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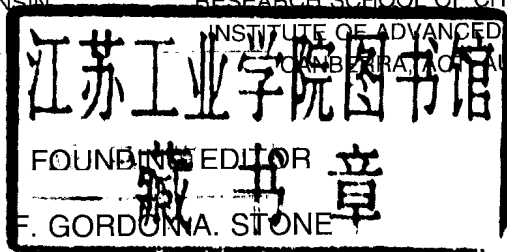
EDITED BY

ROBERT WEST

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

ANTHONY F. HILL

AUSTRALIAN NATIONAL UNIVERSITY
RESEARCH SCHOOL OF CHEMISTRY
INSTITUTE OF ADVANCED STUDIES
CANBERRA, AUSTRALIA



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Contributors

Numbers in parentheses indicate the pages on which the authors' contributors begin.

- THORSTEN KÜHLER and PETER JUTZI (1), Faculty of Chemistry, University of Bielefeld, Universitätsstraße 25, D-33615 Bielefeld, Germany
- NIKOLAI N. ZEMLYANSKY and IRINA V. BORISOVA (35), A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS), 29, Leninsky prospect, 119991-GSP-1, Moscow, Russian Federation
- YURI A. USTYNYUK (35), Department of Chemistry, M. V. Lomonosov Moscow State University, Vorob'evy Gory, 119899 Moscow, Russian Federation
- HANS JOACHIM BREUNIG and IOAN GHESNER (95), Institut für Anorganische und Physikalische Chemie (Fb 2), Universität Bremen, D-28334 Bremen, Germany
- SOICHIRO KYUSHIN and HIDEYUKI MATSUMOTO (133), Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan
- SVEN TOBISCH (167), Institut für Anorganische Chemie der Martin-Luther-Universität Halle-Wittenberg, Fachbereich Chemie, Kurt-Mothes-Straße 2, D-06120 Halle, Germany
- STEPHAN SCHULZ (225), Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany

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Decamethylsilicocene: Synthesis, Structure, Bonding and Chemistry

THORSTEN KÜHLER and PETER JUTZI

Faculty of Chemistry, University of Bielefeld,
Universitätsstraße 25, D-33615 Bielefeld, Germany

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I

INTRODUCTION

The metallocene era started with the synthesis of ferrocene and with the right description of the structure and bonding of this compound.¹ Only a few years after this epochal discovery, the first metallocenes of the group 14 elements tin and lead were synthesized, namely stannocene, $(\text{H}_5\text{C}_5)_2\text{Sn}$,² and plumbocene $(\text{H}_5\text{C}_5)_2\text{Pb}$,³ the analogous germanium compound germanocene, $(\text{H}_5\text{C}_5)_2\text{Ge}$, was prepared nearly two decades later.⁴

Some years later, the introduction of the pentamethylcyclopentadienyl ligand into the π -complex chemistry of the group 14 elements has allowed the synthesis of the deca-methylmetallocenes of germanium, $(\text{Me}_5\text{C}_5)_2\text{Ge}$,⁵ tin, $(\text{Me}_5\text{C}_5)_2\text{Sn}$ ⁵ and lead, $(\text{Me}_5\text{C}_5)_2\text{Pb}$.⁶ The enhanced stability but still high reactivity of these permethylated complexes has led to extensive reactivity studies and to the isolation and characterization of many derivatives.⁷

The decamethylmetallocenes of germanium, tin and lead as well as the parent metallocenes were prepared by reaction of divalent inorganic

substrates (usually halides) with the corresponding cyclopentadienyl transfer agents (usually alkaline metal derivatives). Later on, we could show that the decamethylmetallocenes of germanium and tin can also be prepared by reduction of the tetravalent bis(pentamethylcyclopentadienyl) dihalides of these elements under properly chosen reducing conditions to avoid over reduction and the elimination of the pentamethylcyclopentadienide ligands.⁸ This interesting observation was the starting point for experiments with the aim to synthesize decamethylsilicocene, $(\text{Me}_5\text{C}_5)_2\text{Si}$ (**1**), in an analogous manner. At that time, no monomeric and under ordinary conditions stable inorganic or organometallic species with divalent silicon was known. Such species existed only as reactive and transient intermediates; some of them had been isolated in low-temperature matrices.⁹ To change this situation, π -complexation⁷ seemed to us to be a very promising tool. In this article, we summarize the results concerning synthesis, structure, bonding and chemistry of decamethylsilicocene (**1**), which was the first divalent silicon compound and at the same time also the first stable π -complex with silicon as the central atom. Since the synthesis of **1** in 1986,¹⁰ the field of stable silicon(II) compounds has shown an interesting development. Meanwhile, at least four other classes of compounds have been described in the literature: one containing a hyper-coordinated silicon center (class II),¹¹ and three containing dicoordinated silicon centers (class IIIa,^{12,13} IIIb,^{13,14} IIIc,^{13,15} class IV^{13,16} and class V,¹⁷ see Fig. 1). With regard to other π -complexes with silicon as the central atom, silicon(IV) compounds of

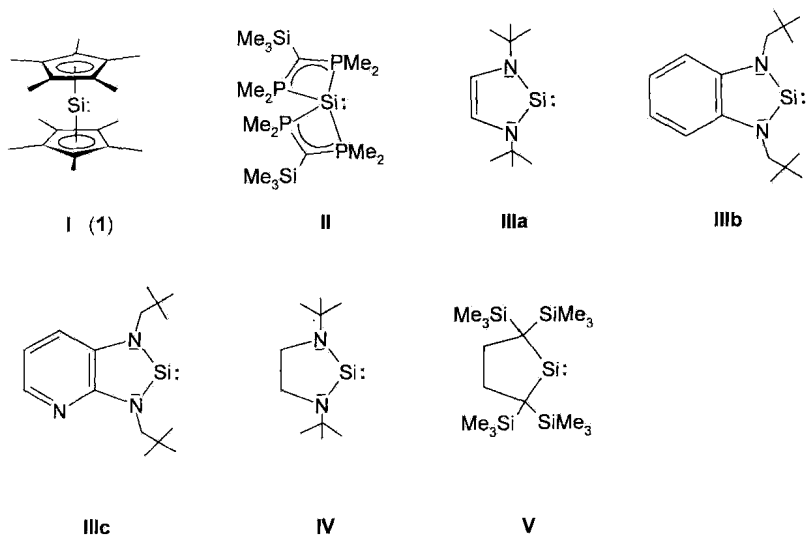
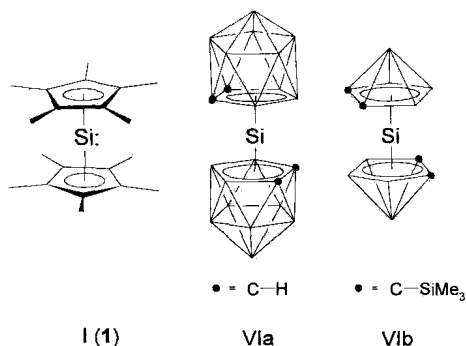


FIG. 1. Classes of stable Si(II) compounds.

FIG. 2. π -Complexes of silicon.

type VIa¹⁸ and VIb¹⁹ containing carbollide ligands were prepared shortly after the synthesis of **1** (see Fig. 2).

II

SYNTHESIS AND STRUCTURE OF DECAMETHYLSILICOCENE

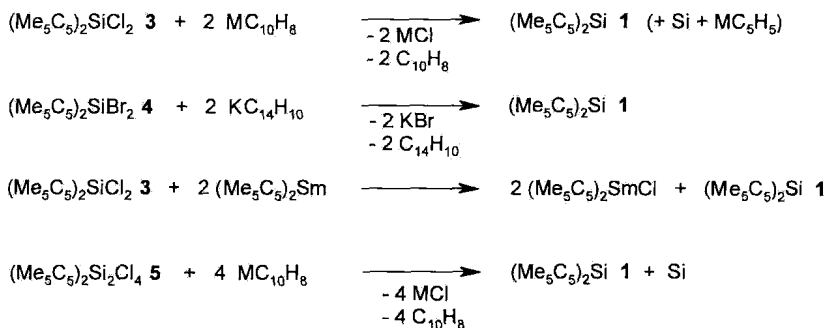
As already mentioned, the tetravalent bis(pentamethylcyclopentadienyl)-silicon dihalides $(\text{Me}_5\text{C}_5)_2\text{Si}(\text{Hal})_2$ ($\text{Hal} = \text{F}$ (**2**), Cl (**3**), Br (**4**)) were used as precursors for the synthesis of **1**. Their preparation was straightforward only in the case of the difluoro compound **2**; due to the steric effects exerted by two pentamethylcyclopentadienyl substituents, the dichloro (**3**) and the dibromo compound **4** could not be synthesized by a simple metathesis route. They were prepared following a strategy where the fifth methyl group at the cyclopentadienyl ring had to be introduced in the last step of the procedure.²⁰ The difluoro compound **2** reacted with alkali metals or with alkali metal naphthalenides to give mainly the corresponding alkali metal cyclopentadienides and a Si-F-containing polymer, thus indicating that in **2** the pentamethylcyclopentadienyl unit is a better leaving group than the fluoro substituent. In the reaction of the dichloro compound **3** with lithium-, sodium-, or potassium-naphthalenide, a grey-black suspension was formed. After filtration, elemental silicon remained as residue. From the colorless solution, **1** could be isolated after removal of the solvent and fractional sublimation. The highest yield of **1** was obtained by performing the reaction at -50°C in dimethoxyethane as the solvent and using a 50% excess of the sodium compound.¹⁰ The undesired formation of elemental silicon was avoided by using the dibromo compound **4** as the precursor and potassium anthracenide as the reducing agent.¹⁰ A clean reduction to

1 without any formation of silicon was observed in the reaction of **3** with decamethylsamarocene.²¹ It was found only recently that the reduction of 1,2-bis(pentamethylcyclopentadienyl)tetrachlorodisilane (**5**) with alkali metal naphthalenides leads to **1** and to elemental silicon in stoichiometric amounts.²² The different strategies for the preparation of **1** are collected in Scheme 1.

Crystallization from *n*-pentane gives colorless crystals of **1**, which are soluble in all common aprotic organic solvents. Compound **1** is monomeric in benzene solution, sensitive towards hydrolysis, but stable in air for short periods of exposure. It melts at 171 °C without decomposition, but decomposes under MOCVD-conditions to elemental silicon at about 600 °C. At room temperature **1** is regarded to be indefinitely persistent in the solid state and in solution; in toluene solution it survives unchanged after heating to 110° for several days.

Cyclic voltammetry measurements in dichloromethane as solvent have shown that **1** cannot be reduced in the region available (up to -1.7 V versus SCE). An irreversible oxidation takes place at $+0.4$ V; presumably the $(\text{Me}_5\text{C}_5)_2\text{Si}^+$ radical cation (**1**⁺) is formed which is unstable due to the easy loss of the pentamethylcyclopentadienyl radical. The fate of the remaining $\text{Me}_5\text{C}_5\text{Si}^+$ cation is uncertain. Further irreversible oxidation processes are observed in the region from $+0.8$ to $+1.5$ V. In the mass spectrum of **1** (EI and CI), the molecular ion $(\text{Me}_5\text{C}_5)_2\text{Si}^+$ (**1**⁺) is not observed; the fragment with the highest mass ($m/z = 163$) corresponds to the $\text{Me}_5\text{C}_5\text{Si}^+$ cation. These observations complete those of the CV studies and demonstrate that **1**⁺ is rather unstable not only in solution, but also in the gas phase.¹⁰

The results of an X-ray crystal structure analysis¹⁰ of **1** are presented in Figs. 3 and 4. Surprisingly, two geometrical isomers, **1a** and **1b**, in the ratio 1:2 are present in the unit cell (space group $C2/c$; $Z = 12$). Isomer **1a** is isostructural with decamethylferrocene, and the silicon lone-pair is not



SCHEME 1. Syntheses of decamethylsilicocene (**1**).

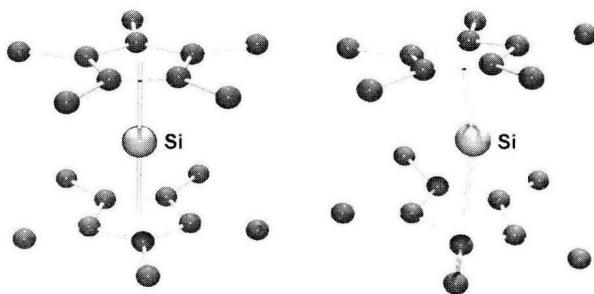


FIG. 3. Molecular structure of the linear (**1a**) (D_{5d}) and of the bent (**1b**) (C_{2v}) isomer of decamethylsilicocene in the solid state.

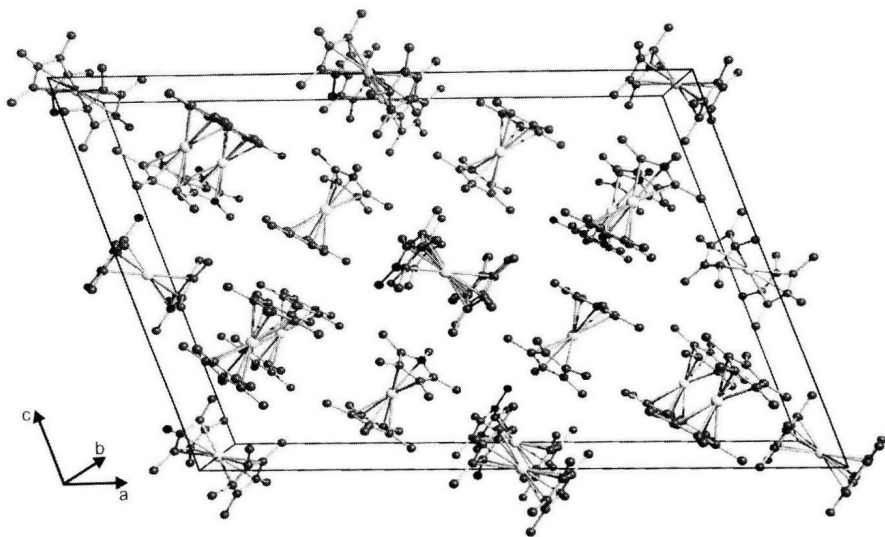


FIG. 4. Representation of the unit cell ($C2/c$) of **1**.

stereochemically active. Isomer **1b** is of the bent-metallocene type with an interplane angle of 25.3° and with pentamethylcyclopentadienyl rings asymmetrically bonded in a staggered conformation; the silicon lone-pair is regarded to be stereochemically active. The Si–C separations are equidistant in **1a** [2.42(1) Å], but different in **1b** [ranging from 2.323(7) to 2.541(7) Å]. The distance between the silicon atom and the cyclopentadienyl ring centroids is 2.11 Å in **1a** and 2.12 Å in **1b**. Space-filling models clearly demonstrate the interplane angle in **1b** to be of the largest possible value. According to GED studies, **1** has a bent-metallocene type structure in the gas phase with an interplane angle of 22.3° .

TABLE I
X-RAY CRYSTAL STRUCTURE AND GED DATA OF THE
DECAMETHYLMETALLOCENES OF SILICON, GERMANIUM, TIN, AND
LEAD

Compound	d [Å] ^a	r _{El-C} [Å] ^b	α [°] ^c
(Me ₅ C ₅) ₂ Si	2.11	2.42(1)	0
	2.12	2.42(6)	25.3
(Me ₅ C ₅) ₂ Ge ^d	2.21	2.52	23
(Me ₅ C ₅) ₂ Sn	2.39	2.68	36
(Me ₅ C ₅) ₂ Pb	2.48	2.79	43

^aDistance from central atom to ring centroid.

^bAveraged El-C distances.

TABLE II
NMR DATA OF THE DECAMETHYLMETALLOCENES OF SILICON, GERMANIUM, TIN, AND LEAD

Compound	El _(solid) ^a	El _(solv)	¹ H	¹³ C
(Me ₅ C ₅) ₂ Si	-403.2, -423.4	-398.0	1.89	10.0, 119.1
(Me ₅ C ₅) ₂ Ge		-	1.99	9.8, 118.1
(Me ₅ C ₅) ₂ Sn	-2136.6, -2140.2	-2146	2.06	10.5, 117.0
(Me ₅ C ₅) ₂ Pb	-4474	-4390	2.18	10.1, 117.4

^a ²⁹Si-, ¹¹⁹Sn-, ²⁰⁷Pb- CP-MAS-NMR of powder samples.

A comparison of some important structural data of the decamethylmetallocenes of silicon, germanium, tin, and lead is given in Table I. As expected, the distance from the respective central atom to the cyclopentadienyl ring centroid or to the ring carbon atoms rises on going to the heavier homologues. In the same direction (with the exception of **1b**), a widening of the angle between the cyclopentadienyl ring planes is observed (see discussion of the bonding situation). The implications of these structural features on bonding and reactivity are discussed elsewhere.⁷

The solid-state CP-MAS ²⁹Si NMR spectrum of **1** reflects the gross structural features known from the X-ray analysis.²³ The nuclear shielding in **1a** (δ = -423.4 ppm) is found to be higher (Δδ = 20.2 ppm) than that in **1b** (δ = -403.2 ppm) (see also Table II). Interestingly, the measured chemical shift values for **1** are at the high-field end of the ²⁹Si NMR scale! The observed small shielding anisotropies Δσ can only be explained if one assumes that the silicon lone-pair in **1a** or **1b** provides a fairly homogeneous source of electron density for the silicon nucleus.

Information concerning the structure of **1** in solution stems from ¹H, ¹³C, and ²⁹Si NMR spectra.¹⁰ They show that only one isomer is present and that this isomer is highly dynamic. A resonance at δ = -398 ppm in the ²⁹SiNMR

spectrum indicates the presence of the bent structure **1b**, and averaged signals in the ^1H and in the ^{13}C NMR spectrum for the ring carbons and for the methyl groups correspond to very rapidly rotating π -pentamethylcyclopentadienyl ligands. The dynamic behavior of **1** is similar to that of the heavier homologues. The NMR data of all the group 14 decamethylmetallocenes are collected in Table II; they are in accord with the general observation for π -complexes of main-group elements, that heteronuclear resonances for the central atoms (here for Si, Sn, and Pb) appear at very high field and that fluxionality within the element-cyclopentadienyl unit leads to averaged ^1H and ^{13}C NMR chemical shifts.^{7,24,25}

III

BONDING IN DECAMETHYLSILICOCENE

Information about the bonding stems from calculations for the parent but still experimentally unknown silicocene molecule ($\text{Si}(\text{C}_5\text{H}_5)_2$) and for the permethylated derivative **1** as well as from the He(I) spectrum of the latter compound. Several calculations have been performed for silicocene, some of them probably at insufficient levels of theory. It is evident that the silicocene potential surface is rather flat with respect to the interconversion between several conformers and to the easy rotation of the cyclopentadienyl rings. At the SCF DZP level, the molecule is predicted to adopt a bent C_s structure. However, the energy difference between the low symmetry conformers (C_s , C_2 , C_{2v}) is only $2.4 \text{ kcal mol}^{-1}$; the D_{5d} conformer is $8.8 \text{ kcal mol}^{-1}$ higher in energy. The total electron population at the silicon center is calculated to be 13.5; d-orbitals at silicon do not play an important role in π -bonding. The Si-(πCp) dissociation energy has been calculated to be in the range of 55 kcal mol^{-1} .²⁶ Quantum chemical calculations for **1** have been performed at the DFT level without any geometrical constraints in the energy optimization.²⁷ The computed structure is in perfect agreement with the solid state structure of the bent isomer. An NBO analysis of silicocene (D_{5d}) assigns a $+0.852$ charge to the silicon atom; for comparison, a $+0.117$ charge is calculated for the iron atom in the ferrocene molecule.

On a more qualitative level, the bonding in the more stable isomer **1b** can be explained on the basis of the general molecular orbital scheme for bent (C_{2v}) metallocenes containing 14 valence electrons, as shown in Fig. 5. The localization of three electron pairs in bonding orbitals (1_{a1} , 2_{b1} , 2_{b2}) is primarily responsible for the Si-Cp interaction; the absence of a silicon orbital of a_2 symmetry imposes the presence of a ligand-based non-bonding orbital. Structural adjustment from D_{5d} (ferrocene type) to C_{2v}

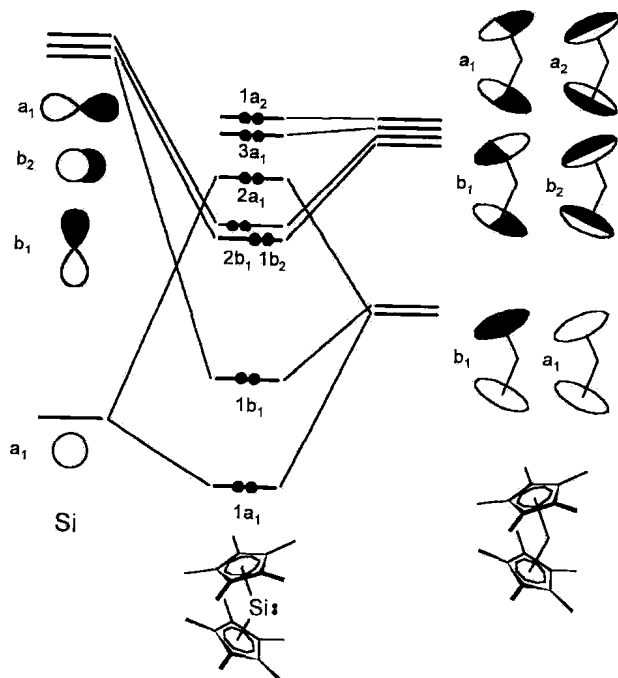


FIG. 5. Schematic MO diagram of decamethylsilicene (1) (only occupied MO's are shown).

TABLE III
PES DATA OF THE DECAMETHYLMETALLOCENES OF SILICON, GERMANIUM, TIN,
AND LEAD

Orbital	(Me ₅ C ₅) ₂ Si	(Me ₅ C ₅) ₂ Ge	(Me ₅ C ₅) ₂ Sn	(Me ₅ C ₅) ₂ Pb
1 _{a2}	6.70	6.60	6.60	6.33
3 _{a1}	6.96	6.75	6.60	6.88
2 _{b1}	8.06	7.91	7.64	7.38
1 _{b2}	8.30	8.05	7.64	7.38
2 _{a1}	7.50	8.36	8.40	8.93

symmetry gives rise to a stabilization of the 2_{a1} orbital as a consequence of the second-order Jahn-Teller effect (incorporation of the a₁ p orbital at silicon). In more simplified terms, the resultant 2_{a1} orbital may be regarded as a non-bonding electron pair, the so-called "lone pair".

Experimental support for the MO sequence in Fig. 5 is provided by the photoelectron spectroscopic (PE) data of 1,¹⁰ which are presented in Table III together with the corresponding data for the heavier homologues. The following conclusions can be drawn from these data: (1) the HOMO's in

all metallocenes are non-bonding with respect to element-Cp interactions; (2) the 2_{h1} and 1_{h2} type orbitals provide the strongest contributions to element-Cp bonding, the respective ionization energies depending strongly on the element involved; (3) the "lone-pair" orbital is rather low in energy for the germanium, tin, and lead compounds, but is higher in energy for the silicon compound. The observed differences in energy have strong implications on the chemical reactivity. The "lone pair" in **1**, which is located in the region of the frontier orbitals, is involved in nearly all reactions performed so far. This is not the case in the chemistry of the heavier homologues.⁷

Summarizing the available bonding information, decamethylsilicocene (**1**) is regarded as an electron-rich silicon(II) compound containing a hypercoordinated silicon atom which is sandwiched between two rather weakly π -bonded pentamethylcyclopentadienyl ligands and thus is effectively shielded; the "lone-pair" orbital at silicon is part of the frontier orbitals of the molecule.

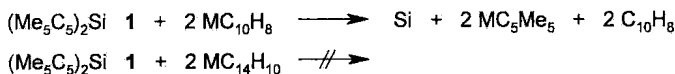
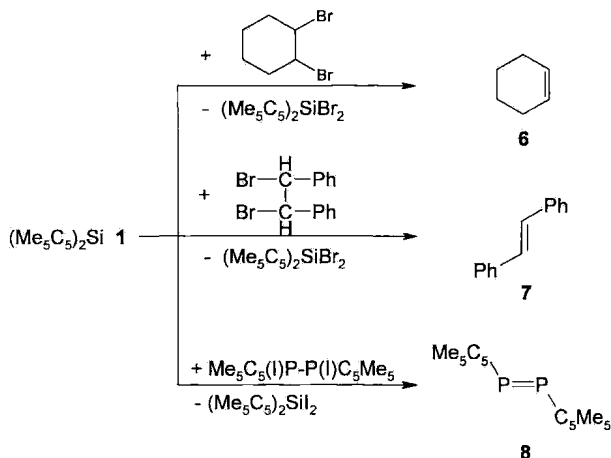
IV

CHEMISTRY OF DECAMETHYLSILICOCENE (**1**)

Experiments performed during the last fifteen years have shown that the chemistry of **1** is mainly determined by the nucleophilicity of the silicon "lone pair" and by the weakness of the π -bonds between silicon and the pentamethylcyclopentadienyl ligands. The "lone-pair" activity is responsible for the donor qualities of **1**. Easy haptotropic shifts ($\eta^5\text{-}\eta^1$) of the cyclopentadienyl ligands cause a vacant orbital at silicon and thus create a silylene-like reaction center; this bonding situation enables oxidative addition and cycloaddition processes. The inherent weakness of the Si- σ Cp bonds in the primary reaction products might cause migration, rearrangement or elimination reactions; as a result, rather complicated and surprising reaction pathways are observed in some cases. In the following, the chemistry of **1** is described in more detail.

A. Attempts to Prepare the Radical Cation and the Radical Anion of **1**

Whereas decamethylferrocene—here regarded as the prototype of a metallocene—can be easily transferred to the corresponding radical cation or anion, this is not the case for decamethylsilicocene (**1**). CV measurements have already shown that the cation **1**⁺ is only a very short-lived transient species.¹⁰ Consequently, chemical experiments to prepare salts containing **1**⁺ have also failed so far. Similar observations have been made concerning

SCHEME 2. Reduction of **1**.SCHEME 3. **1** as reducing agent for vicinal dihalogeno compounds.

the reduction of **1**. It was not possible to stabilize or even to identify the anion $\mathbf{1}^-$, not even in experiments with tunable reducing systems. Thus, reaction with stoichiometric amounts of alkali metal naphthalenides resulted in the quantitative formation of elemental silicon and of the respective alkali metal pentamethylcyclopentadienide, whereas alkali metal anthracenides did not react at all¹⁰ (see Scheme 2). The different reactivity of decamethylferrocene and of **1** can be understood with the help of their MO schemes. Whereas the HOMO in the ferrocene is metal-centered, the HOMO in **1** is centered at the ligands. As a result, single-electron transfer reagents attack compound **1** preferentially at the pentamethylcyclopentadienyl ligands and lead to decomposition. This behavior of **1** is characteristic of cyclopentadienyl compounds of p-block elements.²⁸

B. Reduction of Geminal and Vicinal Dihalogeno Compounds

In the reaction of **1** with vicinal and geminal dihalogeno compounds, dehalogenation under formation of the corresponding bis(pentamethylcyclopentadienyl)dihalogenosilane takes place under mild reaction conditions. In Scheme 3, examples for the reduction of vicinal dibromo- or