The Crystal Structure of [PtCl(OMe)(dicyclopentadiene)]

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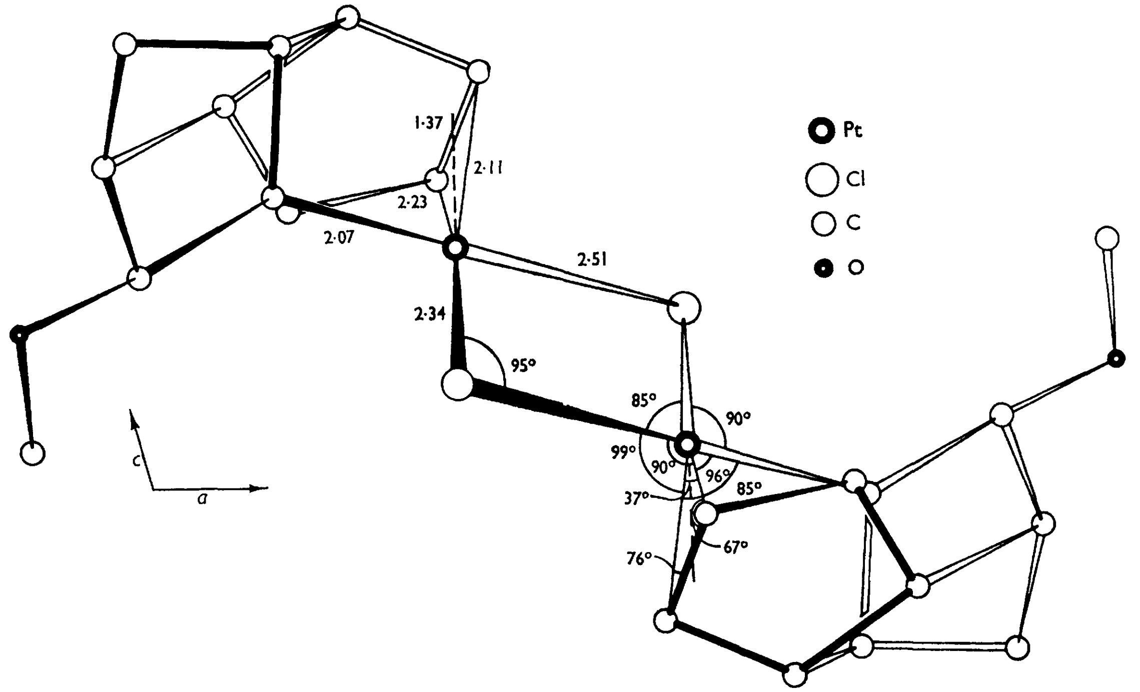
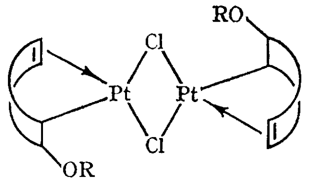
AN investigation by Chatt *et al.*[1] of the compounds prepared by Hofmann and von Narbutt[2] led to the conclusion that complexes [PtCl(OR)(dicyclopentadiene)] were to be formulated as (I). The subsequent discovery that palladium(II) and platinum(II) can form complexes containing π-allylic systems[3] re-opened the question of the structure of compounds (I) as the physical evidence used by Chatt *et al.* for the structural assignment would be equally compatible with the π-allylic structure (II). More recently, however, Stille *et al.*,[4] on the basis of an n.m.r. study of [PtCl(OMe)(dicyclopentadiene)(pyridine)] concluded that structure (I) was correct.

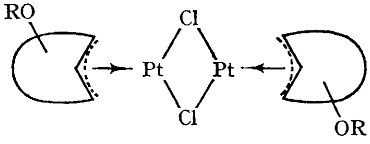
To resolve this uncertainty, a crystal structure determination of [PtCl(OMe)(dicyclopentadiene)] was undertaken. This compound crystallises in the space group $C2/c$ with $a = 24{\cdot}45$, $b = 7{\cdot}50_5$, $c = 12{\cdot}19$ Å, $\beta = 105{\cdot}6°$. For the 2091 photographically observed independent reflections, after



FIGURE



(I)



(II)

four rounds of isotropic least-squares refinement, a value of $R = 11{\cdot}1\%$ was obtained. The compound has structure (I). The environment of the platinum atom is essentially square-planar, each half of the molecule being related to the other half by a crystallographic centre of symmetry. The projection along the *b*-axis of the molecule, with the bond lengths and angles around the platinum atom, is shown in the Figure.

One interesting feature is apparent: the two metal–chlorine distances are significantly different and the longer bond is that in *trans*-position to the carbon atom σ-bonded to the platinum. Bridging Pd–Cl bonds of different lengths have been observed in $[Pd_2Cl_4(PhCH{:}CH_2)_2]$,[5] but in this compound the longer bond is in *trans*-position to the co-ordinated double bond. As there is evidence that lengthening of bond-distances is associated with a strong *trans*-effect,[6] it appears from the present work that a σ-bonded carbon atom exerts a stronger *trans*-effect than a π-bonded olefin.

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