

Protonation of Decamethylsilicocene [Bis(pentamethylcyclopentadienyl)silicon]

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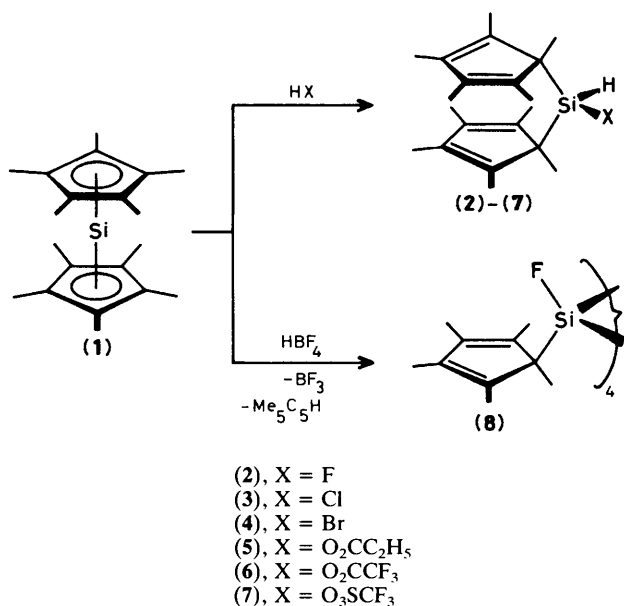
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In general, decamethylsilicocene (**1**) reacts with Brønsted acids under oxidative addition yielding Si^{IV} compounds of the type (Me₅C₅)₂Si(H)X (**2**)—(**7**); as an exception, the cyclotetrasilane (Me₅C₅SiF)₄ (**8**) is formed in the reaction with tetrafluoroboric acid and has been characterized by an X-ray diffraction study.

Recently, we have described the synthesis and structure of decamethylsilicocene, (Me₅C₅)₂Si (**1**), the first silicon(II) compound stable under ordinary conditions, and, at the same time, the first π-complex with silicon as the central atom.¹ The corresponding germanium, tin, and lead compounds have already been described.² Thus, the preparation of (**1**) opens

the possibility of comparative studies concerning the reactivity of the group IV–metallocenes.† Here we describe their differing reactions with protic compounds.

† Though the element silicon is not a metal, compound (**1**) is described as a metallocene in the context of this paper.



Scheme 1. Reaction of decamethylsilicocene (1) with Brønsted acids.

Table 1. Melting points and selected ²⁹Si n.m.r. data for (2)–(7).

	m.p./°C	²⁹ Si(C ₆ D ₆) δ/p.p.m.	¹ J _{SiH} /Hz
(2)	42–43	14.1	229 ^a
(3)	62	16.0	224
(4)	95–97	15.0	232
(5)	78–81	0.8	224
(6)	54	7.6	228
(7)	65–67	–3.6	249

^a ¹J_{SiF} 327 Hz.

The metallocenes (Me₅C₅)₂M of the heavier elements (M = Ge, Sn, or Pb) are attacked by electrophiles exclusively at the π-system of one of the cyclopentadienyl ligands. Thus, reaction with Brønsted acids leads to compounds of the type Me₅C₅MX or Me₅C₅M⁺X[–] with a divalent group IV element, with simultaneous formation of pentamethylcyclopentadiene.² In contrast, attack at the lone-pair is the preferred pathway in silicocene chemistry. As a result, oxidative addition products are obtained in the reaction of (1) with HF, HCl, HBr, and propionic, trifluoroacetic, and trifluoromethanesulphonic acid (see Scheme 1). The addition products (2)–(7) with tetravalent silicon have been characterized by analytical and spectroscopic data (see Table 1).³

In only one experiment did protonation take place at the π-system of the silicon compound.‡ Reaction of (1) with tetrafluoroboric acid leads to the cyclotetrasilane (Me₅C₅SiF)₄ (8). The short-lived ionic species Me₅C₅Si⁺BF₄[–] is formed after elimination of pentamethylcyclopentadiene. In subsequent steps, fluoride abstraction leads to boron trifluoride and the highly reactive silylene (silenediyl) Me₅C₅SiF, which dimerizes to the unstable disilene Me₅C₅(F)Si=Si(F)C₅Me₅.§

‡ Attack at the metal may precede reaction at the ligand; an intermediate of the type (Me₅C₅)₂SiH⁺BF₄[–] has not been observed.

§ The disilene is characterized by the ²⁹Si n.m.r. spectrum of its deep yellow solution: (59.6 MHz, [2H₈]tetrahydrofuran, –70 °C); δ –34.7 p.p.m. (pseudotriplet, ¹J_{SiF} = ²J_{SiF} = 341 Hz).

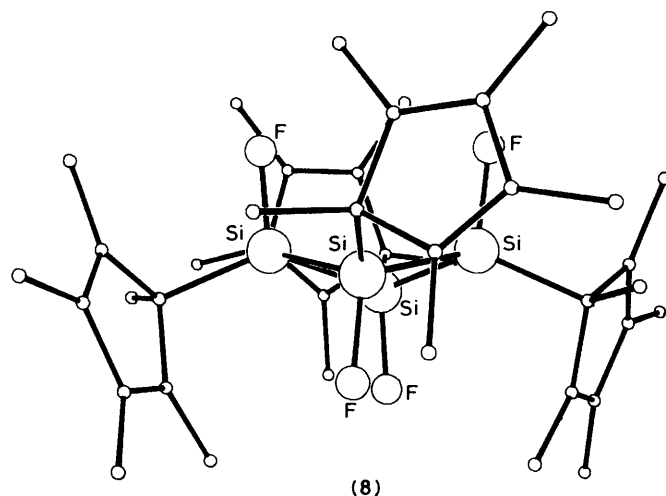


Figure 1. Crystal structure of (8).

which then forms the isolable cyclotetrasilane (8) by a [2 + 2] cycloaddition.

Compound (8)¶ is obtained in the form of pale yellow, air-sensitive needles, which are only sparingly soluble in the common organic solvents. An X-ray analysis of (8) shows a folded four-membered ring of silicon atoms with all-trans orientation of the pentamethylcyclopentadienyl and fluoride ligands (see Figure 1).|| The Si–Si distances [239.1(3) pm] in (8) and the dihedral angle of the Si₄ framework (145.7°) are comparable with known values in other cyclotetrasilanes.^{4,5} With the presence of pentamethylcyclopentadienyl and fluoride ligands, compound (8) possesses two sorts of leaving group.⁶

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¶ (8): m.p. > 320 °C; ¹H n.m.r. ([2H₈]toluene, 50 °C); δ 1.81 (s); ¹⁹F n.m.r. ([2H₈]toluene, 50 °C); δ 188.3 p.p.m. (s, ¹J_{SiF} 381 Hz); mass spec. (70 eV) *m/z* 182 (0.25 M⁺, 0.2%), 163 (Me₅C₅Si⁺, 100%).

|| Crystal data for (8): C₄₀H₆₀F₄Si₄, *M* = 729.25, tetragonal, space group *I4*, *a* = 1547.5(4), *c* = 846.4(2) pm, *U* = 2026.9 × 10⁶ pm³, *Z* = 2, *D_c* = 1.19 g cm^{–3}, μ(Mo-Kα) = 1.86 cm^{–1}, *F*(000) = 784. Diffraction data were collected using a Syntex P21 four circle diffractometer (ω-scan, at 21 °C). The structure was solved by direct methods. The least squares refinement converged at an *R* value of 0.063 for 946 independent reflections [*F_o* > 3.92σ(*F_o*); 4 < 2θ < 52°]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.