A Polynuclear Ruthenium Carbonyl Hydride

By J. W. S. JAMIESON, J. V. KINGSTON, and G. WILKINSON
(*Inorganic Chemistry Laboratories, Imperial College, London, S.W.7*)

ALTHOUGH the hydrido-carbonyl of ruthenium, $H_2Ru(CO)_4$, has been mentioned in Reviews it appears[1] not to exist. In an attempt to obtain this compound by the action of hydrogen and carbon monoxide under pressure (120 atm., 75° c) on a red carbonyl-containing chlororuthenium solution[2] in the presence of silver powder as a halide-acceptor, we have obtained only an orange crystalline compound, m.p., 147° (with decomposition). The latter, which can be recrystallized from dichloromethane and other organic solvents, can be separated from the known carbonyl $Ru_3(CO)_{12}$ by fractional crystallization or by chromatography. It shows a single line in the nuclear magnetic resonance spectrum at τ 27·5 which is characteristic of transition metal–hydrogen bonds. While the mass spectrum is complex due to the presence of the several isotopes of ruthenium the highest peak occurs at mass number 754 and could be attributed to the molecule ion $[H_2Ru_4(CO)_{12}]^+$ containing four ^{104}Ru isotopes. Other peaks indicate successive loss of twelve carbon monoxide molecules and a group of peaks at mass numbers between 393 and 414 with a maximum at 406 denotes the presence of the ion Ru_4^+. Comparison with the mass spectrum[3,4] of $Ru_3(CO)_{12}$ indicates no contamination of the hydrido-species. Chemical analysis and molecular weight are consistent with the formula $H_nRu_4(CO)_{12}$ where $n = 2$ or 3. Integration of the n.m.r. peak and comparison with peaks for known hydrogen compounds gives values of n of 2·8—3·2. The infrared spectrum has bands in the terminal carbonyl region at 2008, 2028, 2063, and 2086 cm.$^{-1}$ but no band unequivocally assignable to Ru–H could be detected.

While the exact structure must await *X*-ray studies now in progress[5] the most likely appears to be one involving a tetrahedron of ruthenium atoms with terminal carbon monoxide groups and, presumably, the hydrogen atoms bonding[6] in the faces.

(*Received, July 20th,* 1966; *Com.* 524.)

---

[1] A. P. Ginsburg, "Transition Metal Chemistry", ed. R. L. Carlin, Vol. 1, p. 147.

[2] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466.

[3] R. B. King, *J. Amer. Chem. Soc.*, 1966, **88**, 2076.

[4] J. Lewis, A. R. Manning, J. R. Miller, and J. Wilson, *J. Chem. Soc. (A)*, 1966, in the press.

[5] By Prof. R. Mason, Sheffield University.

[6] L. B. Hardy, P. M. Treichel, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 366.