

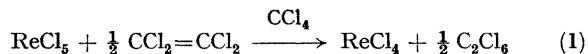
A New Preparation of Rhenium(IV) Chloride

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_2Cl_6 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.



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 described¹ 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 $\text{Re}_2\text{Cl}_8^{2-}$ when tetrabutylammonium bromide is added. The ReCl_4 prepared as described here gives the previously reported reaction with triphenylphosphine.¹

We thank the U.S. Atomic Energy Commission for financial support.

(Received, March 18th, 1971; Com. 345.)

¹ F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, 1967, 6, 223.

² M. J. Bennett, F. A. Cotton, B. M. Foxman, and P. F. Stokely, *J. Amer. Chem. Soc.*, 1967, 89, 2759.

³ P. Frai, A. Guest, and C. J. L. Lock, *Canad. J. Chem.*, 1969, 47, 1069.

⁴ J. H. Canterford and R. Colton, *Inorg. Nuclear Chem. Letters*, 1968, 4, 607.