

SHORT COMMUNICATIONS

CARBONYL HALIDES OF THE GROUP VIII TRANSITION METALS

III.* DICHLOROAQUOCARBONYLRUTHENIUM(II)

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Introduction

In the preparation of dichlorodicarbonylruthenium(II) by the interaction of a mixture of formic acid and hydrochloric acid on ruthenium trichloride, it was observed¹ that the solution turned from its initial red colour to bright green before finally becoming yellow or orange. The dicarbonyl complex was isolated from the orange solution¹ and we now report the isolation of the intermediate compound, dichloroaquocarbonylruthenium(II), from the green solution.

In the course of an elegant kinetic study of this system, Halpern and Kemp² isolated the anion $[\text{RuCO}(\text{H}_2\text{O})\text{Cl}_4]^{2-}$, which is derived from our new aquocarbonyl halide, simply by addition of ammonium chloride to the green solution; and they suggested that dichloroaquocarbonylruthenium(II) was an intermediate in the formation of the dicarbonyl compound.

Results and Discussion

Ruthenium trichloride is readily reduced by formic acid in the presence of hydrochloric acid to give, initially, a green solution.¹ Slow evaporation of this solution in a vacuum desiccator gave pure dichloroaquocarbonylruthenium(II) as a black powder. The complex is involatile and remarkably stable thermally since it can be heated to 200° in vacuum without loss of the coordinated water molecule. However, unlike the corresponding dicarbonyl complex it is susceptible to oxidation in solution. It is soluble in water, hydrochloric acid solution, acetone, methanol, and other coordinating solvents, but insoluble in chloroform, dichloromethane, and carbon tetrachloride. In hydrochloric acid solution it undoubtedly exists as the tetrachloroaquocarbonylruthenate(II) anion, since addition of the chlorides of suitable large cations such as caesium is sufficient to precipitate the appropriate salt of this anion.

Dichloroaquocarbonylruthenium(II) shows two carbonyl stretching modes in the solid state at 2085 and 2025 cm^{-1} , but the tetrachloroaquocarbonylruthenate(II) anion exhibits only a single carbonyl stretch at 1950 cm^{-1} . All of the properties and chemical reactions of dichloroaquocarbonylruthenium(II) are very similar to those of

* Part II, *Aust. J. Chem.*, 1968, **21**, 891.

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¹ Colton, R., and Farthing, R. H., *Aust. J. Chem.*, 1967, **20**, 1283.

² Halpern, J., and Kemp, A. L. W., *J. Am. chem. Soc.*, 1966, **88**, 5147.

the dicarbonyl complex and it is suggested that the structure consists of a kinked chain of $\text{RuCO}(\text{H}_2\text{O})\text{Cl}_4$ units exactly analogous to that found for the dicarbonyl compound. However, when one of the carbonyl groups of the dicarbonyl is replaced with a water molecule, it is still possible to have two types of environment for the remaining carbonyl group, which is consistent with the observed two carbonyl stretching modes. On complex formation, such as in $[\text{RuCO}(\text{H}_2\text{O})\text{Cl}_4]^{2-}$, only one carbonyl stretch would be expected in the discrete octahedral complex in agreement with the observed spectrum.

Dichloroaquocarbonylruthenium(II) in acetone or methanol solution reacts readily with donor ligands in a manner analogous to that already described for the dicarbonyl compound to give, in general, octahedral complexes of the type $\text{RuCO}(\text{H}_2\text{O})\text{Cl}_2\text{L}_2$. Thus, reaction with triphenylphosphine gives diamagnetic $\text{RuCO}(\text{H}_2\text{O})\text{Cl}_2(\text{PPh}_3)_2$.

An interesting observation is that the corresponding dibromo- and diiodo-aquocarbonyl complexes appear to be inherently unstable, in sharp contrast to dibromo- and diiodo-dicarbonylruthenium(II) which are both stable.¹ Attempts to prepare these compounds directly as described above for the dichloro compound resulted only in the isolation of the dicarbonyl compounds, while attempted halogen exchange between the dichloroaquocarbonyl and aqueous hydrobromic or hydriodic acids gave equal amounts of the dihalodicarbonylruthenium(II) and ruthenium trihalides.

Experimental

Dichloroaquocarbonylruthenium(II)

Commercial ruthenium trichloride (0.5 g) was refluxed with 20 ml of a mixed solution of formic and hydrochloric acids (50 : 50 v/v) until the colour of the solution changed from deep red to bright green (usually about 5 hr). The solution was then slowly evaporated at room temperature in a vacuum desiccator. Yield 100% (Found: C, 5.4; Cl, 32.8. Calc. for $\text{RuCO}(\text{H}_2\text{O})\text{Cl}_2$: C, 5.5; Cl, 32.6%).

Caesium Tetrachloroaquocarbonylruthenate(II)

Caesium chloride was added to the green solution described above and pale green crystals precipitated. The crystals were washed with methanol and dried under vacuum (Found: C, 2.3; Cl, 25.9. Calc. for $\text{Cs}_2[\text{RuCO}(\text{H}_2\text{O})\text{Cl}_4]$: C, 2.2; Cl, 25.6%).