Temperature-dependence of the N.m.r. Spectrum of Trisallylrhodium

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RECENTLY Powell and Shaw[1,2] described trisallylrhodium, $Rh(C_3H_5)_3$, made from rhodium dicarbonyl chloride dimer by the following series of reactions:

$$[Rh(CO)_2Cl]_2 \xrightarrow{C_3H_5Cl} [Rh(C_3H_5)_2Cl]_2 \xrightarrow{C_3H_5MgCl} Rh(C_3H_5)_3$$

The n.m.r. spectrum of $Rh(C_3H_5)_3$, which was observed at one temperature only, suggested that of the three symmetrically bonded π-allyl groups, two were equivalent and different from the third. Their explanation is not entirely satisfactory as the proposed structures would be expected to have three nonequivalent allylic ligands, and the experimental results reported[2] require the fortuitous equivalence of one pair of ligands.

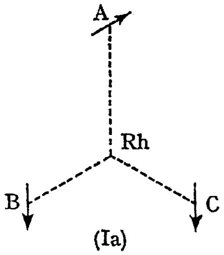
We have therefore repeated the preparation of $Rh(C_3H_5)_3$ by the above route, and also made the compound from anhydrous rhodium trichloride with allylmagnesium chloride at 0° under nitrogen, in a manner analogous to the preparation of other isoleptic* allyl complexes.[3] The compounds obtained by these routes are identical, as shown by their n.m.r. and mass spectra.

The n.m.r. spectrum of $Rh(C_3H_5)_3$ at −74° [Figure (a)] consists of three AM_2X_2-type patterns, showing that the complex has three non-equivalent symmetrically bonded π-allylic ligands. At 10° [Figure (b)] the spectrum is similar to that reported[2] by Powell and Shaw, in which two of the three allylic ligands appear equivalent. Parameters and assignments are given in the Table.

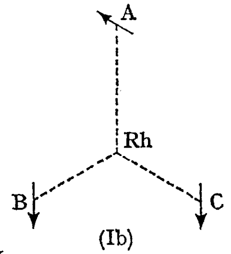
As the temperature is raised from −74° to +10° the doublets at τ 8·29 and 8·67 and the multiplets at τ 5·83 and 6·50 broaden and coalesce giving finally the sharp resonances seen at 10°; these changes are reversible. This behaviour is characteristic of a temperature-dependent exchange between non-equivalent sites. The activation energy for this exchange, estimated by the method of Gutowsky and Holm,[4] is 9·4 ± 2·0 Kcal./mole.

The results may be explained by assuming an equilibrium between two mirror-image structures (Ia) and (Ib). These structures are based on a trigonal prism (each π-allyl ligand occupying two co-ordination sites about the rhodium atom[5]) and have a plane of symmetry through the rhodium atom and the three central carbon atoms of the allyl groups. The diagrammatic representations (Ia) and (Ib) are projections on to this plane of symmetry, the arrow heads indicating the positions of the central carbon atoms. The transition from (Ia) to (Ib) involves rotation of allyl group (A) through 180° about an axis represented by the broken line joining it to the metal atom. This transition has no effect on that part of the n.m.r. spectrum due to allyl group (A) as the two environments are identical. Allyl groups (B) and (C) are, however, in different environments, with (B) and (C) in (Ia) equivalent to (C) and (B) respectively in (Ib). At −74°, therefore, three different types of allyl groups are seen in the n.m.r. spectrum, but at +10° the rotation of (A) is sufficiently rapid to cause averaging of the two environments available to (B) and (C), resulting in the observed coalescence of peaks.

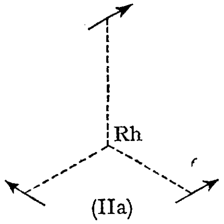
Small doublet splittings due to coupling with the ^{103}Rh nucleus ($I = \frac{1}{2}$) can be discerned, with an expanded field sweep scale, in the resonances of some of the protons in each allyl group, even at



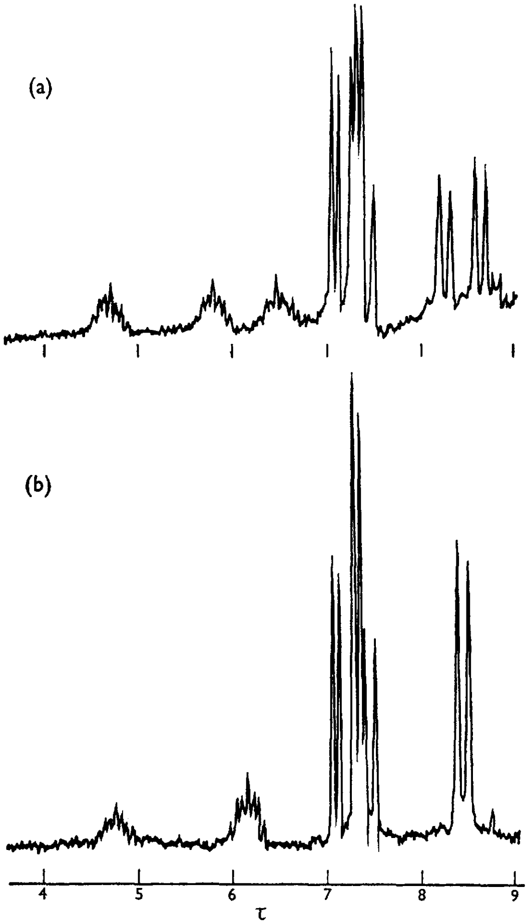
(Ia)



(Ib)



(IIa)



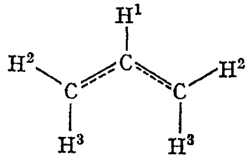
FIGURE

100 *Mc./sec. Proton n.m.r. spectrum of* $Rh(C_3H_5)_3$ *in* $CFCl_3$ *(a) at −74°, (b) at + 10°.*

* We use the term isoleptic to indicate that all the ligands attached to the central metal atom are identical in constitution.

TABLE

Proton n.m.r. parameters for $Rh(C_3H_5)_3$ *in* $CFCl_3$



Temp. °c	Allyl Group	τ_1	τ_2	τ_3	J_{12} c./sec.	J_{13} c./sec.	J(HRh) c./sec.
−74	(A)	4·74	7·13	7·47	7·0	11·0	*
	(B) or (C)	5·83	7·32 or 7·38	8·67	6·5	11·0	*
	(C) or (B)	6·50	7·38 or 7·32	8·29	6·5	11·0	*
+10	(A)	4·75	7·11	7·47	7·0	11·2	$H^1Rh = 1·6$ $H^2Rh < 0·5$ $H^3Rh = 1·5$
	(B), (C)	6·16	7·34	8·46	6·5	11·2	$H^1Rh = 1·0$ $H^2Rh < 0·5$ $H^3Rh = 1·5$

* Rh couplings discernible for some protons but not measured. τ-values in p.p.m., tetramethylsilane internal reference = 10·00. Measurements were made at 100 Mc./sec. and 60 Mc./sec. on a Varian HA-100 and a Perkin-Elmer R.10 spectrometer respectively.

+10° (see Table); thus the averaging process occurring at this temperature cannot involve intermolecular exchange of allylic ligands.

From the fact that the protons of allyl group (A) are considerably less shielded than those of (B) and (C) we conclude that the former group is further away from the rhodium atom than are the other two, and it is probably less strongly bonded to the metal atom. This is consistent with its comparative freedom to rotate.

On the present evidence it is not possible to decide definitely between structures (Ia) and (Ib) as shown and the alternative structures (IIa) and its mirror image (IIb). Also structures based on geometries other than a trigonal prism, *e.g.*, an octahedron,[2] may be possible in which an analogous equilibration can occur.

Above room temperature the spectrum (in chlorobenzene) undergoes changes which indicate further averaging processes. Between room temperature and 100° the resonances due to all the methylene protons broaden, giving at 100° two broad resonances at τ ~7·2 and 8·0. At 120° all the CH_2 resonances are combined in a single broad peak at τ ~ 7·6. At these higher temperatures fairly rapid decomposition occurs. The above changes with temperature are reversible, though there is some loss of peak intensity through decomposition.

The changes observed between room temperature and 100° indicate that averaging of proton environments in each CH_2 group occurs, possibly by rotation of the CH_2 groups as in some other allylic complexes.[3,6] The final averaging of the CH_2 resonances into a single peak at 120°, moreover, suggests that all three allyl groups undergo rapid rotation in the manner proposed above for allyl group (A) at +10°.

The electron-impact mass spectrum of $Rh(C_3H_5)_3$ shows a strong parent ion peak at $m/e = 226$. Peaks due to $Rh(C_3H_5)_2^+$, $Rh(C_3H_5)^+$, and Rh^+ are also observed.

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