Synthesis & Characterisation of Imidodi(thiocarbonic acid O-alkyl ester) Derivatives of Triphenylphosphine Complexes of Rhodium(I) & Ruthenium(II)

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Rhodium(I) complexes of the types \([\text{Rh}(\text{CO})(\text{L-L})(\text{PPh}_3)_2]\) and \([\text{Rh}(\text{LL})(\text{PPh}_3)_3]\) have been synthesised by the replacement of H or Cl and a \(\text{PPh}_3\) by a bidentate chelate ligand, imidodi(thiocarbonic acid O-alkyl ester) from \([\text{RhCl}(\text{CO})(\text{PPh}_3)_3]\) and \([\text{RhH}(\text{PPh}_3)_4]\) respectively. Ruthenium(II) complexes of the types \([\text{RuCl}(\text{CO})(\text{LL})(\text{PPh}_3)_2]\) and \([\text{RuH}(\text{CO})(\text{LL})(\text{PPh}_3)_2]\) have been prepared by the replacement of H or Cl and a \(\text{PPh}_3\) group from \([\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]\) and \([\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]\) respectively. All the complexes have been characterised and structures proposed on the basis of elemental analyses, IR, \(^{31}\text{P}\) NMR, and electronic spectral measurements.

Although the complexes of \(\beta\)-diketones have been investigated with virtually every metal and metalloid, the analogous thio-\(\beta\)-diketonate derivatives have received little attention owing to the difficulty in preparing dithio-\(\beta\)-diketone ligands. Only a few thio-\(\beta\)-diketonate derivatives have been prepared by replacing oxygen atoms in metal-\(\beta\)-diketonates by sulphur atoms. In the recent past, numerous complexes with ligands containing the moiety \(-\text{C}(-\text{S})-(\text{NH})-(\text{CS})-\) have been prepared, but those with the ligands containing \(-\text{CS}-(\text{NH})-(\text{CS})-\) group do not appear to have been reported. Hence we have studied the interactions of imidodi(thiocarbonic acid O-alkyl ester) derivatives with triphenylphosphine complexes of Rh(I) and Ru(II). The complexes thus prepared have been characterised and structures proposed on the basis of spectral (IR, \(^{31}\text{P}\) NMR, electronic) and analytical data.

Materials and Methods

All the reagents used were of CP or AR grade. All the solvents were freshly distilled before use. IR spectra were recorded in KBr or in chloroform on a Perkin-Elmer 597 IR grating spectrophotometer in the range 4000-250 cm\(^{-1}\); electronic spectra in chloroform on a Hitachi-Perkin-Elmer 10/100 recording spectrophotometer; and \(^{31}\text{P}\) NMR spectra on a Bruker WP-80FT instrument. The starting complexes \([\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]\), \([\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]\), \([\text{RhCl}(\text{CO})(\text{PPh}_3)_3]\), \([\text{RhH}(\text{PPh}_3)_4]\) and imidodi(thiocarbonic acid O-alkyl ester) derivatives were prepared by the literature procedures.

The ligands used were of the type \([\text{Ro}-(\text{CS})-(\text{NH})-(\text{CS})-(\text{OR})]\) \(\text{[R}=\text{CH}_3, \text{C}_2\text{H}_5\text{ and CH(\text{CH}_3)_2}\) and are represented as \(\text{L-L}\).

Preparation of complexes.

(i) Complexes of type \([\text{Rh}(\text{CO})(\text{L-L})(\text{PPh}_3)_2]\)

To a solution of \([\text{RhCl}(\text{CO})(\text{PPh}_3)_3]\) (250 mg; 1 mol) in benzene (2 ml) was added the appropriate ligand (58 to 64 mg; 1 mol) and the solution refluxed for 2 hr. It was concentrated on a water-bath to almost dryness and the residue dissolved in minimum amount of dichloromethane. On the addition of methanol a yellow compound separated out, which was filtered, washed several times with methanol and finally with ether and dried; yield, 60-70%.

The brown isomers of the same formula were prepared similarly by taking the rhodium complex and the appropriate ligand in 1:2 ratio; yield, 65-75%.

(ii) Complexes of type \([\text{Rh}(\text{L-L})(\text{PPh}_3)_3]\)

These complexes were prepared as above by taking \([\text{RhH}(\text{PPh}_3)_4]\) and the appropriate ligand in 1:1 ratio; yield, 65-75%.

(iii) Complexes of type \([\text{RuCl}(\text{CO})(\text{L-L})(\text{PPh}_3)_2]\)

To a solution of \([\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]\) (250 mg; 1 mol) in benzene (20 ml) as added the appropriate ligand (36-48 mg; 1 mol) and the solution refluxed for 1 hr. The solvent was evaporated and the residue dissolved in minimum amount of dichloromethane. On the addition of methanol a solid separated out, which was filtered, washed with methanol and finally with ether and dried; yield, 64-72%.

(iv) Complexes of type \([\text{RuH}(\text{CO})(\text{L-L})(\text{PPh}_3)_3]\)

These complexes were prepared as described
Table 1—Analytical Data for Rh(I) and Ru(II) Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>m.p. (°C)</th>
<th>Found (Calc), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Rh(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>Yellow</td>
<td>80-82</td>
<td>60.22</td>
</tr>
<tr>
<td>Rh(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>173</td>
<td>60.86</td>
</tr>
<tr>
<td>Rh(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>177</td>
<td>61.84</td>
</tr>
<tr>
<td>Rh(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>Brown</td>
<td>130</td>
<td>60.14</td>
</tr>
<tr>
<td>Rh(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>135</td>
<td>60.78</td>
</tr>
<tr>
<td>Rh(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>110</td>
<td>61.79</td>
</tr>
<tr>
<td>Rh(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>123-26</td>
<td>66.03</td>
</tr>
<tr>
<td>Rh(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>125-27</td>
<td>66.48</td>
</tr>
<tr>
<td>Rh(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>285-87</td>
<td>66.85</td>
</tr>
<tr>
<td>RuCl(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>Yellow</td>
<td>164-66</td>
<td>57.80</td>
</tr>
<tr>
<td>RuCl(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>153-56</td>
<td>58.49</td>
</tr>
<tr>
<td>RuCl(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>82</td>
<td>59.37</td>
</tr>
<tr>
<td>RuH(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>145-47</td>
<td>60.19</td>
</tr>
<tr>
<td>RuH(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>148-50</td>
<td>60.88</td>
</tr>
<tr>
<td>RuH(CO)(C_4H_6O_2S_2N)(PPh_3)_2</td>
<td>do</td>
<td>144</td>
<td>61.61</td>
</tr>
</tbody>
</table>

*Sulphur was estimated as given by A.I. Vogel, in A textbook of inorganic quantitative analysis (English Language Society, London), 1978.

above taking [RuH_2(CO)(PPh_3)_2], and the appropriate ligand in 1:1 ratio; yield, 60-68%.

Results and Discussion

Rhodium(I) complexes of type [Rh(CO)(LL)(PPh_3)_2]

The yellow and brown complexes of 1:1 ratio; yield, 60-68%.

The yellow and brown complexes of imidodithio ester of the general formula [Rh(CO)(LL)(PPh_3)_2] were obtained by the reaction of [RhCl(CO)(PPh_3)_2] and imidodithio ester in 1:1 and 1:2 molar ratios, respectively. In all the reactions the ligands could replace one of the PPh_3 group and the chloride ligand giving the products. The analytical data of these complexes summarised in Table 1, confirmed the molecular formula [Rh(CO)(LL)(PPh_3)_2]. In the IR spectra of all the compounds, the thioamide bands were present with little shift in their absorptions compared to those of the free ligands indicating coordination of the ligands with the metal ion. Evidence for the presence of S,S'- coordination of the ligands has been provided by the presence of IR absorptions around 1180 cm^{-1} (assignable to vC=S modes), with a shift of around 20 cm^{-1} compared to those of the free ligand. All the compounds exhibited vC=O modes around 1955 cm^{-1} indicating the coordinated carbon monoxide ligand^{10}. In addition to these bands, absorptions due to triphenylphosphine ligand appeared in the expected regions.

Since both the yellow and brown compounds analysed for the same molecular formula [Rh(CO)(LL)(PPh_3)_2], we assume that they are two different isomers. In order to decide on the geometry of the two type of compounds, ^31P NMR spectra of [Rh(CO)(C_4H_6O_2S_2N)(PPh_3)_2] (yellow) and [Rh(CO)(C_6H_6O_2S_2N)(PPh_3)_2] (brown) were taken in toluene. The yellow compound showed two singlets at 35.65 and 31.70 ppm. The brown compound showed only one singlet at 48.40 ppm. This observation leads to three possible structures (I-III) for
these isomeric compounds. Of these I and II should give two singlets and the III should give only one singlet. Hence the brown isomer can be assigned the structure III. The yellow isomer can have either structure I or II. Generally Rh(I) and Co(I) form trigonal bipyramidal compounds rather than the square pyramidal one. Hence, structure II is assigned to the yellow isomer. Moreover, the relative trans influence sequence which shifts $^{31}$P signal to the high field lies in the order $\text{Cl} < P < C < H$.

Based on this, we tentatively assign the signal at 31.7 ppm to the phosphine trans to the carbonyl group and the signal at 35.65 ppm to the other phosphine group. In the brown isomer, the low field signal around 48.40 ppm is due to the two phosphines trans to each other. Based on the above data, we assign structure II for all the yellow isomers and structure III to all the brown isomers of the molecular formula $[\text{Rh}(\text{CO})(\text{LL})(\text{PPh}_3)]$. In all these complexes, the ligand coordinates in the conventional fashion, viz. through two sulphur atoms from the enol form of the ligands.

**Rhodium(I) complexes of type $[\text{Rh}(\text{LL})(\text{PPh}_3)]$**

In the preparation of the compounds of the type $[\text{Rh}(\text{LL})(\text{PPh}_3)]$ (LL = imidodithiocarboxylic O-alkyl ester), the ligand replaces one of the PPh$_3$ group and a hydride to give the product of the molecular formula $[\text{Rh}(\text{LL})(\text{PPh}_3)]$. The analytical data of these complexes are also given in Table 1. In the IR spectra of these complexes the thioamide bands are present with little shifts in their absorptions compared to those of the free ligands indicating their coordination to the metal ion. Evidence for the presence of S,S'-coordinated ligand has been provided by the presence of peaks in the region 1190-1180 cm$^{-1}$, assignable to $\nu C = S$. The absence of a band at 2156 cm$^{-1}$ due to $\nu \text{Rh-H}$ in all the complexes shows that the hydride ligand in the starting material has been replaced by the coordinated bidentate ligand. The striking feature of the IR spectra of the complexes is the absence of bands in the region 3350-3175 cm$^{-1}$ which could be assigned to $\nu C = O$ and $\nu -NH$ modes. This indicates that the ligand is coordinated as an enolate ion. In addition to these, bands due to triphenylphosphine appeared in the expected regions.

The five-coordinate Rh(I) complexes present a problem that is not encountered with four- or six-coordinate complexes. Hence, the $^{31}$P NMR spectra of one complex was studied in order to decide on their geometries. The $^{31}$P NMR spectra of $[\text{Rh}(\text{CS}_3\text{H}_3\text{O}_2\text{S}_2\text{N})(\text{PPh}_3)]$ exhibited two singlets at 48.4 and 35.47 ppm with an intensity ratio of 1:2. Phosphorus-31 NMR studies on ML$_2$-trialkylphosphite complexes of Fe(O), Ru(O), Os(O), Co(I), Rh(I), Ir(I), Ni(I), Pd(I) and Pt(I) showed the structures of these molecules to be trigonal bipyramidal and not square pyramidal. Hence, tentatively a trigonal bipyramidal structure has been proposed for all the compounds of the type $[\text{Rh}(\text{LL})(\text{PPh}_3)]$.

**Ruthenium(I) complexes** $[\text{RuX(CO)(LL)(PPh}_3)]$

[X = Cl or H; LL = imidodithiocarboxylic acid O-methyl/ethyl/isopropyl esters]

All the compounds were prepared by the reaction of either $[\text{RuHCl(CO)(PPh}_3)]$ or $[\text{RuH}_2\text{(CO)(PPh}_3)]$ with the appropriate ligands. Under ordinary conditions, the ligand could replace one of the triphenylphosphines and a hydride ligand from the complex giving the product $[\text{RuX(CO)(LL)(PPh}_3)]$. The analytical data given in Table 1 fit very well with the molecular formula. In the IR spectra of these complexes the thioamide bands are present with little shifts in their absorptions as compared to those of the free ligands. The IR peaks in the region 1190-1175 cm$^{-1}$ (due to $\nu C = S$ mode) clearly indicate the presence of S,S'-coordination of the ligands in the complexes. The $\nu C = O$ modes in the complexes appear in the region 1940-1920 cm$^{-1}$ showing the presence of coordinated carbon monoxide.

All the compounds are diamagnetic which corroborates oxidation state of +2 for ruthenium. The electronic spectra of the complexes in chloroform exhibit two to three bands in the region 600-400 nm. The weak band in the region 440-425 nm can be tentatively assigned to the transition $^1A_{lg} \rightarrow ^1T_{lg}$.
(ref. 16). This and the other band positions indicate an octahedral geometry for all the ruthenium(II) complexes.17,18

References