Crystal and Molecular Structure of Tetrakiscyclopentadienylzirconium

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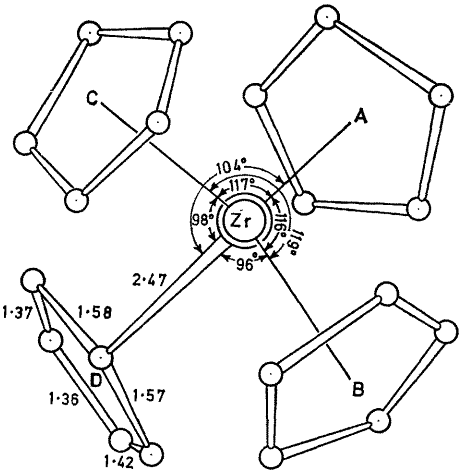
Summary In the crystal form of tetrakiscyclopentadienylzirconium, three cyclopentadienyl rings are π-bonded at a mean Zr–C distance of 2·64 Å, the fourth ring being σ-bonded with a Zr–C distance of 2·47 Å.

THE structures of tetrakiscyclopentadienyl derivatives of zirconium and hafnium cannot be considered as reliably known. Thus the ^{1}H n.m.r. spectra,[1] with one singlet signal, testify to the equivalence of all four C_5H_5 rings in these compounds, whereas their i.r. spectra[1] reveal a distortion of the metal atom co-ordination from tetrahedral local symmetry. Spectral data alone, therefore, are not sufficient for one to draw definite conclusions on either the bonding or the equivalence (or nonequivalence) of the C_5H_5 rings.[1,2] We now report results of an *X*-ray study of $(C_5H_5)_4Zr$. Crystals of $(C_5H_5)_4Zr$ are orthorhombic, with $a = 20{\cdot}83$, $b = 8{\cdot}53$, $c = 8{\cdot}77$ Å; $D_m = 1{\cdot}50$ g. cm^{-3}; $Z = 4$; space group $P2_12_12_1$. The structure was solved by the usual heavy-atom method on the basis of 580 independent reflections (Weissenberg goniometer; unfiltered Cu radiation; visual estimation of intensities). The refinement was accomplished by a full-matrix least-squares method in isotropic approximation to $R = 0{\cdot}083$. The standard deviations are Zr–C, 0·02; C–C, 0·04 Å; C–Zr–C, 1·0°; C–C–C, 2·0°.

The molecular geometry is shown in the Figure. The Zr–C distances for three cyclopentadienyl rings, A, B, and C, vary randomly in the range 2·49—2·73 Å, showing that these rings are π-bonded with the zirconium atom or form a "central σ-bond"[2,3] with it. The average Zr–C π-bonded distance, $2{\cdot}6_4$ Å, is somewhat longer than corresponding values in three previously studied zirconium cyclopentadienyl derivatives having the same type of cyclopentadienyl co-ordination but fewer such ligands: 2·522 Å in $(C_5H_5)_2ZrCl_2$,[4] 2·55 or 2·53 Å in $(C_5H_5)Zr(acac)_2Cl$,[5,6] 2·53 Å in $(C_5H_5)Zr(CF_3{\cdot}CO{\cdot}CHCO{\cdot}CF_3)_3$.[7]

On the other hand, the fourth cyclopentadienyl ring, D, forms a localized two-centre bond (2·47 Å) with the zirconium atom. This bond is not coplanar with the mean plane of the planar D ring, but is inclined to it at an angle of 52°. A similar tilt has been found in other σ-cyclopentadienyl derivatives, *e.g.* $(\pi\text{-}C_5H_5)_2Mo(NO)(\sigma\text{-}C_5H_5)$[8] and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Sn(\sigma\text{-}C_5H_5)_2$.[9]

The C–C bond length in the symmetrically bonded C_5H_5 rings varies randomly in the range 1·31—1·54 Å, but the average value (1·45 Å) is normal for π-bonded C_5H_5 ligands. In the σ-bonded ring there are two C–C bonds of 1·57 and 1·58 Å, respectively; the three other bonds have intermediate lengths. The zirconium atom co-ordination is very close to that found in $(C_5H_5)_3UCl$, where the chlorine atom acts as a σ-bonded ligand. The angles MZrM′ (M and M′ denote the centres of π-bonded C_5H_5 rings) are 116, 117, and 119°; the angles MZrC (σ-bonded) are 104, 96, and 98°. The corresponding angles MUM′ (117°) and MUCl (101°) (average values) are similar.



FIGURE

The molecular structure found in crystalline $(C_5H_5)_4Zr$, with three π-bonded (or central σ-bonded) and one σ-bonded C_5H_5 rings therefore represents a new type of tetrakiscyclopentadienyl transition-metal derivative. A co-ordination of this type had been predicted as a possibility from a quantum-chemical study of metal–ring interactions.[2] The effective equivalence of all four C_5H_5 rings inferred from the ^{1}H n.m.r. spectrum may be attributed to rapid valence tautomerism.

The *X*-ray study of tetrakiscyclopentadienylhafnium is now being carried out. Its crystals are tetragonal, $a = 9{\cdot}80$, $c = 8{\cdot}22$ Å; $Z = 2$; possible space groups $P\bar{4}2_1m$, $P42_12$, and $P4_22_12$. The symmetry of the two-fold special positions in these space groups (*mm*, 4, or 222) shows that, contrary to the situation in $(C_5H_5)_4Zr$, all four C_5H_5 rings are equivalent.

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