Low-Coordinate Silicon

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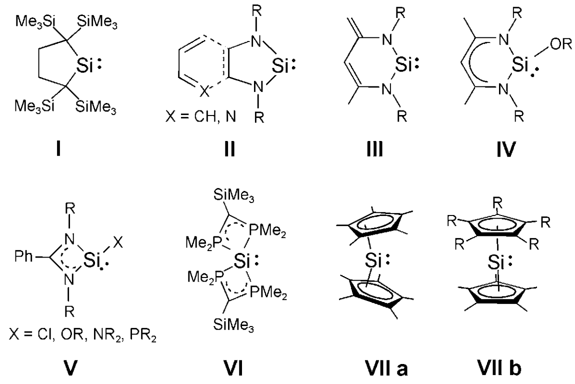
[2,6-(Trip)$_2$H$_3$C$_6$](Cp*)Si: A Stable Monomeric Arylsilicon(II) Compound**

Peter Jutzi, Kinga Leszczyńska, Beate Neumann, Wolfgang W. Schoeller, and Hans-Georg Stammler*

Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

The synthesis of neutral, monomeric silicon(II) compounds that are stable at ambient temperature and pressure has attracted much interest during the last 20 years, but only a few classes of such compounds have been described to date (Scheme 1). Members of only three classes contain two-coordinate silicon atoms (**I–III**) and thus are silylenes in the true sense of the word. All others contain a higher-coordinated silicon atom (**IV–VII**) and should better be described as monomeric silicon(II) compounds. In five of these classes, the substituents of choice are connected to the silicon atom through heteroatoms: nitrogen in **II**,[1,2] **III**,[3] **IV**,[4] and **V**[5]; chlorine in **V**[5]; oxygen in **IV**[4] and **V**[6]; or phosphorous in **V**[6] and **VI**[7]. Organosilicon compounds in the true sense of the word, that is, compounds with C–Si bonds, are present only in class **I** and **VII** compounds: a cyclic alkyl group characterizes the silylene **I**,[8] and π-bound cyclopentadienyl ligands are present in the higher-coordinated sandwich-type Si(II) complexes (**VIIa** and **VIIb**[9,10]).

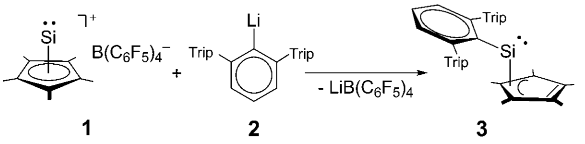


Scheme 1. Silylenes and monomeric silicon(II) compounds.

Interestingly, stable compounds Ar$_2$Si or ArSiR containing aryl (Ar) substituents are unknown to date. Less shielded diarylsilylenes such as Mes$_2$Si (Mes = mesityl)[11] or even Trip$_2$Si (Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$)[12] are only stable up to 77 K and have been characterized by low-temperature UV/Vis spectroscopy. They are reactive intermediates in the classic strategies for the synthesis of stable disilenes.[13] The sterically more congested aryl alkyl silylene Trip(1,2,3-tri-*tert*-butylcyclopropenyl)Si is stable in solution up to 200 K but could not be isolated.[14] The kinetically even better stabilized diaryl silylene Tb(Mes)Si (Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) was generated in solution by thermal dissociation of the corresponding disilene at approximately 70 °C but could also not be isolated.[15]

The synthesis of the salt Me$_5$C$_5$Si$^+$B(C$_6$F$_5$)$_4^-$ (**1**) containing the pentamethylcyclopentadienylsilicon(II) cation (Cp*Si$^+$) opened a novel entrance to the class of low-valent silicon species.[16] Neutral silicon(II) compounds of the type Cp*SiR should be accessible simply by addition of anionic nucleophiles R$^-$. The fate of such compounds (oligomerization, oxidative addition, insertion, or uncontrolled decomposition) will depend on the steric and electronic properties of the respective nucleophile. With sterically very demanding Power-type terphenyl anions Ar*$^-$ (Ar* = 2,6-Trip$_2$C$_6$H$_3$),[17] there should be a chance to prepare stable monomeric aryl pentamethylcyclopentadienylsilicon(II) compounds.

Reaction of **1** with the lithium salt LiAr*·Et$_2$O (**2**)[18] in hexane at −80 °C led to the formation of the salt LiB(C$_6$F$_5$)$_4$ and the silicon(II) compound Me$_5$C$_5$SiAr*·0.5 hexane (**3**·0.5 hexane) [Eq. (1)], which was isolated in high yield as yellow air- and moisture-sensitive crystals after separation of the salt and concentration of the remaining solution. The molecular structure of **3** is presented in Figure 1 from two perspectives. X-ray diffraction data and selected bond lengths and angles are provided in the Supporting Information.



(1)

The molecular structure shows the presence of a monomeric silicon(II) species with an η^3-bonded Cp* ligand and a

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[*] Prof. Dr. P. Jutzi, Dr. K. Leszczyńska, B. Neumann, Prof. Dr. W. W. Schoeller, Dr. H.-G. Stammler
University of Bielefeld, Faculty of Chemistry
Universitätsstrasse 25, 33615 Bielefeld (Germany)
E-mail: peter.jutzi@uni-bielefeld.de
Prof. Dr. W. W. Schoeller
University of California at Riverside (USA)

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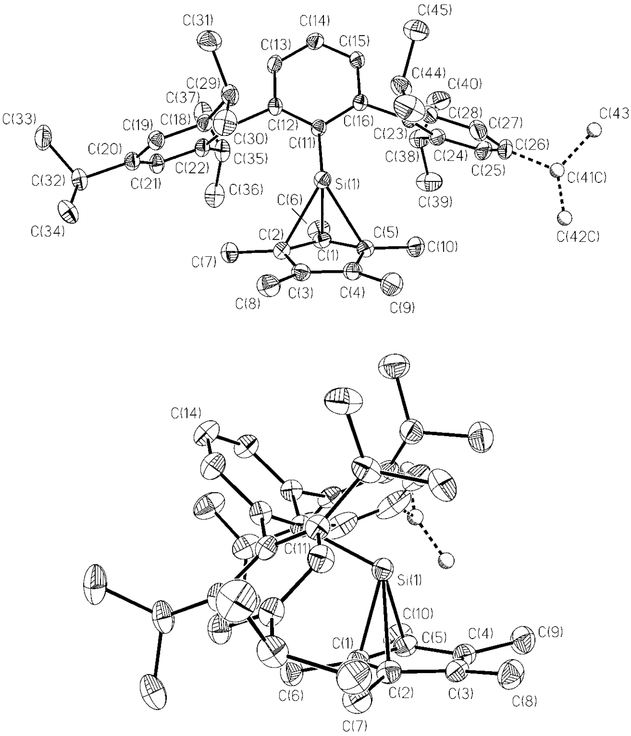
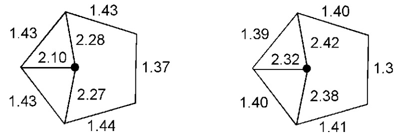


Figure 1. Molecular structure of **3**·0.5 hexane from two perspectives; thermal ellipsoids represent 50% probability. Hydrogen atoms and the hexane molecule were omitted for clarity; one isopropyl group is disordered.

σ-bonded aryl group and a noncrystallographic mirror symmetry in the central unit of the molecule. The geometry at the silicon atom may be qualitatively described (see theoretical calculations below) on the basis of an sp^2 hybridization with one hybrid orbital representing the lone pair and the others engaged in bonding to the substituents. This interpretation is supported by the observed C(1)-Si(1)-C(11) angle of 101.94(7)°. The remaining vacant p orbital at silicon interacts with a filled π orbital at the Cp* fragment. The resulting η^3 bonding of the Cp* ligand is documented by Si–C separations of 2.0965(19) [Si(1)–C(1)], 2.2678(19) [Si(1)–C(2)], and 2.2821(19) Å [Si(1)–C(5)]. This type of bonding leads to C–C bond lengths of 1.43 Å within the allyl unit and a C–C bond length of 1.37 Å in the remaining double-bond fragment. The position of the methyl groups of the allyl unit deviates from the plane of the Cp* ring, as documented by the angles C(6)-C(1)-C(3/4) (169.0°), C(7)-C(2)-C(4/5) (171.2°), and C(10)-C(5)-C(2/3) (172.8°). Despite the rather strong η^3 bonding, the planarity of the C_5 perimeter remains nearly unchanged, unlike the situation in η^3-Cp transition-metal compounds.[19]

The aryl silicon unit is characterized by a sterically enforced conformation of the aryl substituent with the ring plane perpendicular to the mirror plane and by a Si–C bond length of 1.9729(18) Å. C_{aryl}–Si bond lengths in silicon(IV) compounds are in the region of 1.86 Å;[20] as expected for a bonding situation without π back-bonding, a longer distance is observed in the silicon(II) compound **3**. A strong distortion is found at the *ipso* carbon atom of the central aryl group, as documented by a deviation from linearity by 17° of the vectors C(14)–C(11) and C(11)–Si(1). This distortion is caused by the bulk of the terphenyl substituent. The steric requirements also result in short nonbonding distances between outer-aryl carbon atoms and methyl groups from the Cp* ligand. The orientation of the two Trip groups in 2,5-position of the central aryl ring is such as to protect effectively the silicon atom; furthermore, they prevent the compound from dimerization to a disilene.

The structural features of the Cp*Si unit in **3** can be compared with those of the structurally characterized silicon(II) species $Cp^*Si^+B(C_6F_5)_4^-$[16] and Cp^*_2Si.[9] It is expected that the (η^3-Cp*)–Si bond in **3** is stronger than in the bent-sandwich molecule (η^3-Cp*)(η^2-Cp*)Si owing to the competing (η^2-Cp*)–Si bond in the latter. Indeed, a stronger bond in **3** is indicated by shorter Si–C bonds and longer C–C bonds within the allyl unit (Figure 2) and by a pronounced deviation of the allylic methyl groups from the plane of the C_5 perimeter. The shortest Si–C separation in **3** [2.0965(19) Å] is even shorter than each of the Si–C distances in the (η^5-Cp*)Si^+ cation (2.14–2.16 Å).



η^3- Cp* in **3** η^3- Cp* in Cp^*_2Si

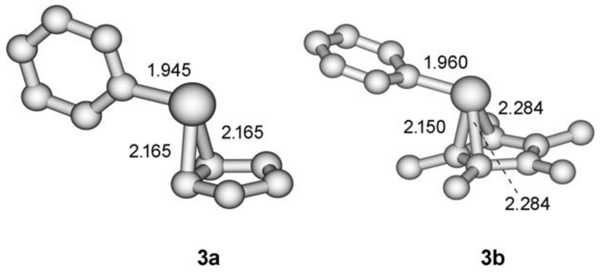
Figure 2. Si–C and C–C bond lengths in the (η^3-Cp*)Si unit in compound **3** and in (η^3-Cp*)(η^2-Cp*)Si.

The ^1H and ^{13}C NMR spectroscopy data of **3**·0.5 hexane (see the Experimental Section) are in accord with the constitution of the compound as derived from the X-ray structure data. They document a fluxional structure in solution, as averaged resonance signals are observed for the methyl groups and the carbon atoms of the Cp* ligand. A fluxional structure in solution is characteristic of η^1- or $\eta^{2,3}$-bound Cp* ligands in the chemistry of main-group elements.[21] The chemical shift for **3** in the ^{29}Si NMR spectrum is observed at $\delta = 51.6$ ppm. Interestingly, the change from the η^5 bonding in Cp^*Si^+[16] to the fluxional η^3 bonding in **3** is connected with a downfield shift of approximately 450 ppm.

The special bonding features were analyzed by DFT calculations on the parent compound PhCpSi (**3a**) and on differently substituted compounds, including **3**.[22] The adiabatic energy separation between the ground state and the corresponding triplet state is 32.5 kcal mol^{-1} for **3** (with ZPE correction), as compared with 35.3 kcal mol^{-1} for PhCp*Si (**3b**). The calculated structure for **3** agrees excellently with the X-ray crystal structure, including the η^3-coordination of the Cp* ring, the stretched Si–C(11) bond (2.006 Å), and the strong tilting at C(11) (Si(1)-C(11)-C(14) 159.7°). The Wiberg bond orders are 0.35 for Si(1)–C(1), Si(1)–C(2), and Si(1)–C(5) and 0.06 for Si(1)–C(3) and Si(1)–C(4). For Si(1)–C(11) the bond order is 0.71, less than a single bond. The overall charge that resides on the Cp*Si fragment is +0.469. A further inspection of the population analysis reveals for the

Si(1)–C(11) interaction a σ bond (population occupancy 1.931) with strong p character at silicon (Si 14 % s, 86 % p; C 30 % s, 70 % p). On this basis, **3** can be viewed as a cationic fragment Cp^*Si^+ interacting with an aryl anion.

Calculations also show that the conformation of the phenyl substituent in the parent compound PhCpSi **3a** is different from that observed in the permethylated compound PhCp*Si **3b** and in **3**, as it allows back-bonding from the phenyl π system into the p orbital at silicon. As a consequence, a shorter Si–C(phenyl) distance and longer Si–C(Cp) distances are found in **3a**.[22] MOLDEN plots of **3a** and **3b** together with calculated bond lengths are presented in Figure 3.



3a **3b**

Figure 3. MOLDEN plots of **3a** and **3b**.

In summary, a bulky σ-bound terphenyl substituent together with a π-bound Cp* ligand enable the isolation and full characterization of the first aryl-substituted monomeric silicon(II) species. Owing to the reactivity patterns of π Cp* complexes of silicon, such compounds can be regarded as the "resting state" of corresponding species with a σ Cp* substituent.[23] In this context, compound **3** is regarded as the "resting state" of a true silylene containing a σ-bound Cp* group. A further interesting potential for reactivity is given by the leaving-group character of the Cp* group. This behavior is often observed in the chemistry of main-group elements.[24]

Experimental Section

Synthesis **3**·0.5 hexane: A suspension of $LiAr^*\cdot Et_2O$ (75 mg, 0.13 mmol;[17] the purity was confirmed by NMR spectroscopy) in hexane (4 mL) was cooled to −78 °C and added by syringe to a stirred suspension of $Cp^*Si^+B(C_6F_5)_4^-$ (112 mg, 0.13 mmol) in hexane (2 mL) cooled to −78 °C. The reaction mixture was warmed to room temperature over 2 h and stirred for additional 1 h at room temperature. The resulting suspension (yellow solution and white solid) was filtered, and the solid was extracted with hexane (ca. 5 mL). The combined hexane solutions were concentrated to approximately 1 mL and left to crystallize at −30 °C. The compound **3**·0.5 hexane was isolated as yellow crystals (yield 74 mg, 81 %). Crystals suitable for X-ray analysis were grown from hexane at −30 °C.

^1H NMR (C_6D_6): $\delta = 0.88$ (t, 3H, CH_3(hexane, $^3J_{HH} = 6.9$ Hz), 1.11 (d, 12H, o-$CH(CH_3)_2$; $^3J_{HH} = 6.8$ Hz), 1.22, 1.27 (br, 2H, $CH_3CH_2CH_2$(hexane); br, 2H, $CH_3CH_2CH_2$(hexane)), 1.32 (d, 12H, p-$CH(CH_3)_2$, $^3J_{HH} = 6.8$ Hz), 1.50 (d, 12H, o-$CH(CH_3)_2$; $^3J_{HH} = 6.8$ Hz), 1.56 (s, 15H, CH_3(Cp*)), 2.89 (sept, 2H, p-$CH(CH_3)_2$; $^3J_{HH} = 6.8$ Hz), 3.24 (br, 4H, o-$CH(CH_3)_2$), 6.99 (d, 2H, m-Ph; $^3J_{HH} = 7.5$ Hz), 7.07 (t, 1H, p-Ph; $^3J_{HH} = 7.5$ Hz), 7.24 ppm (s, 4H, m-CH(Trip)); ^{13}C NMR (C_6D_6): $\delta = 10.1$ (CH_3(Cp*)), 14.3 (CH_3-(hexane)), 23.0, 23.1 (o-$CH(CH_3)_2$, $CH_3CH_2CH_2$(hexane)), 24.4 (p-$CH(CH_3)_2$), 26.8 (o-$CH(CH_3)_2$), 31.8, 31.9 (o-$CH(CH_3)_2$, $CH_3CH_2CH_2$(hexane)), 34.9 (p-$CH(CH_3)_2$), 120.3 (C(Cp*)), 121.8 (m-C(Trip)), 125.9 (p-C(Ph)), 130.7 (m-C(Ph)), 137.9 ($ipso$-C(Trip)), 143.0 (o-C(Ph)), 147.3 (o-C(Trip)), 148.8 (p-C(Trip)), 155.8 ppm ($ipso$-C(Ph)), ^{29}Si NMR (C_6D_6): $\delta = 51.6$ ppm. Elemental analysis (%) calcd for $C_{49}H_{71}Si$: C 85.52, H 10.40; found C 85.45, H 10.43.

CCDC-716947 contains the supplementary crystallographic data for compound **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[22] All computational results were obtained by full structural optimization at the RI-BP86 level utilizing a triple-zeta (TZVP) AO basis set. All structures were identified as energy minima by vibrational analysis. For details and references, see the Supporting Information.

[23] For comparison: The species (η^5-Cp*)Si$^+$ and (η^2-Cp*)(η^3-Cp*)Si are resting states for (η^1-Cp*)Si[16] and (η^1-Cp*)$_2$Si fragments,[21] respectively.

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