Nuclear Magnetic Resonance Study of Bisallylrhodium Chloride

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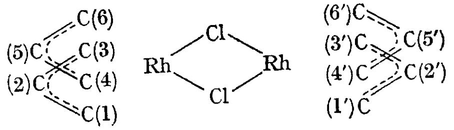
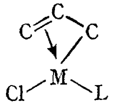
RECENT *X*-ray crystallographic studies of bisallylrhodium chloride[1] and triphenylphosphine methallylpalladium chloride[2] have yielded unusual features concerning metal–allyl bonds. The investigators[1,2] chose as an extreme representation, structure (I), a σ-bonded allyl group with metal–olefin interaction, rather than (II), a π-bonded allyl group, with unequal bonding between the metal and the two terminal carbon atoms of the allyl group. A number of nuclear magnetic

TABLE

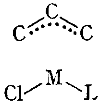
^1H n.m.r. parameters of bisallylrhodium chloride



Solvent	Temp.	Chemical shift (τ) 1,6(*cis*)	2,5	1,6(*trans*)	3,4(*cis*)	3,4(*trans*)	Coupling constants (c./sec.)
$CDCl_3$	$-20°$	4·92	5·24	5·98	7·50	8·18	$J_{1cis,2}$ = 6·8 $J_{1trans,2}$ = 12·0 $J_{3cis,2}$ = 6·0 $J_{3trans,2}$ = 10·8
			2,5		1, 3, 4, and 6		
o-$C_6H_4Cl_2$ ..	140°		5·38		6·80		$J_{2,1} = J_{2,3}$ = 9·3 $J_{Rh,2}$ = 2·3



(I)



(II)

resonance studies[3] on a variety of metal allyl complexes have been reported. These data are more easily interpreted in terms of structure (II). This conclusion, based in part upon the observed near-zero coupling between the two nonequivalent protons on C-3 of triphenylphosphinemethallylpalladium chloride[3a] is, however, not an unambiguous test for a σ-bonded methylene group,[4] since other factors such as electronegativity may produce similar results.

An analysis of the temperature dependence of the 100 Mc./sec. n.m.r. spectrum of bisallylrhodium chloride has yielded further clarification of the asymmetric nature of the allyl groups. The Figure shows the spectra of bisallylrhodium chloride dimer in solution in $CDCl_3$ and o-$C_6H_4Cl_2$ as obtained at $-20°$ and 140°, respectively. The n.m.r. parameters of the low-temperature species show that the allyl groups are asymmetric. This is indicated by the chemical shifts for the protons attached to C-3 and C-4 which appear at higher fields than do those bonded to C-1 and C-6. Furthermore, the small differences between $J_{cis(1,2)}$ and $J_{cis(3,2)}$ and $J_{trans(1,2)}$ and $J_{trans(3,2)}$ taken collectively with the near-zero coupling between the two nonequivalent protons bonded to C-3 and C-4, and C-1 and C-6 suggest near-planar π-bonded allyl groups, structure (II), rather than structure (I).

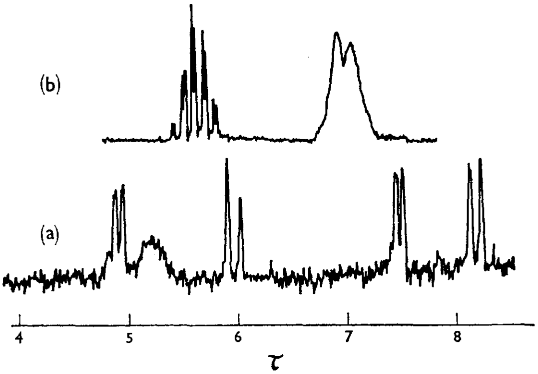


FIGURE. *Nuclear magnetic resonance spectra of bisallylrhodium chloride in solution in:* (a) $CDCl_3$ *at* $-20°$, *and* (b) o-$C_6H_4Cl_2$ *at* 140°.

The spectrum of bisallylrhodium chloride dimer at 140°, is of the AX_4 type corresponding to a dynamic system which is a consequence of a rapid equilibration between the asymmetric π-bond and σ-bond.

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