N.m.r. Study of Hindered Internal Rotation in Transition-metal π-Allyl Complexes

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ON the evidence of proton n.m.r. spectra it has been claimed that allylic ligands in complexes with transition metals are capable of bonding to the metal atom in three distinct ways:—

(i) σ-bonding, *e.g.*, allylmanganese pentacarbonyl,[1]

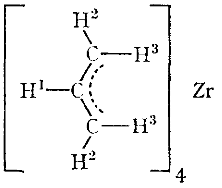
(ii) π-bonding, which gives an AM_2X_2-type spectrum,

(iii) a dynamic bonding[2] which gives an AX_4-type spectrum.

Type (iii) has been visualised as a rapid exchange in which each of the terminal carbon atoms in turn is σ-bonded to the metal atom.[3] Our results on $Zr(allyl)_4$ and $[(allyl)PdCl]_2$ provide clear evidence that some examples of type (iii) are π-bonded, and differ from type (ii) only in having relatively fast internal rotation of the CH_2 groups.

$Zr(allyl)_4$ was prepared from anhydrous $ZrCl_4$ and (allyl)MgCl under nitrogen at −80°c. and characterised by its mass spectrum (to be published). The n.m.r. spectrum is temperature-dependent as briefly reported by Wilke *et al.*[2] We examined a solution in $CFCl_3$ at temperatures from −74°c to 0°c, and found that a change from AM_2X_2-type to AX_4-type occurs within this range, the CH_2 peaks coalescing at −40°c. The peak widths in the transitional range were unaffected by changes in the solution concentration; this rules out any mechanism involving intermolecular ligand exchange. Data at two extreme temperatures are given in the Table.

The observations are consistent with a π-bonded structure (I) in which hindered rotation of the CH_2 groups about the C–C bonds linking them to the central carbon atom occurs at a rate dependent on the temperature. This readily explains the following features of our results:—



(I)

(a) the chemical shift of H¹ remains unaltered as the spectrum changes from AM_2X_2 to AX_4,

(b) the chemical shift of the doublet in the AX_4 spectrum is midway between the chemical shifts of the two doublets in the AM_2X_2 spectrum,

(c) the single coupling constant in the AX_4 spectrum is half the sum of the two coupling constants in the AM_2X_2 spectrum.

We have measured the activation energy for internal rotation using the method of Gutowsky and Holm[4] and obtained the value $10{\cdot}5 \pm 1{\cdot}0$ kcal./mole.

TABLE

Proton n.m.r. spectra of Zr(allyl)$_4$ *in* $CFCl_3$

−10°c. (AX_4-type)	−74°c. (AM_2X_2-type)
$\tau_1 = 4{\cdot}81$ (quintet, intensity 1)	$\tau_1 = 4{\cdot}82$ (multiplet, intensity 1)
	$\tau_2 = 6{\cdot}72$ (doublet, intensity 2)
$\tau_2 = \tau_3 = 7{\cdot}37$ (doublet, intensity 4)	$\tau_3 = 8{\cdot}10$ (doublet, intensity 2)
$J_{1,2} = J_{1,3} = 12{\cdot}5$ c./sec.	$J_{1,2} = 8{\cdot}5$ c./sec.
	$J_{1,3} = 15{\cdot}5$ c./sec.
	$J_{2,3} < 0{\cdot}5$ c./sec.

τ-Values in p.p.m., tetramethylsilane internal reference $= 10{\cdot}00$. Subscripts refer to numbering in formula (I).

Wilke *et al.*[2] put forward, as a possibility to explain the temperature dependence of the Zr(allyl)$_4$ and Th(allyl)$_4$ spectra, rotation of the CH_2 groups but visualised this as involving a structural transition to a "dynamic" form. As we have shown no such structural change need be involved for Zr(allyl)$_4$. The chemical shifts for Th(allyl)$_4$, quoted but not commented on by Wilke *et al.*,[2] show the features (a) and (b) above and can therefore be explained exactly as for Zr(allyl)$_4$.

[(Allyl)PdCl]$_2$ as a solution in $CDCl_3$ has an AM_2X_2-type n.m.r. spectrum[5] consistent with the symmetrical π-bonded structure. A solution in dimethyl sulphoxide (DMSO) was reported to give an AX_4-type spectrum[3] at an unspecified temperature but Shaw *et al.*[6] later found a sharp quintet and a broad single peak at 33·5°c.

We have examined [(allyl)PdCl]$_2$ as a solution in dried hexadeutero-DMSO from 25 to 65°c. We found at relatively low temperatures a spectrum similar to that reported by Shaw *et al.*[6] The width of the CH_2 peak was unaffected either by the solution concentration or by the addition of small amounts of water to the solution. At 65°c the CH_2 resonance had sharpened sufficiently to reveal a doublet splitting which was the same as the quintet splitting ($J = 9{\cdot}8$ c./sec.). This coupling constant is, to a good approximation, half the sum of the two coupling constants ($J_{1,2} = 6{\cdot}4$, $J_{1,3} = 12{\cdot}8$ c./sec.) found[5] for the AM_2X_2 spectrum in chloroform. The relatively high freezing point of DMSO prevents one's lowering the solution temperature sufficiently to get an AM_2X_2 spectrum. The results lead us to believe that this too is a case of hindered internal rotation, which apparently occurs much more rapidly in DMSO solution than in $CDCl_3$ at a given temperature.

Wilke *et al.*[2] suggest that the relative ease of internal rotation in Zr(allyl)$_4$ (in contrast with the majority of transition-metal π-allyl complexes) is explained by the absence of *d*-electrons available for back-donation to the allyl groups. We support this view, and further suggest that for [(allyl)PdCl]$_2$ in DMSO, the solvent acts as a ligand on the metal atom, accepting back-donated *d*-electrons and thereby reducing the back-bonding to the allyl group. A similar mechanism probably plays a part in the changes observed[2,6] when phosphines are added to solutions of π-allyl compounds.

N.m.r. measurements were made at 100 Mc./sec. on a Varian HA-100 spectrometer.

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