The Crystal and Molecular Structure of (1–5-η-Fluorenyl)(1–3-η-Fluorenyl) dichlorozirconium(IV)

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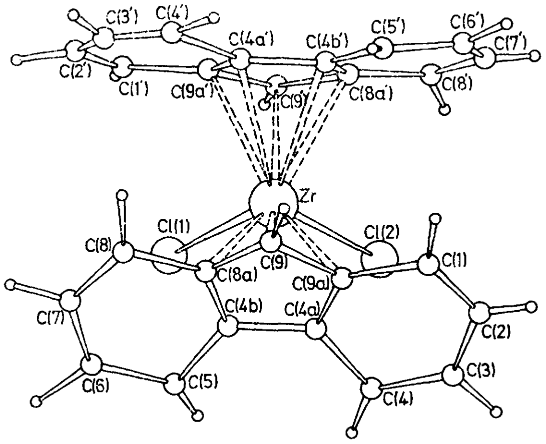
Summary Steric interaction between the tetrahedrally co-ordinated ligands in $(fl)_2ZrCl_2$ (fl = fluorenyl) is avoided by opening the fl–Zr–fl angle and displacement of one fl unit, thus reducing a normally pentahapto system to one which is trihapto (π-allylic).

The complex $(fl)_2ZrCl_2$ has been prepared from zirconium tetrachloride and the dioxan complex of sodium fluorenide in dimethoxyethane.[1] Sublimation at 200°, 10^{-3} mmHg, of the total reaction product gave orange prisms as well as extensive decomposition of the residue. A crystal structure analysis of the orange sublimate was undertaken.

Crystal data: $C_{26}H_{18}Cl_2Zr$; M.Wt. = 492, monoclinic; $a = 12{\cdot}347$, $b = 13{\cdot}771$, $c = 11{\cdot}922$ Å, $\beta = 98{\cdot}2°$, $U = 2006$ Å^3, $Z = 4$, $D_c = 1{\cdot}63$, $\mu = 87{\cdot}13$ cm^{-1}, space group $P2_1/n$. The cell dimensions and intensity for 2697 independent reflexions were measured with a Canberra Industries automated 4-circle Siemens diffractometer using the θ-2θ scanning mode ($2\theta < 130°$) and Ni-filtered Cu-K radiation.



The Zr and Cl sites were located from a three-dimensional Patterson function and the resultant electron density map revealed the locations of all C atoms. Least squares refinement reduced the discrepancy factor R to 0·063. All hydrogen atoms were subsequently located to yield a final value of $R = 0{\cdot}058$.

A perspective view of the complex is shown in the Figure.

The stereochemistry may be discussed in terms of a distorted tetrahedral co-ordination in which the fl–Zr–fl angle is 125·5° and the Cl–Zr–Cl angle is 93·6°. This latter value is similar to many which have been found in comparable π-complexes and which have been discussed in terms of molecular orbitals.[2]

The bonding of one fluorenyl group to Zr can be described as 9,9a,4a,4b,8a-η since the five Zr to C distances range from 2·40 to 2·65 Å. The other fluorenyl group is, however, π-allylically bound to zirconium, the Zr to C(4a) and C(4b) distances being 2·82 Å while those to C(9), C(9a) and C(8a) are 2·40, 2·52 and 2·59° respectively. This is the first reported case of 1—3-η bonding in a planar π-bonded ring system and is of particular interest in the light of Cotton's critical comments on the concept of trihapto bonding of cyclopentadienyl rings.[3]

It would appear that the combination of the wide fl–Zr–fl angle and the 1—3-η bonding together allow the otherwise impossibly close contacts to be avoided in this molecule.

All other features of the molecular structure and crystal packing are normal and will be reported in detail elsewhere.

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