Triallylrhodium(III) and a Crotyl–Butadiene Complex of Rhodium

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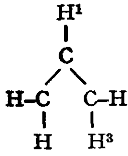
WE have recently described[1] a diallylrhodium complex $[RhCl(C_3H_5)_2]_2$, prepared from rhodium chlorocarbonyl, allyl chloride, and water. We now find that treatment of $[RhCl(C_3H_5)_2]_2$ with allylmagnesium chloride gives triallylrhodium(III) as a volatile pale yellow solid, m.p. 80—85°, with a camphoraceous odour. Triallylrhodium has a novel type of stereochemistry since its n.m.r. spectrum shows two types of symmetrically bonded π-allyl ligands to be present (two of one kind, one of the other). The n.m.r. data ($CDCl_3$ solution) are given below, with the hydrogens numbered as shown. The peaks in pattern X have twice the intensity of the corresponding peaks in pattern Y.



	τ_1	τ_2	τ_3	J_{12}c/sec.	J_{13}c/sec.
Pattern X	5·98[a]	7·19[b]	8·36[b]	7	11·5
Pattern Y	4·62[a]	6·98[b]	7·36[c]	6·5	~12·5

[a] Septet (should be nonet but two peaks unresolved). [b] Doublet.
[c] Doublet, partially overlapping a more intense resonance (pattern X, τ_2)

π-Allylic ligands are μ- or "sandwich" bonded to metals and may be regarded as occupying two co-ordination positions in such complexes.[2] Thus triallylrhodium is essentially a six-co-ordinated complex, the arrangement of the π-allyl groups about the rhodium atom probably being based on a trigonal prism or octahedron as shown in Figures 1 and 2. In Figures 1 and 2 the arrows represent the arrangement of the allyl groups with the arrow head indicating the position of the central carbon atom; in Figure 1 the planes of the allyl groups are vertical to the plane of the paper. An allyl group represented by the dotted arrow could then give the resonance pattern Y; the other two allyl groups must be so nearly equivalent as to give only one resonance pattern, X. The structure of triallylrhodium is being determined by X-ray diffraction; more complicated structures than the ones outlined above are of course possible.

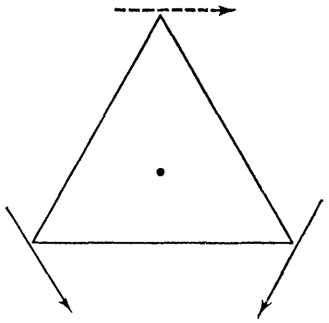


FIGURE 1

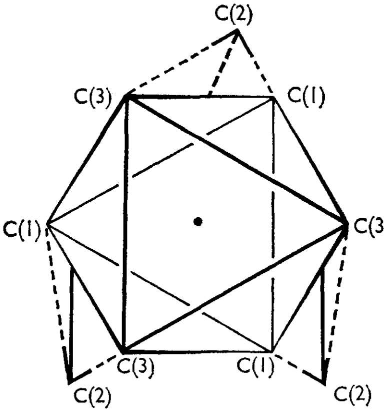


FIGURE 2

As reported previously[1] $[RhCl(C_3H_5)_2]_2$ reacts with cyclopentadienylthallium to give $[Rh(C_3H_5)_2C_5H_5]$. We now find this cyclopentadienyl complex to react with hydrochloric acid successively giving $[RhCl(C_3H_5)(C_5H_5)]$ and $[RhCl_2(C_5H_5)]_x$ (probably $x = 2$).

Rhodium trichloride reacts with butadiene in ethanol to give a binuclear complex $[Rh_2Cl_4(C_{12}H_{20})]$; previously this complex was mentioned by us and incorrectly formulated as $[Rh_2Cl_4(C_{12}H_{18})]$.[3] N.m.r. studies on the reaction of this complex with pyridine (2 mol. per Rh atom) in $CDCl_3$ solution show the liberation of butadiene (1 mol. per 2 Rh atoms) and the formation of 2 mol. of a π-crotyl complex $[RhCl_2(C_4H_7)(py)_2]$, which can be readily isolated. $[Rh_2Cl_4C_{12}H_{20}]$ reacts with bipyridyl to give $[RhCl_2(C_4H_7)(bipy)]$ and with cyclopentadienylthallium to give $[RhCl(C_4H_7)(C_5H_5)]$ ($C_4H_7 = \pi$-crotyl) {analogous to the complex $[RhCl(C_3H_5)(C_5H_5)]$ referred to above}.

We formulate $[Rh_2Cl_4(C_{12}H_{20})]$ as $[C_4H_7RhCl_2(C_4H_6)Cl_2RhC_4H_7]$ with two bridging and two terminal chlorines and a bridging butadiene ligand [infrared data (cm.$^{-1}$) = bands at 1535 (m) (co-ordinated C=C of butadiene), 320 (vs) (terminal Rh–Cl stretch), 240 (vs) (bridging Rh–Cl–Rh stretch)]. The n.m.r. spectrum of [$Rh_2Cl_4C_{12}H_{20}$] is very complicated and the crotyl (C_4H_7) ligands are probably asymmetrically bonded as in [$RhCl(C_3H_5)_2$].[1]

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[1] J. Powell and B. L. Shaw, *Chem. Comm.*, 1966, 236.

[2] M. L. H. Green and P. L. I. Nagy, *Adv. Organometallic Chem.*, 1964, **2**, 325.

[3] J. E. Lydon, J. K. Nicholson, B. L. Shaw, and M. R. Truter, *Proc. Chem. Soc.*, 1964, 421.