since they fall well below 250 nm.

Based on the results of analytical and spectral data it appears that one molecule of PPh$_3$ and a Cl$^-$ ion in the complex [RuH(CO)Cl(PPh$_3$)$_3$] are substituted by two molecules of pyrazole or imidazole. The coordination of the pyrazole or imidazole was found to be through ring nitrogen and not through NH nitrogen after deprotonation. Secondly, methyl or ethyl substituted imidazole did not react with [RuH(CO)Cl(PPh$_3$)$_3$] possibly because of steric hindrance.

Acknowledgement
We are thankful to Dr. Lallan Mishra, Department of Chemistry, BHU, Varanasi, Dr. R P Tripathi, Medicinal Chemistry Division, CDRI, Lucknow and Mr. N Ahmed, Chemistry Department, IIT, Kanpur, for their constant help.

References