Synthesis and Structure of Rhodium(I) Complexes with Anthranilic Acid

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Summary

Rhodium chloride hydrate RhCl₃·3H₂O reacts with anthranilic acid (HA; C₆H₄(COOH)NH₂) in boiling dimethylformamide (DMF) yielding dicarbonylanthranilatorhodium(I) [Rh(CO)₂(A)], (1). In the reaction of (1) with an excess of triphenylphosphine in DMF one carbonyl ligand is substituted by phosphine and carbonyltriphosphineanthranilatotorhodium(I) [Rh(CO)(PPh₃)A], (2) is formed.

Introduction

Aliphatic aminoacids or their esters, form many complexes with copper, cobalt and nickel[1-9]. There are also complexes with two different aminoacids M(A) (B) (M = CuII or PdII; A - acidic aminoacid, e.g. L- or D-asparagine or glutamine, cysteine; B - basic aminoacid, e.g. arginine)[9].

Only a few papers deal with the rhodium complexes with aminoacids. Beck et al. prepared a number of PdII, PtII and RhI complexes with N,N-bis(diphenylphosphino) esters of α-aminoacids[10]. Carboxylrhodium(I) complexes with aliphatic aminoacids such as alanine, glycine, leucine are also known[7]. Attempts to synthesize rhodium complexes with aromatic aminoacids have been reported for a considerable period. Khidekel et al. prepared a rhodium complex with N-phenylanlanthranilic acid for which the formula H[Rh(FA)₂Cl] was assumed[8]. However, there is no convincing evidence for the structure suggested[11, 12].

Transition metal complexes with aminoacids, particularly aromatic aminoacids, are frequently good catalysts for the hydrogenation of aromatic compounds[8, 9, 15] and do not undergo any deactivation during the hydrogenation process[14, 15]. These compounds also show catalytic properties in hydroformylation reactions, particularly in systems modified by phosphines.

In the present work we attempted to prepare a rhodium(I) dicarbonyl complex with anthranilic acid, and its derivative with triphenylphosphine. The latter complex may be the active form in a catalytic system containing the dicarbonyl complex and free phosphine.

Results and Discussion

Carbonyl rhodium complexes are synthesized most frequently from the bis(dicarbonylchlororhodium) [(Rh(CO)₂Cl)₂][16, 17]. Rusina and Vlček[18] prepared the complex [Rh(CO)(PPh₃)]Cl by heating rhodium chloride RhCl₃·3H₂O in the presence of triphenylphosphine at the boiling point of DMF. Similarly, Varszavskii[19] prepared [Rh(CO)₂(acac)]. This method simplifies the preparation considerably making thus possible to avoid the synthesis of [(Rh(CO)₂Cl)₂]. For this reason this method, with some modifications, was applied to prepare a rhodium(I) complex with anthranilic acid.

The reaction of RhCl₃·3H₂O with anthranilic acid in boiling DMF under nitrogen yields a yellow amorphous compound [Rh(CO)₂(A)], (1). On heating with DMF in the presence of an excess of triphenylphosphine compound (1) loses one carbonyl for a PPh₃ and a brown amorphous complex [Rh(CO)(PPh₃)A], (2), is formed. Analytical data indicate that both complexes are pure and do not contain any solvent. A discrepancy between the calculated and found rhodium percentages for complex (2) results from the presence of phosphine (see Experimental). Under the conditions of thermogravimetric analysis (0-1000°C) unidentified non-volatile phosphorus compounds, partly fused with the metal may form causing an overestimation of the rhodium content.

Because of the two functional groups (~NH₂, ~COOH) anthranilic acid can give rise to a mono-negative chelating ligand. Coordination of the carboxyl group to the metal may be demonstrated by infrared spectroscopy. A comparison of the i.r. spectra of (1) and (2) with that of the free carboxylate ion (according to references[20, 23], the sodium or potassium salt of the respective acid is considered to contain such an ion) indicates that the carboxylate group frequencies v(CO) (OCCO) lie in the 1590-1570 cm⁻¹ region, while the v(b) (OCCO) lies in the 1375-1350 cm⁻¹ region. The differences Δν = ν(CO)-ν(CO) are 200 cm⁻¹ for a free carboxylate ion, 225 cm⁻¹ for complex (1) and 225 cm⁻¹ for complex (2), respectively (Table 1). Comparison with the reference data[20, 25] suggests that the carboxyl group of the anthranilate is coordinated to the sodium as a monodentate ligand with both oxygen atoms remaining equivalent because Δν both for (1) and (2) are only slightly higher than that for the free ion (Table 1). However, an ionic bond between the ~C~O group and metal is in this case highly improbable.

Alternatively, one can assume that the spectrum of the carboxyl group is a consequence of simultaneous coordination of one oxygen atom to rhodium and the other oxygen via hydro- bond formation in the infrared spectra.

The amine group of anthranilic acid may be coordinated to the metal via the free electron pair of nitrogen. In potassium

<p>| Table 1. I.r. spectra of potassium anthranilate and of complexes (1) and (2). |
|-----------------|----------------|-----------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>Frequencies cm⁻¹</th>
<th>[C₆H₄NH₂COOK]</th>
<th>[Rh(CO)₂(A)]</th>
<th>[Rh(CO)(PPh₃)A]</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3420</td>
<td>3170</td>
<td>3175</td>
<td>ν(CO)</td>
<td>ν(CO)</td>
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<tr>
<td>3315</td>
<td>3070</td>
<td>3075</td>
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<td>1575</td>
<td>1585</td>
<td>1575</td>
<td>ν(CO)</td>
<td>ν(CO)</td>
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<tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td>ν(P-C₃H₃)</td>
<td>ν(P-C₃H₃)</td>
</tr>
</tbody>
</table>

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make it difficult to interpret the electron spectra since their rhodium(I) complexes. The solvents used (DMF, benzene) 365 nm for complex and the latter from ligand-metal electron transitions.

ing from charge-transfer transitions in the phosphine ligand kmax = 365 nm (emax = 614.5), the former being a band resulting also exhibits two bands: Xm~x = 268 nm (emax = 4160) and

potassium anthranilate. 2 - [Rh(CO)₂(A)], Figure 1. Electron absorption spectra of

0.26 g) in DMF (10 cm³) was treated with a two-fold excess of anthranilic acid (1.5 mmole, 0.2 g) and the mixture was heated under reflux for two hours. During the first 10 minutes of heating the solution changed its colour from dark red to yellow. The solution was cooled to about 20 °C and diluted with a double volume of water (20 cm³). During dilution a yellow precipitate formed. The solution with its precipitate was cooled to +5 °C for 1 hour and then filtered off, washed with H₂O and Me₂CO and dried in vacuo. The yellow powder is soluble in DMF, slightly soluble in THF and insoluble in most organic solvents. Analysis: for C₉H₆NO₄Rh; Found: C, 36.3; H, 2.3; N, 4.6; Rh, 34.7%. Calcd.: C, 36.5; H, 2.1; N, 4.7; Rh, 34.7%.

Carbonyltriphosphineanthranilatorhodium(I) [Rh(CO)(PPh₃)(A)], (2)

A deoxygenated solution of RhCl₃ · 3H₂O (0.75 mmole, 0.25 g) in DMF (10 cm³) was treated with a two-fold excess of anthranilic acid (1.5 mmole, 0.2 g) and the mixture was heated under reflux for two hours. During the first 10 minutes of heating the solution changed its colour from dark red to yellow. The solution was cooled to about 20 °C and diluted with a double volume of water (20 cm³). During dilution a yellow precipitate formed. The solution with its precipitate was cooled to +5 °C for 1 hour and then filtered off, washed with H₂O and Me₂CO and dried in vacuo. The yellow powder is soluble in DMF, slightly soluble in THF and insoluble in most organic solvents. Analysis: for C₉H₆NO₄Rh; Found: C, 59.1; H, 4.4; N, 2.1; Rh, 22.5%. Calcd.: C, 58.8; H, 4.2; N, 2.6; Rh, 19.5%.

References