

Ruthenium Trichloride and Its Applications

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Since the war there has been much work on the chemistry of ruthenium. The first stimulus for this came from the observation that ruthenium is one of the main products of the nuclear fission of heavy atoms, while the other and more recent reason has been the realisation that many ruthenium complexes have unusual structures and reactivities, and that some have valuable or potentially valuable catalytic properties.

Ruthenium trichloride is by far the best starting material for the synthesis of compounds of the metal. Like osmium, ruthenium exhibits a wide range of oxidation states in its complexes (VIII to -II), and all of these may be reached from RuCl_3 since, although it is stable, it can easily be oxidised or reduced. It is most commonly used in the hydrated form, this being soluble in many solvents, but for anhydrous or solid-state reactions $\beta\text{-RuCl}_3$ is the best source.

History and Preparation

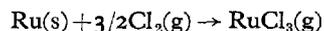
Ruthenium was discovered in 1844 by Claus (1), and in the course of his extensive and classic investigations he isolated a brown material formed by chlorination of the metal at low red heat. This was $\beta\text{-RuCl}_3$ but he mistakenly believed it to be the dichloride. The material which he formulated as " Ru_2Cl_6 ", made by the digestion of higher ruthenium oxides in hydrochloric acid, was probably a complex mixture of ruthenium(IV) poly hydroxo-chloro species. The present-day commercial product is made in a similar way, and from this the hydrated salt $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (where n is approximately 3) can be obtained by recrystallisation from concentrated hydrochloric acid. Such purifica-

tion is, however, unnecessary for most of the reactions described below.

The anhydrous salt exists in two modifications: the black α -form, made by chlorination of the metal at 700°C (2) or by the prolonged action of sulphuryl chloride under pressure on ruthenium at 300°C (3), and the more reactive β -form which is made by the same methods but at lower temperatures (350°C and 300°C respectively (2, 3)).

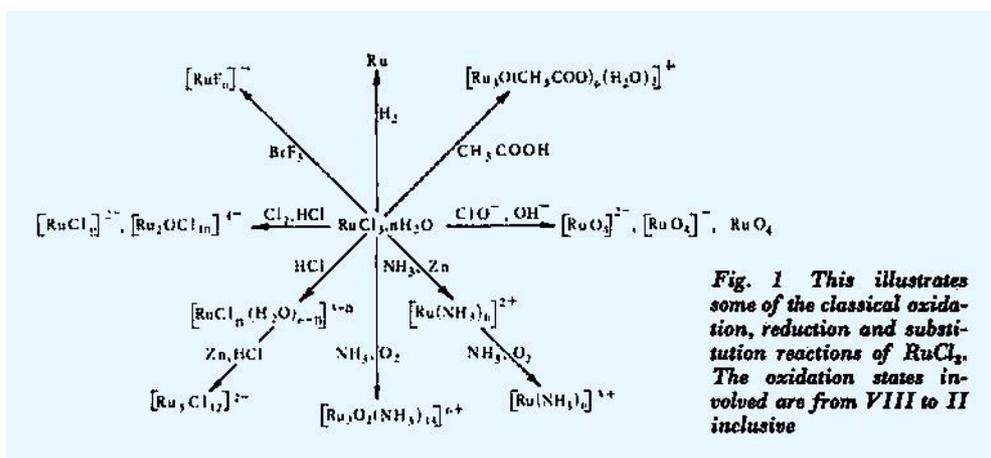
Physical Properties

The hydrate $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ is very soluble in water and in a wide range of polar organic solvents. The α modification of anhydrous RuCl_3 forms black crystals, chemically rather inert, and insoluble in most solvents, while the more reactive β -form is brown, hygroscopic and soluble in some polar solvents. X-ray data show that both α - and $\beta\text{-RuCl}_3$ contain octahedrally co-ordinated ruthenium with a Ru-Cl distance of 2.36 Å (2, 4). Thermodynamic data are available for $\beta\text{-RuCl}_3$ (5) and for the reaction (6):



Chemical Properties

Some of these properties of ruthenium trichloride are summarised in Fig. 1, which gives some of the classical oxidation, reduction or substitution reactions with normal σ -donor ligands, and in Fig. 2 which is concerned mainly with organometallic complexes of π -acceptor ligands. In both diagrams some of the products listed are, or may become, of industrial interest. References are usually to recent review articles rather than to the original papers.

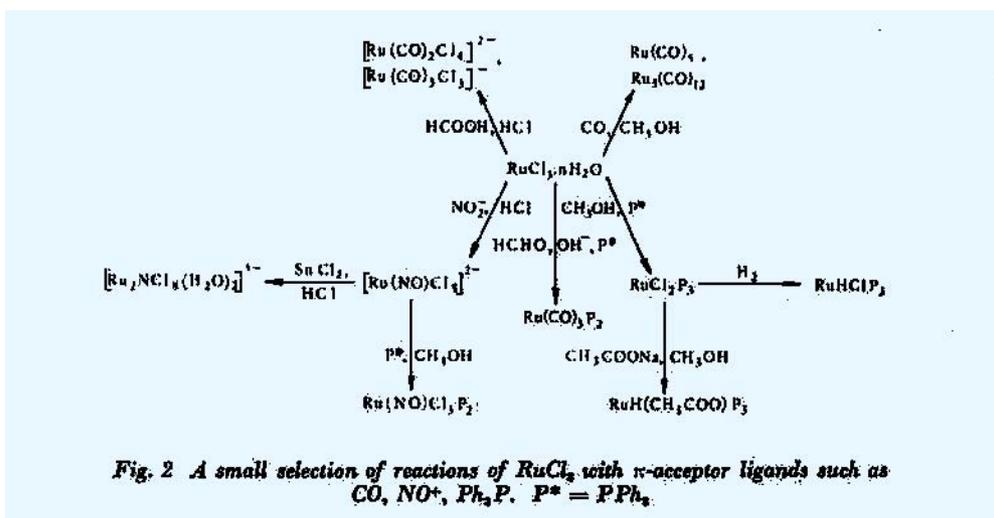


Oxidation of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ directly to ruthenium tetroxide can be achieved with periodate or hypochlorite. The tetroxide is increasingly being used for specific oxidation of organic materials (e.g. of olefins to ketones, for carbohydrate or steroid oxidations (7), and its applications as a fixative and stain for biological tissues have been explored (8). The reaction of RuCl_3 with ammonia in air gives the intensely red dye $[\text{Ru}_2\text{O}_2(\text{NH}_3)_4]\text{Cl}_6$ ("ruthenium red") and this has also found extensive use for staining work in electron microscopy (8).

Reduction of RuCl_3 in acid solution leads to the intensely blue cluster complex

$[\text{Ru}_5\text{Cl}_{12}]^{2-}$, a useful source of other ruthenium(II) complexes (9). Forty years before ruthenium was isolated, Fourcroy and Vauquelin observed this colour in acid solution of platinum metal concentrates reduced by zinc, but did not identify the source (10). The ammine chemistry of the metal was significantly extended recently by the work of Lever and Powell (11) who generated $[\text{Ru}(\text{NH}_3)_6]^{2+}$ from reduced RuCl_3 and ammonia, and prepared many other ammine salts from this.

Carbonyls and carbonyl phosphines have been well reviewed (12). Water-soluble carbonyl chloro complexes are readily ob-



tained by decarbonylation of RuCl_3 by formic acid (13). By far the greatest part of ruthenium carbonyl chemistry has been conducted in non-aqueous solvents, however. Bradford (14) has reviewed the preparation and properties of $\text{Ru}(\text{CO})_5$ and the intriguing cluster complex $\text{Ru}_3(\text{CO})_{12}$; these can be made from methanolic solutions of RuCl_3 in carbon monoxide under pressure. The main emphasis of recent research in this field has been on carbonyl phosphines; reduction of RuCl_3 in alcohols with tertiary phosphines (usually triphenylphosphine) in the presence of carbon monoxide gives complexes such as $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$, and this can be converted to the dihydride by treatment with lithium aluminium hydride. The ruthenium (0) complex $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ is one of the most efficient hydroformylation catalysts yet discovered, converting ethylene quantitatively to propionaldehyde (15).

Phosphine and hydrido phosphine (12) complexes have been extensively studied, especially from the viewpoint of the homogeneous hydrogenation of terminal olefins in which respect $\text{RuCl}_2(\text{PPh}_3)_3$ (another useful source of many ruthenium(II) complexes) and $\text{RuH}(\text{CH}_3\text{COO})(\text{PPh}_3)_3$ are particularly effective (15). The mechanism of such catalysis probably involves cationic species, $[\text{Ru}(\text{PPh}_3)_n]^{2+}$ (16).

Ruthenium forms more nitrosyl complexes than any other element; many of these, particularly nitrosyl phosphines, have unusual stereochemistries, oxidation states and reactivities. The oxidation states involved are formally ruthenium(II), (0) or $-(\text{II})$; and the stereochemistries tetrahedral, trigonal or square-based pyramidal, or octahedral (17). The absorption of molecular nitrogen by RuCl_3 in the presence of reducing agents or by $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$ has been a fruitful and continuing field of study (18).

Direct Applications

Undoubtedly the main value of RuCl_3 is as a source of other ruthenium complexes, and it is on this aspect that this article has

been chiefly concerned. The salt has, however, been used successfully, either alone or with other transition metal species, for the catalytic conversion of acetylene to acetaldehyde, the oxidation of ethylene, conversion of propylene to acetone and the polymerisation of olefins, and acetylenes (15). It will function as an electroplating agent for ruthenium plating (19), but this purpose is better achieved by the bridged nitrido species $[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]^{3-}$ which may also be made from ruthenium trichloride (20).

References

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