

A Low-pressure Synthesis of $\text{Ru}_3(\text{CO})_{12}$

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THE orange ruthenium carbonyl reported by Manchot and Manchot¹ as $\text{Ru}_2(\text{CO})_9$ has been shown to be the trinuclear $\text{Ru}_3(\text{CO})_{12}$ by Corey and Dahl.² Previous syntheses of this compound have involved decomposition, either at 50° or in sunlight, of $\text{Ru}(\text{CO})_5$ formed by carbonylation of ruthenium black,¹ ruthenium sulphide,³ or ruthenium stearate⁴ at high pressures (180—220 atm.) and temperatures (180—200°). Recently, Wilkinson and his co-workers have reported⁵ the formation of a carbonyl hydride, possibly $\text{H}_3\text{Ru}_4(\text{CO})_{12}$, together with $\text{Ru}_3(\text{CO})_{12}$, by treatment of a red carbonyl-containing chlororuthenium solution with

hydrogen and carbon monoxide (120 atm., 75°) in the presence of silver as a halide-acceptor.

We now report a simple, low-pressure synthesis of $\text{Ru}_3(\text{CO})_{12}$. Carbonylation (< 10 atm., 65°) of ruthenium trichloride in methanol in the presence of a suitable halogen acceptor, *e.g.*, zinc, gives the carbonyl in 75% yield. The product separates as large hexagonal crystals from the reaction mixture, and is essentially pure. If necessary, the carbonyl may be sublimed at 80—100° (0.1 mm), or recrystallised from cyclohexane or benzene as fine orange crystals, m.p. 154—155° (ν_{CO} 2062, 2032, 2011 cm^{-1} ; lit.⁶ 2061, 2032, 2015 cm^{-1} , both in CCl_4).

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³ W. Hieber and H. Fischer, German Patent 695,589.

⁴ Imperial Chemical Industries, Ltd., British Patent 983,792

⁵ J. W. S. Jamieson, J. V. Kingston, and G. Wilkinson, *Chem. Comm.*, 1966, 569.

⁶ W. Beck and K. Lottes, *Chem. Ber.*, 1961, **94**, 2578.