

Synthesis of Ammonium Salt of Pentachloro-nitrosylruthenate(II): A New Approach

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The new convenient route for the synthesis of complex $(\text{NH}_4)_2[\text{Ru}(\text{NO})\text{Cl}_5]$ involves reaction of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ with NOCl in ethanolic medium in the presence of triphenylphosphine. Tetraphenylarsonium salt of the complex has also been prepared.

The use of NOX ($X = \text{Cl}$ or Br) as suitable nitrosylating agent for synthesizing transition metal nitrosyl complexes has been extensively investigated¹⁻¹⁰. We now wish to report a new use of NOCl in the preparation in ethanolic medium of the known complex, $(\text{NH}_4)_2[\text{Ru}(\text{NO})\text{Cl}_5]$, by reacting $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ with nitrosyl chloride in the presence of Ph_3P . NOCl acts not only as a nitrosylating agent but also gets reduced to ammonia in this reaction. Although a few rather involved procedures for synthesizing this compound are known¹¹, the one reported in this note is quick and facile and the pure compound is obtained in considerably high yield.

Hot ethanolic solution of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.5 g, 40 ml) was mixed with a boiling ethanolic solution of triphenylphosphine (2.5 g, 25 ml) and to this was added, a freshly prepared saturated solution (10 ml) of NOCl in dichloromethane. The resulting solution was vigorously stirred and heated for another 2 min. On cooling it to room temperature shining crystals of $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ were obtained which were separated by centrifugation. To the centrifugate (containing unreacted triphenylphosphine) an excess of NOCl was further added and the crystals of $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$, if further appeared in small amount were filtered off. The filtrate was evaporated to nearly half the volume on a water-bath when a pink coloured compound started precipitating. The evaporation of the solution was continued till there was no more precipitation and the solution became almost colourless. The precipitate was separated by centrifugation, washed thoroughly with dichloromethane, ether and dried *in vacuo*. It analysed for $(\text{NH}_4)_2[\text{Ru}(\text{NO})\text{Cl}_5]$ (1) and did not melt up to 300°C.

Tetraphenylarsonium salt of the complex was precipitated by adding tetraphenylarsonium chloride to an aqueous solution of 1. The precipitate was separated by centrifugation washed successively with ethanol, ether and dried *in vacuo*. It analysed for $(\text{Ph}_4\text{As})_2[\text{Ru}(\text{NO})\text{Cl}_5]$ (2).

The pink complex (1) and its tetraphenylarsonium salt (2) are air-stable and insoluble in most of the organic solvents (CH_2Cl_2 , CHCl_3 , CCl_4 , C_6H_6 , ether etc). On eluting the aqueous solution of 1 through an anion exchange column (Dowex-1X8, 50-100 mesh, Cl^- -form), the pink coloured ion of the complex was absorbed on the column indicating the presence of an anionic species in the complex. The eluent on analyzing showed the presence of ammonium chloride corresponding to the two ammonium ions per molecule of the complex taken.

The IR data of 1 was almost identical with those reported in literature¹¹ [IR: 3190s (νNH), 1390s (δNH), 1895 cm^{-1} (νNO). The aqueous solution of 1 on repeated evaporation in hydrohalic acid, yielded the corresponding compound $(\text{NH}_4)_2[\text{Ru}(\text{NO})\text{X}_5]$ ($X = \text{Br}$, I).

It was observed that the presence of excess of NOCl , $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and triphenylphosphine was essential for the formation of 1. The most interesting and unusual aspect of the reaction is the reduction of NO to ammonia. Possibly during the course of reaction the odd electron bearing species NO interacted with $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ with the formation of $[\text{Ru}(\text{NO})\text{Cl}_5]^{2-}$ and $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ in the presence of triphenylphosphine, but at the same time it oxidized triphenylphosphine to its oxide in the presence of ethanol and during the process got reduced to the ammonium ion. Since the formation of ammonium ions was observed by the reaction of NOCl with PPh_3 in the absence of metal chloride, it appears that the presence of ruthenium ion is not absolutely essential for the reduction of NO to NH_4^+ .

Attempts to rationalise the reduction of NO by triphenylphosphine are underway and the results will be published elsewhere.

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