The Molecular Structure of π-1,3-Dimethylallylpalladium Chloride Dimer

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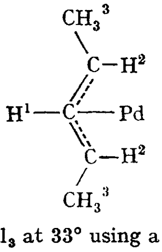
THE prediction from n.m.r. studies that π-allyl complexes should have sandwich structures has been verified in a number of cases by X-ray structural determinations.[1] It has also been shown that in 2-methylallyl derivatives [$Ni(C_4H_7)_2$[2] and $(C_4H_7)PdCl(PPh_3)$ [3]], the methyl group is displaced out of the plane of the three allyl carbon atoms towards the metal atom. The loss of planarity has important theoretical implications[4] as it indicates a loss of resonance energy in the π-electron system of the allyl group, which is compensated for by stronger binding between the metal and the allyl group. In order to determine whether groups substituted on the terminal carbon atom of the allyl group are also displaced out of the allyl plane, and if so in which direction, we have prepared, and carried out a 3-dimensional X-ray analysis on, π-1,3-dimethylallylpalladium chloride dimer (I).

The complex was prepared from 4-chloropent-2-ene and sodium chloropalladite using a method analogous to that described by Dent, Long, and Wilkinson[5] for the preparation of allylpalladium chloride dimer. The n.m.r. spectrum in $CDCl_3$ and benzene indicates, as found for $\{(C_3H_5)PdCl\}_2$,[6] that each allyl group in solution is equivalent and symmetrically bonded to the palladium atom (see also reference 7). The coupling J_{12} indicates that the protons H^2 occupy a position *trans* to H^1 as shown in the diagram.

τ_1 = 4·86 (triplet)†
τ_2 = 6·38 (six-line multiplet)
τ_3 = 8·83 (doublet)
J_{12} = 10·7 c./sec.
J_{23} = 6·3 c./sec.



Compound (I) was recrystallized from chloroform or benzene as pale yellow crystals which decomposed without melting from about 160°. The crystals are monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14); $a = 9{\cdot}967 \pm 0{\cdot}009$, $b = 11{\cdot}125 \pm 0{\cdot}005$, $c = 12{\cdot}709 \pm 0{\cdot}014$ Å, $\beta = 90{\cdot}65 \pm 0{\cdot}08°$, $U = 1409{\cdot}16$ Å^3, D_m (by flotation) $= 1{\cdot}999$, $D_c = 1{\cdot}988$, for $Z = 4$, $M = 422{\cdot}0$.

1080 independent structure amplitudes were determined, using a Picker 4-circle Single-Crystal Diffractometer with Mo-K_α radiation. The structure was determined using Patterson and Fourier syntheses and refined to an R value of 12·4%; attempted further refinement was unsuccessful because of disorder or of strong thermal vibration in the allyl group. The carbon atoms are thus less well defined than expected and to overcome this we are re-determining the structure at low temperature. Nevertheless some conclusions can be drawn at this stage.

For each allyl ligand, the three Pd–C distances are unequal (see Figure) the variation being the same in both groups. A similar variation in allyl metal–carbon distances has been found in the complexes $(C_4H_7)PdCl(PPh_3)$ [3] and $\{(C_3H_5)_2RhCl\}_2$.[8] In those compounds the bonding may

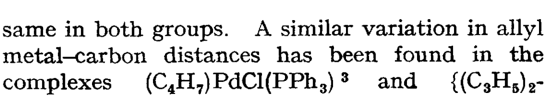


FIGURE. *Structure of* $[(C_5H_9)PdCl]_2$

Pd(2)–C(2) 2·14(4) Å	Pd(1)–C(9) 2·14(4) Å
Pd(2)–C(3) 2·07(4)	Pd(1)–C(8) 2·08(3)
Pd(2)–C(4) 2·04(3)	Pd(1)–C(7) 2·05(3)

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† Measurements were made in $CDCl_3$ at 33° using a 60 Mc./sec. Perkin-Elmer R.10 spectrometer.

be modified by the different groups *trans* to the allyl ligand. In the present complex no such effect can occur and we believe that the lack of symmetry in the solid state results from an inherent lack of rigidity in molecules of this type, involving multi-centre bonds, which allows some distortion to be caused by crystal packing forces.

The dihedral angles between the allyl C_3 planes and the palladium co-ordination planes [defined by PdCl(1)Cl(2)] for the two allyl groups are 123° and 127°, values similar to those found in other allyl complexes.[1] The methyl groups are not all co-planar with the allyl plane; three of them are displaced towards the metal atom (by 0·4, 0·2 and 0·1 Å) whilst the fourth appears to be co-planar with the allyl group but is the least well-defined atom in the molecule.

The Pd–Cl distances [2·40 (1) Å] are all equal and the same as those found in $\{(C_3H_5)PdCl\}_2$,[9] but longer (and therefore presumably weaker) than in $[PdCl_2]_n$, 2·31 Å,[10] and $[PdCl_4]^{2-}$, 2·30 Å.[11] The bridge is unusual in being non-planar, with an angle of 150° between the two metal co-ordination planes. There is no reason to suppose that this molecule is affected by metal–metal bonding, unlike $[Rh(CO)_2Cl]_2$[12] and $[(C_2H_4)_2RhCl]_2$,[13] the only other known examples of non-planar chloro-bridged complexes. The dipole moments of (I) and $[(C_3H_5)PdCl]_2$ ($\mu = 2{\cdot}30$ and 2·16 D respectively, in benzene at 25°) indicate that both complexes are non-planar in solution.‡ The reasons for this non-planarity are not clear. We suggest that the weak Pd–Cl bonding in both complexes allows bending of the bridge to occur easily in solution, whilst in the solid state the conformations are mainly determined by intermolecular forces which lead to a planar bridge in $[(C_3H_5)PdCl]_2$ and a non-planar bridge in compound (I).

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‡ Non-planarity (ref. 9b, 14) and dissociation (ref. 15) of the bridge have previously been proposed to explain the dipole moment of halogen-bridged dinuclear allyl complexes.

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