

Products Formed from 2-Methylallyl Alcohol and Rhodium Trichloride Trihydrate. Determination of the Structure of $[\text{RhCl}_2(\text{C}_8\text{H}_{15}\text{O})(4\text{-methylpyridine})_2]_2$ by X-Ray Crystallography

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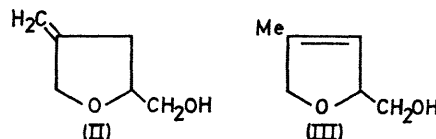
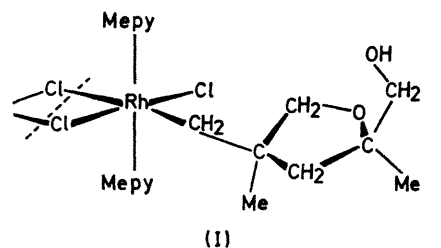
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Summary Rhodium trichloride trihydrate and 2-methylallyl alcohol react to give $[\text{RhCl}_2(\text{C}_8\text{H}_{15}\text{O}_2)]_n$ which with 4-methylpyridine gives $[\text{RhCl}_2(\text{C}_8\text{H}_{15}\text{O}_2)(4\text{-methylpyridine})_2]_2$, the structure of which has been determined by X-ray diffraction.

When a solution of rhodium trichloride trihydrate in 2-methylallyl alcohol-methanol is heated under reflux for 1 minute isobutene is evolved and on cooling yellow-brown crystals of a complex $[\text{RhCl}_2(\text{C}_8\text{H}_{15}\text{O}_2)]_n$ are deposited. This complex is too insoluble for an accurate determination of molecular weight. Its i.r. spectrum shows the presence of an OH group and of a bridging chloride system. Treatment of $[\text{RhCl}_2(\text{C}_8\text{H}_{15}\text{O}_2)]_n$ with lithium bromide gives the corresponding bromo-complex and with neutral monodentate ligands ($L = \text{pyridine}$, PPh_3 , or AsMe_2Ph) complexes of the type $[\text{RhCl}_2(\text{C}_8\text{H}_{15}\text{O}_2)L]_2$ are formed. These show i.r. absorptions at *ca.* 330 $[\nu(\text{Cl-Rh-Cl})]$, *ca.* 245 $[\nu(\text{RhCl}_2\text{Rh})]$, and at *ca.* 3390 cm^{-1} $[\nu(\text{OH})]$. Treatment of $[\text{RhCl}_2(\text{C}_8\text{H}_{15}\text{O}_2)]_n$ with 4-methylpyridine (2 mol. equiv. per Rh atom) gives $[\text{RhCl}_2(\text{C}_8\text{H}_{15}\text{O}_2)(4\text{-methylpyridine})_2]_2$ which also shows i.r. absorptions due to terminal chlorine, bridging chlorine, and hydroxy-groups. The structure of this 4-methylpyridine complex has now been determined by X-ray diffraction.

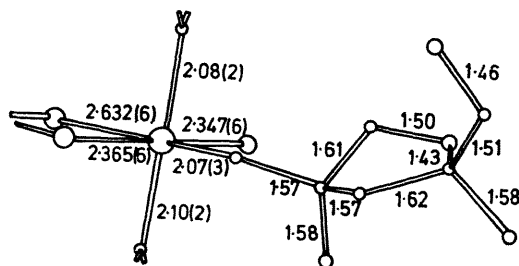
Crystal data: $\text{C}_{40}\text{H}_{58}\text{Cl}_4\text{N}_4\text{O}_4\text{Rh}_2$, $M = 948.1$, monoclinic, $a = 16.14$, $b = 15.04$, $c = 20.99$ Å, $\beta = 103.9^\circ$, $U = 4943$ Å³, $Z = 4$, $D_c = 1.29$. Space group $C2/c$. 1580 Independent reflections measured by Stoe Weissenberg

diffractometer, $\text{Cu-K}\alpha$ radiation, $R = 0.106$ by block-diagonal least-squares refinement, Rh and Cl atoms anisotropic at the present stage of refinement.



The complex is a centrosymmetric dimer with two bridging chlorine atoms; one half of the molecule is represented by (I) (Mepy is 4-methylpyridine). Details of the stereochemistry and selected bond lengths are shown in the Figure. The two oxygen atoms were identified from comparisons of bond lengths, and the observation that abnormally low isotropic temperature factors resulted from least-squares refinement when the two atoms were given

carbon scattering factors ($B = 2$ and 4 for the ring and terminal O, respectively, whereas B for neighbouring atoms averaged $5-6 \text{ \AA}^2$). A final difference Fourier analysis revealed *ca.* 0.5 mol of unco-ordinated 4-methylpyridine in the crystal lattice.



Molecular structure of the rhodium complex. Only one half of the dimer is shown, and only the N atom of each co-ordinated 4-methylpyridine group. E.s.d.s of rhodium bond lengths are in parentheses, all others shown are $\pm 0.04 \text{ \AA}$.

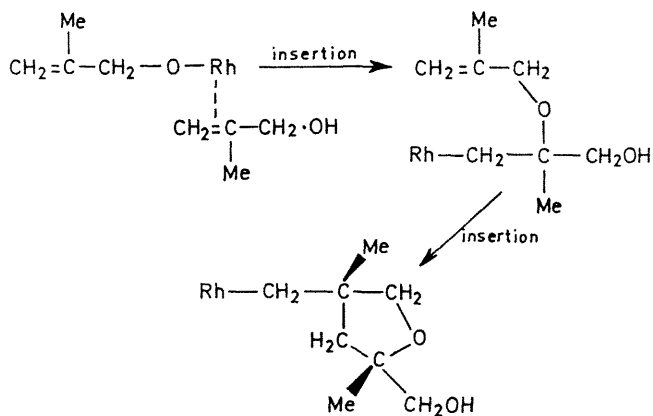
Although there are two asymmetric carbon atoms in the substituted furan ligand, both enantiomers are present in the molecule by virtue of the centre of symmetry. The two methyl groups are *cis* with respect to the furan ring.

Rhodium-ligand distances demonstrate the large *trans*-influence of a saturated carbon ligand¹ compared with a chlorine atom. Bond lengths within the ring are consistent with a fully saturated system.

¹ R. Mason and A. D. C. Towl, *J. Chem. Soc. (A)*, 1970, 1601.

² W. Hafner, H. Prigge, and J. Smidt, *Annalen*, 1966, **693**, 109; W. H. Urry and M. B. Sullivan, American Chemical Society Meeting, Minneapolis, 1969, Division of Petroleum Chemistry Abstracts.

The substituted furan-ring-rhodium system in (I) may be formed as shown in the Scheme. The ring system is



SCHEME

analogous to that of two of the products (II) and (III), formed when allyl alcohol is treated with palladium chloride.² Product (II) is probably formed by insertion reactions analogous to those of our rhodium-2-methylallyl alcohol system with elimination of a palladium hydride species at the final step and (III) by isomerisation of (II).

We thank the S.R.C. and Johnson, Matthey Ltd. for generous support.

(Received, May 20th, 1971; Com. 810.)