The Short Fe–Ge Bond in Two Crystalline Modifications of π-Butadiene-π-cyclopentadienyldichloromethylgermyliron: an *X*-Ray Crystallographic Study

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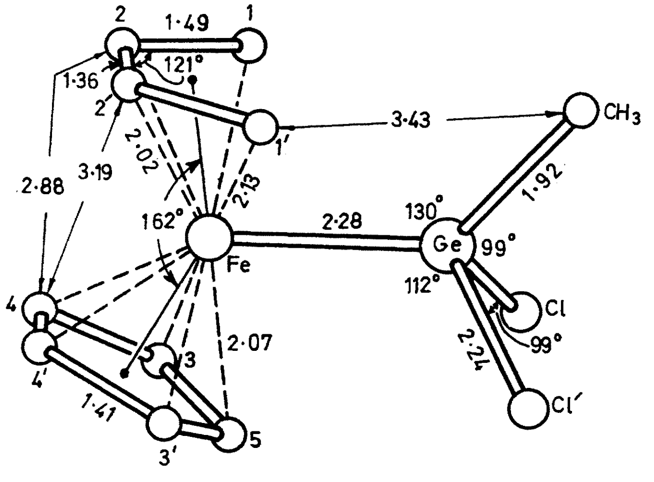
Summary A significant shortening of Fe–Ge bond in the title compound (2·28 and 2·29 Å as against 2·56 Å, the sum of the covalent radii, is probably caused by a strong d_π(Fe) → d_π(Ge) interaction.

PREVIOUS investigations[1–5] of iron complexes containing Fe–Ge bonds have shown a marked dependence of this bond length both on the ligands attached to the iron atom and on the general molecular stereochemistry. All compounds studied up to now have been carbonyl complexes of iron, so it seemed interesting to find out how the Fe–Ge bond length would vary on replacement of the carbonyl ligand by weaker π-acceptor groups. We therefore undertook the *X*-ray study of π-butadiene-π-cyclopentadienyldichloromethylgermyliron, $(\pi\text{-}C_5H_5)(\pi\text{-}C_4H_6)FeGeCl_2CH_3$ obtained by photochemical reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}GeCl_2CH_3$ with butadiene.[6] The compound was dimorphous in the crystalline state.

Crystal data: modification (I) is orthorhombic, $a = 11{\cdot}83$, $b = 10{\cdot}78$, $c = 9{\cdot}71$ Å, $U = 1238$ Å^3, $D_m = 1{\cdot}7$, $D_c = 1{\cdot}69$ g cm^{-3} for $Z = 4$, space group *Pnma* with the molecule in special position on a mirror plane. Modification (II) is triclinic, $a = 8{\cdot}02$, $b = 12{\cdot}39$, $c = 7{\cdot}40$ Å, $\alpha = 116{\cdot}9°$, $\beta = 107{\cdot}4°$, $\gamma = 92{\cdot}0°$, $U = 613$ Å^3, $D_c = 1{\cdot}70$ g cm^{-3} for $Z = 2$, space group $P\bar{1}$. *X*-Ray photographs taken with an equi-inclination Weissenberg goniometer with unfiltered iron [for (I)] and copper [for (II)] radiation contain *ca.* 500 and 1200 independent reflections, respectively. The structures of (I) and (II) were solved by the heavy-atom technique and refined by the full-matrix least-squares method with isotropic temperature factors. At the present stage of refinement $R_F = 0{\cdot}13$ and $0{\cdot}14$ for (I) and (II), respectively.

The molecular configuration (Figure), almost the same in both modifications, is of a wedge-like sandwich type and we give values only for the orthorhombic one. The Fe atom co-ordination can be described as distorted octahedral, and that of the Ge atom is distorted tetrahedral. Distortions are caused at least partly by steric hindrance between ligands. Thus, the angle subtended by normals from the C_5H_5 and C_4H_6 ligands is increased from 144·7° (the angle made by the threefold and twofold axes of the ideal octahedron) to 162° in accordance with the considerably shortened distances C(2) · · · C(4) 2·88 and

C(2) · · · C(4′) 3·19 Å between these ligands. The increase of the Fe–Ge–CH_3 angle from 109·5° to 130° accords with the shortened distance $C(1)H_2 \cdots C(6)H_3$ 3·43 Å. The cyclopentadienyl and butadiene ligands are planar, with the usual bond lengths. The Fe–C distances are also close to those previously found in Fe complexes with these ligands.



FIGURE

The most interesting feature of the molecular geometry is the Fe–Ge bond length, 2·28 ± 0·01 Å in (I) and 2·29 ± 0·01 Å in (II), the shortest yet found; *cf.* 2·357 Å in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2GeCl_2$,[1] 2·398 Å in $[Fe(CO)_4Ge(C_2H_5)_2]_2$,[2] 2·422 Å in $[Ge(C_6H_5)_2]_2Fe_2(CO)_7$,[3] 2·433 Å in $[(\pi\text{-}C_5H_5)Co(CO)]_2[GeCl_2]_2Fe(CO)_4$,[4] and 2·49 Å in $[Ge(CH_3)_2]_3Fe_2(CO)_6$.[5] The bond length found in (I) and (II) is considerably shorter than the sum of the single-bonded covalent radii (Fe 1·3$_4$ Å,[7] Ge 1·22 Å [8]). Such contraction of the Fe–Ge bond, or an increase in its order, can most probably be ascribed to a strong $d_\pi(Fe) \rightarrow d_\pi(Ge)$ back-donation, which is favoured in the present case both by the relatively weak π-acceptor ability of the Fe atom ligands (C_5H_5 and C_4H_6) and by the electronegative substituents, chlorine atoms, at the Ge atom.

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