A New Preparation of Rhenium(IV) Chloride

By (MRS.) A. BRIGNOLE and F. A. COTTON*

(*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts* 02139)

Summary Rhenium(IV) chloride can be prepared by heating $ReCl_5$ in a mixture of CCl_4 and C_2Cl_4.

RHENIUM(IV) CHLORIDE was discovered and characterized by accident.[1,2] Later, two methods for its preparation were developed;[3,4] both required expensive chloride acceptors (Re_9Cl_9 and $SbCl_3$) to reduce $ReCl_5$, and used cumbersome sealed tube reactions. We report a cheaper and more convenient procedure [using reaction (1)] which does not, however, give as highly crystalline a product.

$$ReCl_5 + \tfrac{1}{2}\,CCl_2{=}CCl_2 \xrightarrow{CCl_4} ReCl_4 + \tfrac{1}{2}\,C_2Cl_6 \qquad (1)$$

The solvents were dried by heating under reflux over P_2O_5, and then distilled under nitrogen. C_2Cl_4 was distilled under reduced pressure to avoid decomposition. $ReCl_5$ was purified by vacuum sublimation at 50 °C and 0·1 Torr.

The reaction was carried out in a three-necked flask provided with a condenser and stopcock. This system was evacuated and flushed with N_2. $ReCl_5$ (1·1 g) was transferred from a Schlenk tube and the degassed solvents (16 ml CCl_4 and 6 ml of C_2Cl_4) were added with a syringe. $ReCl_5$ is soluble in the reaction mixture. The solution was heated at 70—80 °C for 42 h. The $ReCl_4$ formed is insoluble in CCl_4, and a brown suspension is thus formed, which was filtered off under nitrogen, and washed with degassed and distilled CCl_4 until the filtrate was colourless to remove unchanged $ReCl_5$. The $ReCl_4$ was transferred to a Schlenk tube and dried overnight under vacuum and gave on analysis Cl, 43·5 and 43·3% (calcd. value 43·25%).

The yield was *ca.* 80% based on $ReCl_5$. If the reaction time is extended to 4 days the yield diminishes (38%) and the analysis gives Cl 41·2%. The yield also decreases if the solvents are not freshly distilled and if air is not strictly excluded from the apparatus.

The $ReCl_4$, obtained as a brown powder, is best stored under nitrogen. Its i.r. spectrum in the 3000—600 cm^{-1} region is blank. It is insoluble in benzene and CCl_4 but soluble in acetone, tetrahydrofuran, and acetonitrile giving green solutions. The sample of $ReCl_4$ previously described[1] was insoluble in tetrahydrofuran and acetonitrile. Evaporation of the solution in dry, degassed acetonitrile yields a sticky brown-black solid, which is soluble in HCl and gives $Re_2Cl_8^{2-}$ when tetrabutylammonium bromide is added. The $ReCl_4$ prepared as described here gives the previously reported reaction with triphenylphosphine.[1]

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