Synthesis of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ at Atmospheric Pressure

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HIEBER and LAGALLY,[1] by reaction of dry rhodium trichloride and copper or zinc with carbon monoxide at 200 atm. and different temperatures, obtained $Rh_4(CO)_{12}$ (< 80°) or $Rh_6(CO)_{16}$ (>80°). Recently $Rh_6(CO)_{16}$ has been prepared in high yields by treating rhodium trichloride trihydrate in methanol with carbon monoxide at 50 atm. and 60°.[2] 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 $[Rh(CO)_2Cl]_2$, which is easily prepared from rhodium trichloride trihydrate and carbon monoxide at 100°.[3]

By addition of water (about 5%) to a solution of $[Rh(CO)_2Cl]_2$ in an organic solvent (such as methanol, acetone, or tetrahydrofuran) saturated with carbon monoxide, a slow formation of $Rh_6(CO)_{16}$ takes place according to the equation:

$$3[Rh(CO)_2Cl]_2 + 7CO + 3H_2O \rightarrow Rh_6(CO)_{16} + 3CO_2 + 6HCl \quad (1)$$

The yield of $Rh_6(CO)_{16}$ is low (30—40%) owing to the side reaction between the hydrochloric acid liberated in the above reaction and the tetracarbonyldichlorodirhodium[4]:

$$[Rh(CO_2Cl]_2 + 2HCl \rightleftarrows 2H[Rh(CO)_2Cl_2].$$

Under these conditions $Rh_6(CO)_{16}$ is the only insoluble product and can be obtained in a pure state[5] by filtration; the tetracarbonyldichlorodirhodium can be recovered from the solution by evaporation to dryness. Hydrochloric acid and carbon dioxide determinations give full confirmation of equation (1).

The $Rh_6(CO)_{16}$ 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. $Rh_6(CO)_{16}$ can be purified by slow extraction with chloroform or methylene chloride in nitrogen atmosphere.

Similarly a mixture of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ is obtained by reducing a solution of $[Rh(CO)_2Cl]_2$ 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°, giving red crystals of pure $Rh_4(CO)_{12}$ (71%). The residual solid is washed with water, leaving $Rh_6(CO)_{16}$ (11%) on the filter.

Surprisingly, the direct reduction with zinc of a pentane solution of $[Rh(CO)_2Cl]_2$ gives only low yields of $Rh_4(CO)_{12}$ (15—25%), owing to the formation of considerable amounts of a zinc carbonylrhodiate. In this type of synthesis, carbonylrhodiates are important intermediates or by-products; these compounds will be the object of a separate communication.

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