Di-μ-chloro-bis-(π-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II) and its Structure

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THE ethanolysis of diketen is accelerated by the addition of sodium tetrachloropalladate(II). Yellow crystals separated at the end of this reaction were identified as the π-allylic palladium(II) complex of ethyl acetoacetate. The same compound was also prepared directly by reaction of palladium(II) chloride with the ester in water. [Correct analysis for $PdCl(C_6H_9O_3)$; *M* 502 (ebullioscopic, benzene) indicating a dimer.]

The palladium(II) complex of acetylacetone is known to have the usual structure of an enolate chelate,[1] as has bis(benzoylacetonato)palladium(II) in the crystal.[2] The corresponding acetoacetate complex has not yet been reported. The following i.r. data (KBr disc) reveal that instead of the usual chelate structure, the complex may have a π-allylic linkage: 3200m (O–H str.), 3080w (end methylene str.), 1675vs (C=O str.), 1445s (delocalized C–C str.), 1205vs (C–O–C asym. str.), 545m (π-allyl skeletal deform.). The stretching absorption bands of OH and C=O groups are both shifted to lower frequency, indicating the existence of intra- or inter-molecular hydrogen bonding.

In order to determine the exact structure of this complex, a three-dimensional X-ray analysis was carried out. Crystals are triclinic; $a = 4{\cdot}798$, $b = 10{\cdot}311$, $c = 10{\cdot}639$ Å, $\alpha = 117{\cdot}35$, $\beta = 102{\cdot}29$, $\gamma = 84{\cdot}07°$; $D_m = 1{\cdot}97$; $Z = 1$ (as a dimer, $M = 542{\cdot}0$); space group $P\bar{1}$; $\mu = 98$ cm.$^{-1}$ (for Cu-K_α). Multi-film equi-inclination Weissenberg photographs were taken about the a and c axes, and 1323 independent reflexions were collected. The positions of palladium and chlorine atoms were determined from the three-dimensional Patterson function. All of the light atoms except hydrogen were found on the three-dimensional electron density map; the heavy atom method being applied. The positional and isotropic thermal parameters were refined by a block-diagonal least-squares procedure (R 0·16, five cycles).

The molecular structure is shown in the Figure. Two palladium and two chlorine atoms form a square-planar structure, and the enol tautomer of ethyl acetoacetate co-ordinates to palladium as a π-allyl ligand, to give a dimer, as previously assumed. The average value of three Pd–C distances for the allyl ligand is 2·14 Å, comparable to those found in $(C_3H_5PdCl)_2$.[3,4] The Pd–Cl and Pd–Pd distances are 2·42 and 3·46 Å, respectively, which agree with previous values.[5] The dihedral angle between the metal co-ordination plane and the π-allyl ligand is 108°. The hydrogen bonding between the enolic hydroxy-group and the carbonyl group of the molecule related by the centre of symmetry forms endless sheets of molecules extended along the c axis. The hydrogen bond distance is 2·81 Å.

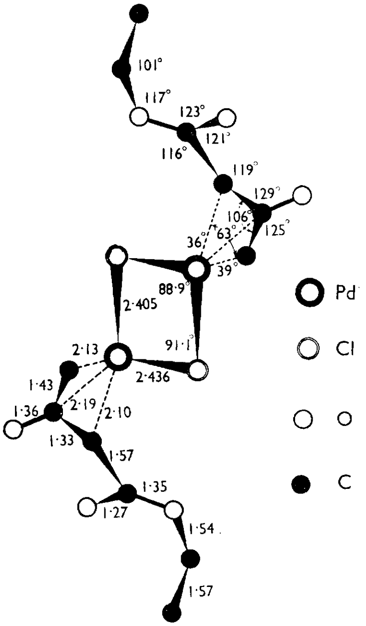

FIGURE. *Molecular structure of* $PdCl(C_6H_9O_3)$.

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