

## Synthesis of $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ at Atmospheric Pressure

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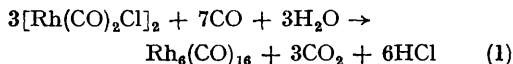
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HIEBER and LAGALLY,<sup>1</sup> by reaction of dry rhodium trichloride and copper or zinc with carbon monoxide at 200 atm. and different temperatures, obtained  $\text{Rh}_4(\text{CO})_{12}$  (< 80°) or  $\text{Rh}_6(\text{CO})_{16}$  (> 80°). Recently  $\text{Rh}_6(\text{CO})_{16}$  has been prepared in high yields by treating rhodium trichloride trihydrate in methanol with carbon monoxide at 50 atm. and 60°.<sup>2</sup> Both syntheses require high-pressure equipment that is not always available. We report a

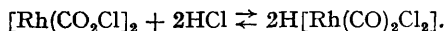
synthesis which operates at atmospheric pressure and does not require any special equipment. The starting material for the new synthesis is  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ , which is easily prepared from rhodium trichloride trihydrate and carbon monoxide at 100°.<sup>3</sup>

By addition of water (about 5%) to a solution of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  in an organic solvent (such as methanol, acetone, or tetrahydrofuran) saturated

with carbon monoxide, a slow formation of  $\text{Rh}_6(\text{CO})_{16}$  takes place according to the equation:



The yield of  $\text{Rh}_6(\text{CO})_{16}$  is low (30—40%) owing to the side reaction between the hydrochloric acid liberated in the above reaction and the tetracarbonyldichlorodirrhodium<sup>4</sup>:



Under these conditions  $\text{Rh}_6(\text{CO})_{16}$  is the only insoluble product and can be obtained in a pure state<sup>5</sup> by filtration; the tetracarbonyldichlorodirrhodium can be recovered from the solution by evaporation to dryness. Hydrochloric acid and carbon dioxide determinations give full confirmation of equation (1).

The  $\text{Rh}_6(\text{CO})_{16}$  yield can be raised to 80—90% by neutralizing the free acidity with potassium hydroxide or, better, by buffering the solution with lithium acetate. The reaction time is about two or three days at room temperature.

$\text{Rh}_6(\text{CO})_{16}$  can be purified by slow extraction with chloroform or methylene chloride in nitrogen atmosphere.

Similarly a mixture of  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$  is obtained by reducing a solution of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  in n-heptane with carbon monoxide in the presence of sodium hydrogen carbonate. After stirring for 48 hr. at room temperature, the suspension is filtered and the solid is extracted with more n-heptane; the combined solution is cooled to  $-70^\circ$ , giving red crystals of pure  $\text{Rh}_4(\text{CO})_{12}$  (71%). The residual solid is washed with water, leaving  $\text{Rh}_6(\text{CO})_{16}$  (11%) on the filter.

Surprisingly, the direct reduction with zinc of a pentane solution of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  gives only low yields of  $\text{Rh}_4(\text{CO})_{12}$  (15—25%), owing to the formation of considerable amounts of a zinc carbonylrhodiato. In this type of synthesis, carbonylrhodiates are important intermediates or by-products; these compounds will be the object of a separate communication.

We thank the C.N.R. for financial support.

(Received, December 19th, 1967; Com. 1357.)

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<sup>3</sup> J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.

<sup>4</sup> L. Vallarino, *Inorg. Chem.*, 1965, **4**, 161.

<sup>5</sup> P. Chini, *Chem. Comm.*, 1967, 440.