Tetrahedron Letters No.47, pp. 4187-4189, 1965. Pergamon Press Ltd.
Printed in Great Britain.

FORMATION OF DICHLORO(2,7-DIMETHYL-OCTA-2,6-DIENE-1,8-DIYL)RUTHENIUM(IV) FROM $RuCl_3$ AND ISOPRENE

L. Porri, M. C. Gallazzi, A. Colombo, G. Allegra
Istituto di Chimica Industriale del Politecnico, Milano, and
Centro Nazionale di Chimica delle Macromolecole, Sez. I, Milano, Italy.

(Received 1 October 1965)

Recently it has been reported (1) that $RuCl_3$, on reacting with butadiene at 100°C in methoxyethanol, yields a crystalline complex, $RuCl_2C_{12}H_{18}$, which, on the basis of X-ray evidence, was formulated as Dichloro(dodeca-2,6,10-triene-1,12-diyl)ruthenium(IV).

We have studied the reaction between $RuCl_3$ and isoprene, and isolated a red-brown complex which shows interesting differences, from the chemical and structural standpoint, from the one obtained from butadiene. The complex was obtained by heating at 60-70°C for 40 hours a solution of $RuCl_3$ in ethanol (0.1 g in 2 cc.) with a large excess (10 cc.) of isoprene. The complex, which is diamagnetic, is fairly soluble in CH_2Cl_2 and $CHCl_3$, much less in CCl_4, nearly insoluble in benzene and ethyl alcohol. Its elemental analysis is in accord with the formula $RuCl_2C_{10}H_{16}$.

Solutions of $RuCl_2C_{10}H_{16}$ in CH_2Cl_2 react with H_2 at room temperature and atmospheric pressure yielding 2,7-dimethyl-octa-2,6-diene in nearly a quantitative amount. This shows that the organic ligand is a linear tail-to-tail dimer of isoprene. On reacting CO at room temperature and atmospheric pressure with a CH_2Cl_2 solution of $RuCl_2C_{10}H_{16}$, a new complex, $RuCl_2C_{10}H_{16}\cdot CO$, of yellow colour, is obtained. This further reacts in CH_3OH solution with CO giving eventually $RuCl_2(CO)_4$ and polymeric products. Analogously, pyridine reacts with $RuCl_2C_{10}H_{16}$ giving first the complex $RuCl_2C_{10}H_{16} \cdot C_6H_5N$ (red-purple crystals), and finally $RuCl_2(C_6H_5N)_4$, together with polymeric products.

The formation of $RuCl_2(C_{10}H_{16})CO$ and $RuCl_2C_{10}H_{16}(C_6H_5N)$ suggests that the complex $RuCl_2C_{10}H_{16}$ is dimeric with a chloro-bridge between the ruthenium atoms. The formation of polymeric products, from the organic ligand, in the reactions of the complex with CO or C_6H_5N, indicates that the organic ligand is bonded to Ru by π-allylic bonds. In fact if it were bound by a simple olefinic complexation a linear dimer, rather than a polymer product, would have been obtained on reaction with CO or pyridine.

The NMR spectrum of $RuCl_2C_{10}H_{16}(CO)$ shows two singlets at τ 6.31 and 5.18, most probably attributable to the two terminal allylic hydrogens, and a sharp singlet at τ 7.66, attributable to methyl groups. This evidently means that the two methyl groups of the tail-to-tail dimer are equivalent.

All the above evidences are fully confirmed by the preliminary study of the complex by X-ray spectroscopy.

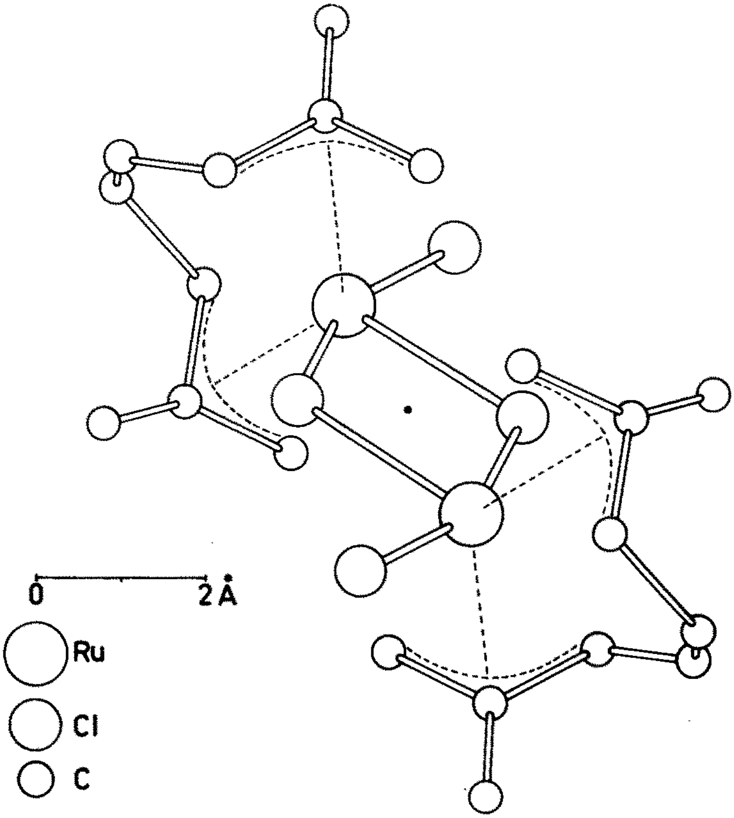
Preliminary results of our single crystal analysis show that the dimensions of the triclinic unit cell are:

$a = 9.45 \pm 0.04$ Å; $b = 8.43 \pm 0.04$ Å; $c = 7.71 \pm 0.03$ Å;
$\alpha = 107.8 \pm 0.5°$; $\beta = 75.2 \pm 0.5°$; $\gamma = 101.5 \pm 0.5°$; $V = 561 \pm 5$ Å^3

Only one molecule is contained in the unit cell, and the calculated density ($d = 1.82$ g/cm^3) is in good agreement with the experimental value ($d = 1.80$ g/cm^3). The two-dimensional refinement on the (*ab*) and (*bc*) projections has shown that the molecule is centrosymmetrical (space group $P\bar{1}$), the resulting molecular structure being represented in the figure.

Within the accuracy of the present stage of refinement, the organic group possesses a twofold axis which connects the two chemically equivalent isoprene units and passes through the Ru atom. The distance between Ru and the allylic carbon atoms is on the average 2.25 Å. The type of coordination around the Ru atoms may be roughly described as a trigonal bipyramid, the upper and lower vertices being represented by two chlorine atoms and the three equatorial vertices by a chlorine atom and the two allylic groups.

The disagreement index between observed and calculated structure factors is 0.10 for 470 observed reflections. The tridimensional refinement is in progress.



References

1. J. E. Lydon, J. K. Nicholson, B. L. Show, M. R. Truter, Proc. Chem. Soc., 421 (1964).