Crystal and Molecular Structure of Tetrabenzylzirconium at −40 °C

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Summary The crystal structure of tetrabenzylzirconium (at −40 °C) shows the molecule to have approximate $\bar{4}$ symmetry with distorted tetrahedral co-ordination (average Zr–C 2·27 Å); the benzyl groups are σ-bonded to the metal atom but the angles at the methylene carbon atoms are unexpectedly small, ranging from 85° to 101°.

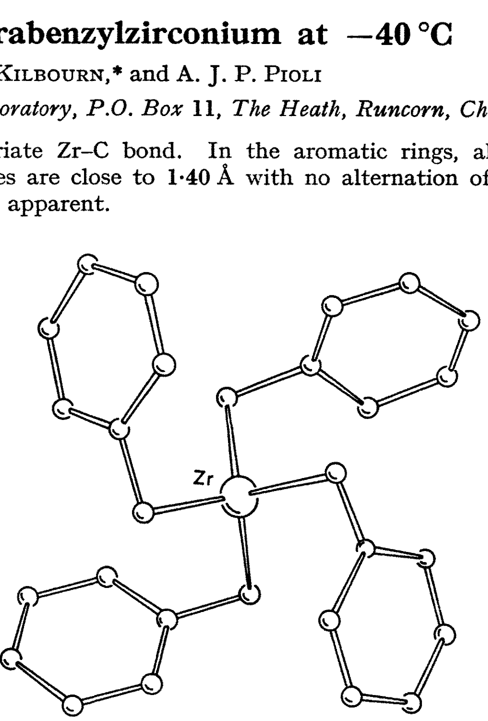
LITTLE is known about the structure and stereochemistry of covalent organic compounds of titanium and zirconium or about the nature of the σ-bond between the transition metal and carbon in such compounds. We report a preliminary account of the full three-dimensional structure analysis of single crystals of tetrabenzylzirconium.

The compound was prepared in an analogous manner to tetrabenzyltitanium[1] and recrystallized from toluene at −25 °C. After preliminary photography to identify the space group, full three-dimensional data ($\leqslant 2\theta = 44°$) were collected using a Picker automatic diffractometer. The crystal was kept at *ca.* −40 °C while being orientated and during data collection by using special attachments for the diffractometer.[2] The structure has been solved by conventional methods and refined to an R value of 0·102 for 2216 terms with F (observed) $> 2{\cdot}8e$.

Crystal data: $C_{28}H_{28}Zr$, orange plates, $M = 455{\cdot}5$, $a = 19{\cdot}95 \pm 0{\cdot}01$, $b = 13{\cdot}72 \pm 0{\cdot}01$, $c = 16{\cdot}31 \pm 0{\cdot}01$ Å, $U = 4461$ Å^3, space group *Pbca*, $D_c = 1{\cdot}36$ when $Z = 8$, $F(000) = 1888$, Mo-K_α radiation (Nb filter), $\mu = 5{\cdot}0$ cm^{-1}.

There is *no* crystallographic symmetry imposed on the molecule which does, however, approach $\bar{4}$ symmetry. The Figure shows the molecule viewed down this 'pseudo' $\bar{4}$ axis.

The co-ordination geometry around the central zirconium atom, as defined by the four Zr–C σ-bonds, is a distorted tetrahedron with the molecule stretched along the $\bar{4}$ axis. The C–Zr–C angles bisected by this pseudo-symmetry axis are 94 and 96°; the other angles are 118 and 122, and 113 and 116°. The Zr–C σ-bonds are 2·23, 2·26, 2·28, and 2·29 (0·015) Å; none is significantly different from the average of 2·27 Å. All seven carbon atoms of each benzyl ligand are effectively co-planar and nearly perpendicular to the appropriate Zr–C bond. In the aromatic rings, all C–C distances are close to 1·40 Å with no alternation of bond lengths apparent.



FIGURE

The average angle at the methylene carbon atom is unexpectedly small, Zr–C–C 85, 90, 92, and 101(1)°, (mean Zr–C–C, 92°) and less than the usual angle at $-CH_2-$. Associated with this, the atom of the aromatic ring bonded to the methylene carbon is closer to the metal than would be expected (average Zr $\cdots$ C is 2·74 Å). The co-ordination arrangement of the ligand seems to be slightly distorted from a 'normal' M–C σ-bond (M–C–C, 112°).

In $(h^3\text{-}4\text{-}MeC_6H_4{\cdot}CH_2)(h^5\text{-}C_5H_5)(CO)_2Mo$[3], three carbon atoms of the benzylic ligand are approximately equidistant from the metal atom and the benzyl group acts as a π-allylic ligand. It is obvious that tetrabenzylzirconium does not contain such a π-benzyl group but that the benzyl group is essentially σ-bonded.

(*Received, April* 8*th*, 1971; *Com.* 525.)

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