

THE NATURE OF THE BONDING IN  $\pi$ -ALLYL COMPLEXES OF TRANSITION METAL IONS

S. F. A. KETTLE AND R. MASON

*Department of Chemistry, University of Sheffield (England)*

(Received September 27th, 1965)

Allyl complexes of transition metal ions are of particular interest on two grounds: the allyl ligand can be regarded as intermediate in type between olefins and conjugated aromatic systems and various complexes have considerable catalytic properties. X-ray structural analyses<sup>1,2,3,4</sup> have shown that in  $\pi$ -allylpalladium-chloride and -acetate the plane defined by three carbon atoms of the allyl group is tilted with respect to the plane defined by the palladium and the two remaining atoms coordinated to it. If the bonding between the allyl radical and the palladium atom were analogous to that usually postulated for ethylene-platinum complexes<sup>5</sup>, a dihedral angle of  $90^\circ$  is to be expected. This is to be compared with the values of  $125^\circ$ ,  $110^\circ$  (ref. 4) and  $108^\circ$  (ref. 3) observed in the acetate and chloride complexes respectively.

There are two distinct mechanisms by which bonding between an allyl radical and a transition metal atom can occur and which differ in the orientation of the radical with respect to the metal ion and remaining ligands (Fig. 1).

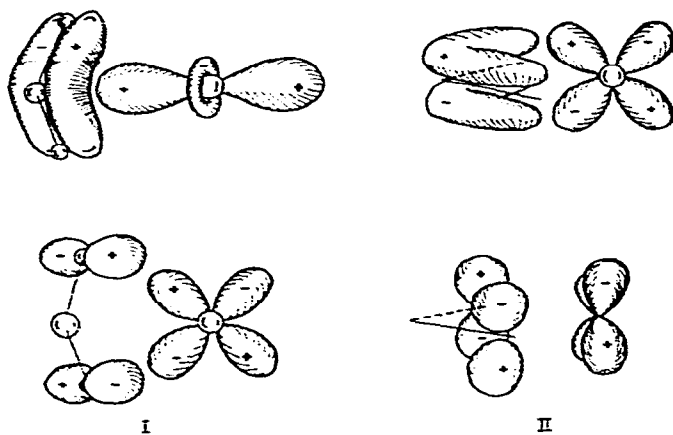


Fig. 1. Alternative orientations for allyl-metal interaction. The interaction between allyl  $b_1(1)$  (top) and  $a_2$  (bottom) molecular orbitals are shown for each orientation.

In the first orientation (I) the geometry is such that a line drawn from the palladium atom to the mid-point of the line joining the two equivalent carbon atoms of the allyl group, the former being taken as the  $z$  axis, is perpendicular to the plane defined by the carbon atoms of the allyl group (the dihedral angle is  $90^\circ$ ). In the second

orientation (II) these carbon atoms are co-planar with the palladium atom ( $\chi$  is  $180^\circ$ ). The three  $\pi$  molecular orbitals of the allyl ligand are of  $b_1$  (twice) and of  $a_2$  symmetry of the  $C_{2v}$  group. In both of the above and in all intermediate orientations these molecular orbitals overlap with orbitals centred on, say, a palladium ion. The observation of an orientation intermediate between the two extremes makes it evident that it is a poor approximation to regard either as exclusively responsible for the allyl-palladium bonding. In Table 1 the palladium orbitals which interact significantly with the allyl molecular orbitals in the two extreme orientations are given together with the resultant overlap integrals. The latter were calculated using Slater orbitals assuming a palladium-carbon bond length of  $2.08 \text{ \AA}$ . Tables of  $2p_x-4d_x$  overlap integrals are not available and so these overlap integrals are taken as the mean of  $2p_x-3d_x$  and  $2p_x-5d_x$ . The functional form of Slater functions at these large inter-nuclear distances is not good and we rely only on the trend of the overlap integrals rather than their absolute values. It should be noted that we have taken the  $x$  axis of the complex as parallel to the line joining the two equivalent atoms of the allyl group.

The symmetry of the atomic arrangement in orientation 1 is only  $C_s$  and consequently the following additional overlap integrals are not required, by symmetry, to be zero:  $S[b_1(1), d_{xz}-yz] = 0.030$ ,  $S[b_1(1), d_{yz}] = 0.128$ ,  $S[b_1(2), d_{xz}-yz] = 0.062$ ,  $S[b_1(2), d_{yz}] = 0.128$  and  $S[a_2, d_{xy}] = 0$ . These interactions are later shown to be unimportant and can be ignored for the moment.

It is significant that different metal orbitals are involved in the bonding in the two extreme orientations (Table 1). Overlap integrals involving the  $b_1(2)$  orbital are small and we shall also ignore these interactions in our subsequent discussion; in doing so we note that the allyl group differs, say, from ethylene, where the back-donation process is considerable.

TABLE 1  
ALLYL-PALLADIUM OVERLAP INTEGRALS<sup>a</sup>

	Allyl orbital			
	$b_1(1)$	$a_2$	$b_1(2)$	$\chi$
Energy	$x + \sqrt{2}\beta$	$x$	$x - \sqrt{2}\beta$	
Orientation 1	$0.426$	$0.365$	$0.073$	$90^\circ$
Palladium orbital	$d_{z^2}$	$d_{z^2}$	$d_{z^2}$	
Orientation 2	$0.285$	$0.166$	$0.015$	$180^\circ$
Palladium orbital	$d_{yz}$	$d_{xy}$	$d_{yz}$	

<sup>a</sup> Hückel orbitals and energies are used for the allyl radical<sup>6</sup>.

The extent of the interaction between the allyl and palladium orbitals will depend on the overlap integral - it will vary roughly as its square\* - and on the energy difference between the interacting orbitals. For the present the latter dependence will be neglected since, to a good approximation, it will be independent of the angle that the allyl group makes with the palladium system.

\* This follows if the resonance integrals in the secular determinants are set proportional to the corresponding overlap integral and the stabilisation which they give evaluated according to second order perturbation theory.

The total bonding energy,  $E$ , of the allyl-palladium bond may accordingly be expressed as the sum of the bonding energies ( $\epsilon_1$  and  $\epsilon_2$ ) of the two separate overlap mechanisms discussed above,

$$E = \epsilon_1 \cos \Theta + \epsilon_2 \sin \Theta$$

where the suffixes 1 and 2 refer to mechanisms 1 and 2 (Table 1) and  $\Theta$  is ( $\chi - 90^\circ$ ). The dihedral angle at which the total bonding energy is maximised is

$$\left( 180^\circ - \tan^{-1} \frac{\epsilon_1}{\epsilon_2} \right)$$

The  $\epsilon$ 's are assumed to be proportional to  $S^2$  so that this expression becomes

$$\left( 180^\circ - \tan^{-1} \left( \frac{S_1}{S_2} \right)^2 \right)$$

and with the values of  $S$  given in Table 1 we find that the dihedral angles predicted separately from the  $b_1(1)$  and  $a_2$  interactions are  $114^\circ$  and  $102^\circ$  respectively, values which may be compared with the experimental values of  $125^\circ$  and  $110^\circ$  (ref. 4) and  $108^\circ$  (ref. 3). If the other overlap integrals given earlier for orientation 1 are included, then  $S_1^2$  must be replaced by  $\sum_j S_{1j}^2$ , the summation extending over all overlap integrals. This more complete calculation shows that the  $b_1(1)$  and  $a_2$  interactions are maximised at dihedral angles of  $112^\circ$  and  $102^\circ$  respectively, results which are close to those given for the simpler calculation.

In order to decide which of these two interactions determines the geometry of the allyl complex it is necessary to discuss the relative energies of the  $\pi$  orbitals of the allyl system and the  $d$  orbitals of palladium. The ionisation potential of the allyl radical is 5.2 eV<sup>7</sup> and this we equate with the energy of the  $a_2$  orbital. Taking the value of the resonance integral,  $\beta$ , as 2.5 eV the  $b_1(1)$  orbital lies at 11.7 eV and the  $b_1(2)$  at 4.7 eV. The first and second ionisation potentials of palladium are 8.3 eV and 19.4 eV respectively. If in the complex the palladium carried a fractional positive charge (we have elsewhere drawn analogies with  $d^8$  and  $d^9$  systems<sup>4</sup>) the energy of the  $d$  orbitals of palladium lies between 8.3 and 19.4 eV. It therefore seems probable that the  $b_1(1)$  orbital plays the major role in the palladium-allyl bonding. In Pd<sup>I</sup> the 5s orbital lies approximately 4.0 eV above the  $d$  orbitals while the 5p orbitals lie at approximately 9.0 eV above the 4d levels<sup>8</sup>. The 5p orbitals are much lower-lying in Pd<sup>0</sup>, being about 4.2 eV above the 4d orbitals, whilst the 5s orbital is slightly less stable than the 4d orbitals.

It is difficult to discuss the interaction of the 5s and 5p orbitals at all quantitatively since they will doubtless be contracted. The  $2p_\sigma$ -5s overlap integral, calculated for Slater orbitals assuming a  $4d^8 5s^1$  configuration for palladium, is 0.04, which is undoubtedly much too small. It does not appear likely that they participate greatly in the molecular orbitals primarily responsible for the bonding although they may participate to some extent in relatively weakly bonding molecular orbitals. Since their contribution is somewhat uncertain, they have not been included in the schematic molecular orbital energy diagram which is given in Fig. 2, although it should be

pointed out that a valence bond description would be based on the use of hybrid  $dsp^2$  palladium orbitals.

It is of interest to examine the allyl-metal interaction in the isoelectronic nickel and platinum complexes, for which the overlap integrals and related data are collected in Table 2.

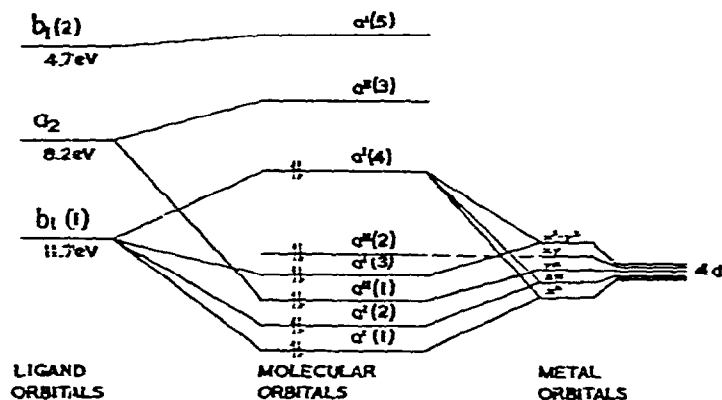


Fig. 2. Schematic energy level scheme for Pd-allyl group interaction.

In the absence of accurate structure analyses of nickel- and platinum-allyl complexes, we have assumed identical geometrical parameters to those in the palladium-allyl example. It seems likely that we have, in this way, underestimated the nickel-allyl overlap integrals and overestimated them in the case of the platinum complex so that it is not possible, at the present time, to make comparisons about the

TABLE 2

OVERLAP INTEGRALS AND PREDICTED DIHEDRAL ANGLES IN NICKEL- AND PLATINUM-ALLYL COMPLEXES

Ion	$b_1$ interaction			$a_2$ interaction		
	S Orientation 1	S Orientation 2	$\chi$	S Orientation 1	S Orientation 2	$\chi$
Ni <sup>I</sup>	0.242	0.129	106°	0.159	0.075	103°
Pt <sup>I</sup>	0.511	0.304	117°	0.300	0.212	116°

relative stability of allyl complexes of different metal ions with any confidence. But it would be surprising if the dihedral angles of the allyl group in nickel and platinum complexes did not follow the pattern observed in the allylpalladium-acetate and -chloride.

The explanation of dihedral angles advanced in this paper is not confined to the case of the allyl radical. In tricarbonyl(octafluoro-1-3-cyclohexa-diene)iron the dihedral angle of the co-ordinated butadiene fragment is 111° (ref. 9), that in  $\pi$ -cyclopentadienylhexakis(trifluoromethyl)benzenerhodium is 99° (ref. 10), the corresponding values in  $\pi$ -cyclopentadienyl(1-phenylcyclopentadiene)cobalt<sup>11</sup> and [tetrakis(tri-

fluoromethyl)cyclopentadienone]tricarbonyl iron<sup>12</sup> being 95° and 96.6° respectively. It seems reasonable to believe that a similar model to that which we have elaborated here will rationalise these results.

#### SUMMARY

The bonding electron distribution in allyl complexes of transition metal ions is discussed and related to the observed stereochemistries of  $\pi$ -allylpalladium-chloride and -acetate. Some general comments are made on the application of the theory to the bonding in other organometallic molecules.

#### REFERENCES

- 1 J. M. ROWE, *Proc. Chem. Soc.*, (1962) 66.
- 2 A. E. SMITH, *Acta Cryst.*, 18 (1965) 331.
- 3 W. E. OBERHANSLI AND L. F. DAHL, *J. Organometal. Chem.*, 3 (1965) 43.
- 4 M. R. CHURCHILL AND R. MASON, *Nature*, 204 (1964) 777.
- 5 J. CHATT AND L. A. DUNCANSON, *J. Chem. Soc.*, (1953) 2939.
- 6 F. A. COTTON, *Chemical Application of Group Theory*, Interscience, 1963, p. 156.
- 7 A. G. HARRISON AND F. P. LOSSING, *J. Am. Chem. Soc.*, 82 (1960) 1052.
- 8 C. E. MOORE, *Atomic Energy Levels*, U.S. National Bureau of Standards, Circular 467.
- 9 M. R. CHURCHILL AND R. MASON, *Proc. Chem. Soc.*, (1964) 226.
- 10 M. R. CHURCHILL AND R. MASON, *Proc. Roy. Soc. (London)*, Ser. A, 279 (1964) 191.
- 11 M. GERLOCH AND R. MASON, *Proc. Roy. Soc. (London)*, Ser. A, 279 (1964) 170.
- 12 N. A. BAILEY, M. GERLOCH AND R. MASON, *Nature*, 201 (1964) 72.

*J. Organometal. Chem.*, 5 (1966) 573-577

## SHORT COMMUNICATIONS

---

### PMR spectra of some neopentyl derivatives of mercury. Long-range <sup>199</sup>Hg-<sup>1</sup>H coupling

Recently we reported<sup>1,2</sup> spin-spin coupling between protons and phosphorus through four  $\sigma$  bonds. In continuation of our work on the long-range interaction of protons with hetero nuclei, we have now found that mercury (isotope <sup>199</sup>Hg, spin 1/2, 16.86% natural abundance) couples strongly with protons over four single bonds. A very recent communication by Kiefer and Waters<sup>3</sup> on the coupling of mercury with  $\gamma$  protons prompts us to report our findings on this subject.

Neopentyl derivatives, prepared by the usual methods\*, were used as model compounds because of the simplicity of their PMR spectra. The <sup>199</sup>Hg-H <sub>$\gamma$</sub>  coupling could be measured easily as the two peaks of the split  $\gamma$  protons were located symmetrically about the resonance of the corresponding unsplit protons (Fig. 1). The pertinent data are summarized in Table 1.

\* The preparation of neopentylmagnesium chloride and its further reactions with appropriate mercuric halides were carried out in dry tetrahydrofuran<sup>2</sup>.