

New Rhodium Complexes Containing a Hydrogen-Metal Bond

PREPARATION AND PROPERTIES OF AMMINOHYDRIDO COMPOUNDS

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New and unexpectedly stable compounds of rhodium with hydrogen directly co-ordinated to the metal have been prepared. They are soluble in water, and their cold aqueous solutions readily take up ethylene and acetylene with the formation of ethyl and vinyl derivatives in which the organic radical is co-ordinated directly to the metal. These hydrido-compounds have a potential usefulness as catalysts for the hydrogenation of unsaturated organic acids.

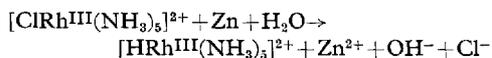
In the past two decades there has been a vast increase in the knowledge of the chemistry of the platinum group metals and yet not a great deal of effort has been directed towards the isolation and characterisation of ammino complexes. Lever and Powell (1) have described the preparation and properties of hexamminoruthenium (II) chloride which was first separated from a solution obtained by boiling with zinc dust an ammoniacal ammonium chloride solution of hydroxotetramminonitrosylruthenium chloride. The crystals are isomorphous with the hexammine chlorides of bivalent iron, cobalt and nickel but unlike these compounds, which are decomposed by hydrochloric acid into simple chlorides of the metal and ammonium chloride, hexamminoruthenium (II) chloride is converted to the deep blue aquochlorotriammine $[\text{Ru}^{\text{III}}(\text{NH}_3)_3\text{H}_2\text{OCl}_2]\text{Cl}$ with evolution of hydrogen and deposition of a little metallic ruthenium.

In view of this interesting behaviour of ruthenium, attempts have been made to prepare the analogous rhodium compound with somewhat surprising results. The most common and easily prepared rhodium ammine is chloropentamminorhodium (III)

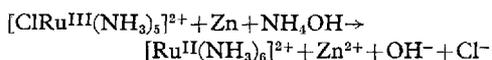
chloride, which has only a small solubility in water and is even less soluble in ammoniacal ammonium chloride solution. If a suspension of this compound in such a solution is boiled with mechanical stirring and treated with zinc dust the rhodium ammine rapidly dissolves and only a small amount of metal is precipitated. From the cold filtered solution saturation with ammonium chloride and ammonia results in the separation of small nearly colourless crystals which are very soluble in water and difficult to free entirely from ammonium salts for analysis. They contain Rh, NH_3 and Cl in the ratio 1:5:2 and the infra-red spectrum shows a sharp peak at 2080 cm^{-1} which is ascribed to a Rh-H stretching frequency. A much better yield is obtained by using ammonium sulphate in place of ammonium chloride in the preparation. In this case the sulphate of the new ammine may be readily obtained in 80 per cent yield or better by saturating the solution from the zinc treatment with gaseous ammonia while cooling in ice-water. The substance separates in very pale yellow acicular crystals which are very soluble in water but only slightly soluble in cold saturated ammonia solution which can there-

fore be used to wash them completely free from zinc and ammonium salts. After final washes with acetone and air-drying, analysis of the crystals and infra-red spectrometry show them to be hydridopentamminorhodium (III) sulphate $[\text{HRh}^{\text{III}}(\text{NH}_3)_5]\text{SO}_4$.

This compound is the first pure hydrido-complex of a transition metal with a non- π -bonding ligand to be prepared. In the dry state it is remarkably stable, remaining unchanged after many months' exposure to the air. In solution, however, one ammonia molecule is liberated and replaced by a water molecule; addition of acetone precipitates white air-stable trans-hydrido-aqua-tetramminorhodium (III) sulphate $[\text{HRh}(\text{NH}_3)_4\text{H}_2\text{O}]\text{SO}_4 \cdot 2$. Unlike salts of the ruthenium amines, therefore, chloropentamminorhodium salts are not reduced to complexes of bivalent rhodium by treatment with zinc in ammoniacal solution; instead the chlorine in the complex is replaced by hydrogen by the reaction



With chloropentamminoruthenium salt the reaction with zinc in ammoniacal solution is:



Reactions of Hydridorhodium Amines

The reactions of the hydridorhodium amines are extremely interesting and in this field there is scope for a considerable amount of investigation. Boiling with dilute hydrochloric acid results in deposition of about 60 per cent of the rhodium as metal, the balance being converted to *trans*-dichloro-tetramminorhodium chloride whereas with more concentrated acid no rhodium is precipitated but hydrogen is evolved and a pink microcrystalline salt, so far unidentified, separates. By boiling with acetic acid complete break-up of the ammine is achieved, half the rhodium being precipitated as metal and the remainder being converted to the green rhodium (II) acetate, $\text{Rh}^{\text{II}}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$,

which crystallises from the solution. Boiling with ammoniacal silver sulphate solution precipitates two atoms of silver per atom of rhodium and the rhodium is converted into hexammine with a little aquopentammine. Boiling the slightly acid sulphate solution with copper sulphate results in the precipitation of one atom of copper per atom of rhodium and conversion of the rhodium to a very soluble tetrammine, but no copper is precipitated from ammoniacal or acid chloride solutions, Cu(II) being reduced only to Cu(I). Shaking the cold solution with ethylene results in absorption of one mole of C_2H_4 per atom of rhodium and saturation of the cold solution with ammonia causes separation of pale yellow crystals of the alkyl derivative $[\text{C}_2\text{H}_5\text{Rh}(\text{NH}_3)_5]\text{SO}_4$. The reactions with oxygen, mercuric salts and sulphur dioxide have been noted but are obviously complex and, so far, have not been studied in detail.

Catalytic Properties

There are indications that this type of compound has interesting catalytic properties. Hydridopentamminorhodium sulphate in aqueous solution has been shown to be a moderately good catalyst for the hydrogenation of water-soluble unsaturated carboxylic acids at 60°C. Linear rates of hydrogen uptake in the range 0.1–0.3 ml.min.⁻¹ were observed using 0.3–0.6 M solutions of maleic, crotonic and acrylic acids and 0.05 M solutions of the ammine. The reactions are obviously complex since the colours of the solutions show marked change after reaction varying from deep yellow to green. There is, however, no precipitation of rhodium metal whereas, in the absence of a carboxylic acid, aqueous solutions of the complex slowly deposit metallic rhodium when treated with hydrogen at 60°C.

References

- 1 F. M. Lever and A. R. Powell, Intern. Conf. Coord. Chem., Chem. Soc. Special Publ. No. 13, 1959, p. 135
- 2 J. A. Osborn, A. R. Powell and G. Wilkinson, *Chem. Comm.*, 1966, 461