Dibutadienerhodium(I) Chloride

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ALTHOUGH several complexes of rhodium with chelating dienes are known,[1] no complex of this metal with an acyclic conjugated diene has yet been described.

We have obtained a butadiene complex of rhodium, $(C_4H_6)_2RhCl$, which forms yellow crystals. The latter are sensitive to air, but stable under nitrogen at temperatures below about 40°. The new complex has been obtained by two routes: (*a*) by direct reaction of rhodium trichloride with butadiene, and (*b*) by reaction of rhodium trichloride with cyclo-octene, followed by treatment of the resulting complex, $(C_8H_{14})_2RhCl$, with butadiene.

In method (*a*), butadiene (0·7 g.) and rhodium trichloride (0·1 g.) are dissolved in 99·5%-ethanol (6 ml.) and kept at about $-5°$ for 8—10 days.* During this period of time, well-shaped yellow crystals formed on the bottom of the container.

In method (*b*), cyclo-octene (3 ml.) and rhodium trichloride (1 g.) are dissolved in 99·5%-ethanol (20 ml.) and the solution is kept at room temperature for 3 days, after which time red–brown crystals (0·85 g.) of composition $(C_8H_{14})_2RhCl$ have been formed. The complex reacts rapidly with liquid butadiene to give cyclo-octene and a yellow microcrystalline powder, of which the infrared spectrum, *X*-ray powder spectrum, and

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* If the reaction is performed above 0°, a different crystalline complex is obtained: this is currently under investigation.

[1] See, for example, E. O. Fischer and M. Werner, "Metall-π-Komplexe mit di- und oligo-olefinischen Liganden," Verlag Chemie, 1963.

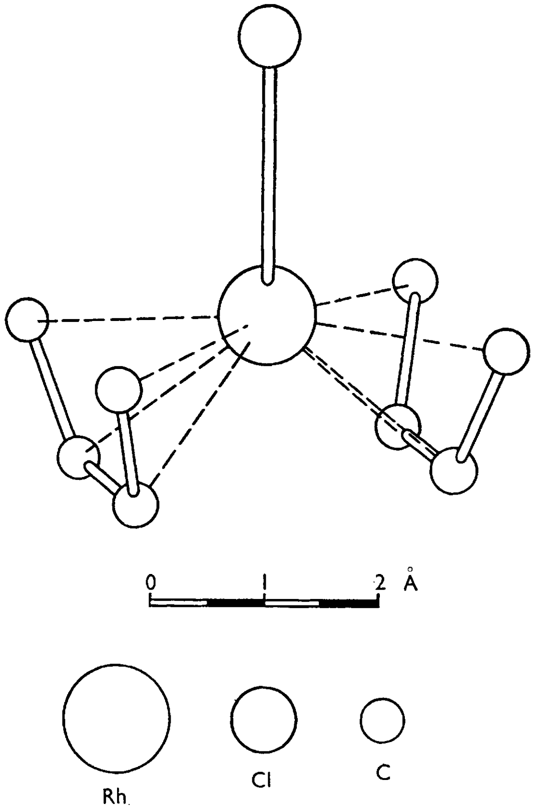
elemental analysis were identical with those of the complex obtained by method (*a*).

Satisfactory elemental analyses were obtained for $(C_4H_6)_2RhCl$ and for $(C_8H_{14})_2RhCl$. The complex $(C_4H_6)_2RhCl$ reacts with a solution of triphenylphosphine in benzene to give two molecules of butadiene for each atom of rhodium.

If we formally assume each butadiene molecule to contribute four electrons to rhodium in the complex, the electronic configuration of xenon is attained; this picture is in agreement with the observed diamagnetism of the complex. The infrared spectrum of $(C_4H_6)_2RhCl$ exhibits two bands at about 1479 and 1375 cm.$^{-1}$, but no band characteristic of the conjugated double bonds, or of the vinyl group.

Single crystals of $(C_4H_6)_2RhCl$ have been examined by the usual X-ray Weissenberg methods using Mo-$K\alpha$ radiation. The space group of the tetragonal unit cell is $P\bar{4}2_1m$, and the cell dimensions are: $a = b = 7{\cdot}90 \pm 0{\cdot}03$ Å, $c = 6{\cdot}92 \pm 0{\cdot}03$Å. The experimental value of the density ($d_{\text{exp.}} = 1{\cdot}87$ g. cm.$^{-3}$) is in agreement with the presence of two molecules in the unit cell ($d_{\text{calc}} = 1{\cdot}90$ g. cm.$^{-3}$). Each molecule mus tbe placed on a twofold axis which contains the rhodium and chlorine atoms, and also on two orthogonal mirror planes. Therefore the molecular symmetry is C_{2v}. The preliminary results of the structural refinement [$R = 12{\cdot}1\%$ on the (hkl) reflections with ($h + k = 0$) and ($h + k = 1$)] indicate that, in the crystalline state, the structure of the molecule is as shown in the Figure. The Rh–Cl bond length is $2{\cdot}45 \pm 0{\cdot}03$ Å; the Rh–C distances are 2·20 Å on the average ($\pm 0{\cdot}05$ Å). The three dimensional refinement is in progress in order to clarify the details of the molecular geometry.

The complex $(C_4H_6)_2RhCl$ is soluble at room temperature in such solvents as benzene, chloroform, and carbon tetrachloride. A rapid reaction occurs, however, with formation of insoluble products. The behaviour of the complex in solution and the nature of the transformation products will be described in a subsequent paper.



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