Products formed from Rhodium Trichloride Trihydrate and Allyl Alcohol or Diallyl Ether; The Crystal and Molecular Structure of $[Rh_2Cl_4(C_6H_{11}O)_2],CH_3OH$

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Summary The structure of the complex $[Rh_2Cl_4(C_6H_{11}O)_2],CH_3OH$ formed from $RhCl_3,3H_2O$ and allyl alcohol is reported as well as a very efficient rhodium-catalysed cyclisation of diallyl ether.

WHEN a solution of rhodium trichloride trihydrate in a mixture of allyl alcohol and methanol is heated under reflux for 1 min, propene is evolved and, on cooling, yellow-brown crystals of a compound $[RhCl_2(C_6H_{11}O)]_n,n/2CH_3OH$-are deposited.

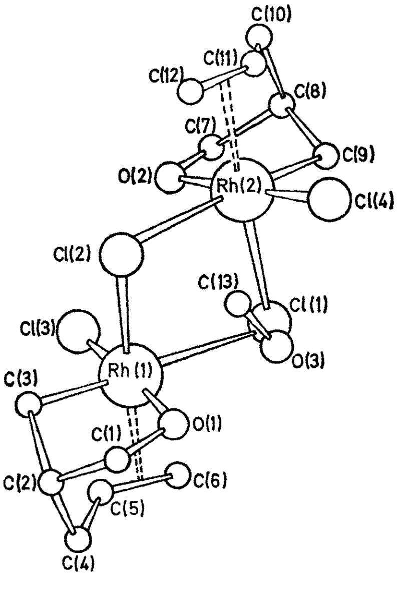
Other products formed in this reaction include propionaldehyde, propionaldehyde diallyl acetal, acraldehyde, and traces of ethylene.[1,2] The compound $[RhCl_2(C_6H_{11}O)]_n,$-$n/2CH_3OH$ is rather insoluble and its ^1H n.m.r. spectrum is very complex. The i.r. spectrum shows absorptions in the regions characteristic of a bridging chloride system and of a hydroxy-group. The structure of the compound has been determined by single-crystal *X*-ray diffraction.

Crystal data: $[Rh_2Cl_4(C_6H_{11}O)_2],CH_3OH$, $M = 578·0$, orthorhombic, $a = 10·70(1)$, $b = 15·00(2)$, $c = 11·88(1)$ Å, $U = 1906·3$ Å^3, $D_O = 1·98$, $D_c = 2·01$ g cm^{-3}, $Z = 4$; space group $Pn2_1a$. The intensities of 2948 independent non-zero reflections were estimated visually from equi-inclination Weissenberg photographs taken with Mo-K_α radiation. The structure was determined by standard Patterson and Fourier techniques and was refined by least-squares with allowance for isotropic temperature factors for all atoms to $R = 8·7\%$. Anisotropic refinement is continuing.

The molecule is shown in the Figure and the principal dimensions are given in the Table.

Principal bond lengths (Å)

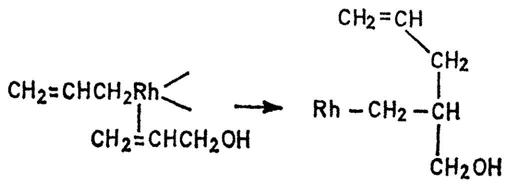
Rh–Cl (*trans* to σ-bonded carbon) = 2·616(4); mean of 2
Rh–Cl (*trans* to π-bonded olefin) = 2·386(4); mean of 2
Rh–Cl (*trans* to co-ordinated oxygen) = 2·301(6); mean of 2
C–C [olefinic; *i.e.* C(5)–C(6) and C(11)–C(12)] = 1·36(3); mean of 2
Other C–C distances are normal single bonds.
O(1)–O(3) = 2·58(2)
O(2)–Cl(3) = 3·07(2)
O(3)–Cl(4) = 3·06(2)



FIGURE

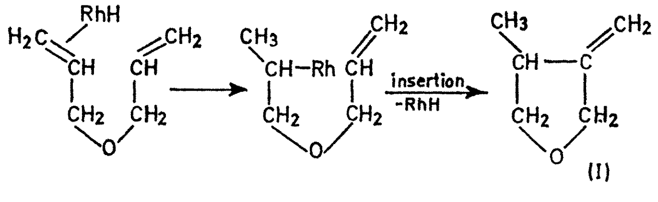
The dimeric molecule is folded by 18·2° across the Cl(1)–Cl(2) line, thus producing a Cl(3) · · · O(2) separation which is appropriate to hydrogen bonding while, at the same time, allowing the methanol molecule to bridge Cl(4) and O(1) by the formation of two more hydrogen bonds. The atoms Rh(1,2), Cl(3,4), O(1,2,3) are very nearly coplanar (r.m.s. distance of atoms from mean plane = 0·1 Å).

The novel tridentate ligand $C_6H_{11}O$ probably arises by the 1,2-addition of a σ-allylrhodium system to a co-ordinated allyl alcohol. The σ-allylrhodium system could be generated in several ways. One possibility would be as in the reaction between palladium chloride and allyl alcohol which gives allylpalladium chloride.[3,4]



The complex $[RhCl_2(C_6H_{11}O)]_2,CH_3OH$ reacts with neutral monodentate ligands, L, (pyridine, 4-methylpyridine, PMe_2Ph, PPh_3 or $AsPh_3$) (one mole per Rh atom) to give binuclear complexes of type $[RhCl_2(C_6H_{11}O)L]_2$. With two moles of neutral ligands, L, per Rh atom, binuclear complexes of the type $[RhCl_2(C_6H_{11}O)L_2]_2$ (L = py or $AsPh_3$) are formed. Similarly bipyridyl gives $[RhCl_2(C_6H_{11}O)$-$(bipy)]_2$. All these complexes show i.r. absorptions due to OH and to terminal Cl–Rh–Cl and bridging $RhCl_2Rh$ systems. The neutral ligands, L, presumably successively displace the co-ordinated OH and C=C of the tridentate ligand $C_6H_{11}O$ from the rhodium. With thallium acetylacetonate $[RhCl(acac)(C_6H_{11}O)]_2$ is formed.

We also find that when diallyl ether containing a few percent of allyl alcohol is heated with either rhodium trichloride trihydrate or $[RhCl_2(C_6H_{11}O)]_2,CH_3OH$ as catalyst, rapid conversion of diallyl ether into the cyclised product (I) occurs. The conversion possibly involves two insertions with a rhodium hydride intermediate. One mole of rhodium will catalyse conversion of 10^4 moles of diallyl ether into (I) without apparent loss in efficiency. Allyl phenyl ether is isomerized by rhodium trichloride trihydrate to a mixture of *cis*- and *trans*-phenyl propenyl ethers.



We thank the Science Research Council, Imperial Chemical Industries Ltd., and Johnson Matthey Ltd. for generous support.

(*Received, May* 13*th*, 1971; *Com.* 763.)

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