

## Reversible Transformation of a Stable Monomeric Silicon(II) Compound into a Stable Disilene by Phase Transfer: Experimental and Theoretical Studies of the System $\{[(\text{Me}_3\text{Si})_2\text{N}](\text{Me}_5\text{C}_5\text{Si})\}_n$ with $n = 1, 2$

Peter Jutzi,<sup>\*,†</sup> Andreas Mix,<sup>†</sup> Beate Neumann,<sup>†</sup> Britta Rummel,<sup>†</sup>  
Wolfgang W. Schoeller,<sup>\*,†,‡</sup> Hans-Georg Stammer,<sup>†</sup> and A. B. Rozhenko<sup>†,§</sup>

Faculty of Chemistry, University of Bielefeld, 33615 Bielefeld, FRG, Department of Chemistry, University of California, Riverside, California 92521-0403, and Department of Chemistry, Institute of Organic Chemistry, National Academy of Sciences of Ukraine, 5 Murmanskaya str., 02660, Kiev, Ukraine

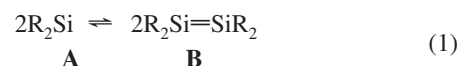
Received March 19, 2009; E-mail: peter.jutzi@uni-bielefeld.de

**Abstract:** The salt ( $\eta^5$ -pentamethylcyclopentadienyl)silicon(II) tetrakis(pentafluorophenyl)borate (**5**) reacts at  $-78$  °C with lithium bis(trimethylsilyl)amide in dimethoxyethane (DME) as solvent to give quantitatively the compound [bis(trimethylsilyl)amino][pentamethylcyclopentadienyl]silicon(II) **6A** in the form of a colorless viscous oil. The reaction performed at  $-40$  °C leads to the silicon(IV) compound **7**, the formal oxidative addition product of **6A** with DME. Cycloaddition is observed in the reaction of **6A** with 2,3-dimethylbutadiene to give the silicon(IV) compound **8**. Upon attempts to crystallize **6A** from organic solvents such as hexane, THF, or toluene, the deep yellow compound *trans*-1,2-bis[bis(trimethylsilyl)amino]-1,2-bis(pentamethylcyclopentadienyl)disilene (**6B**), the formal dimer of **6A**, crystallizes from the colorless solution, but only after several days or even weeks. Upon attempts to dissolve the disilene **6B** in the described organic solvents, a colorless solution is obtained after prolonged vigorous shaking or ultrasound treatment. From this solution, pure **6A** can be recovered after solvent evaporation. This transformation process can be repeated several times. In a mass spectroscopic investigation of **6B**, Si=Si bond cleavage is observed to give the molecular ion with the composition of **6A** as the fragment with the highest mass. The X-ray crystal structure analysis of the disilene **6B** supports a molecule with a short Si=Si bond (2.168 Å) with efficiently packed, rigid  $\sigma$ -bonded cyclopentadienyl substituents and silylamino groups. The conformation of the latter does not allow electron donation to the central silicon atom. Theoretical calculations at the density functional level (RI-BP86 and B3LYP, TZVP basis set) confirm the structure of **6B** and reveal for silylene **6A** the presence of an  $\eta^2$ -bonded cyclopentadienyl ligand and of a silylamino group in a conformation that prevents electron back-donation. Further theoretical calculations for the silicon(II) compound **6A**, the disilene **6B**, and the two species **11** and **11\*** derived from **6A** (which derive from Si=Si bond cleavage) support the experimental findings. The reversible phase-dependent transformation between **6A** and **6B** is caused by (a) different stereoelectronic and steric effects exerted by the pentamethylcyclopentadienyl group in **6A** and **6B**, (b) some energy storage in the solid state structure of **6B** (molecular jack in the box), (c) a small energy difference between **6A** and **6B**, (d) a low activation barrier for the equilibration process, and (e) the gain in entropy upon monomer formation.

### Introduction

During the past several decades, thermally stable silylenes or higher coordinated silicon(II) compounds ( $\text{R}_2\text{Si}$ )<sup>1–13</sup> and several stable disilenes ( $\text{R}_2\text{Si}=\text{SiR}_2$ )<sup>14,15</sup> have been synthesized and characterized in terms of their structure, bonding, and chemistry. An interesting aspect of the chemistry of these classes

of compounds is their reversible transformation according to eq 1:



Although many disilenes (**B**) have been prepared from highly reactive silylenes (**A**) as intermediates, only a few examples are documented in the literature where an equilibrium between **A** and **B** is observed. In the reported examples (see Chart 1), at least one component is described to be thermally rather unstable and, thus, not isolable under normal conditions of temperature and pressure.

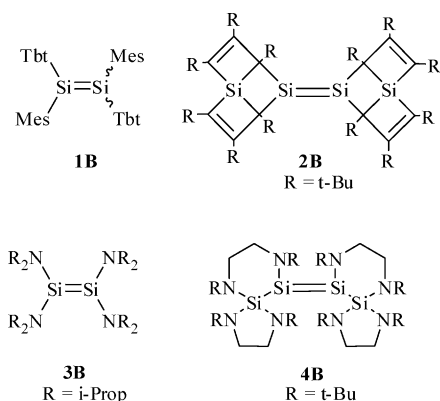
<sup>†</sup> University of Bielefeld.

<sup>‡</sup> University of California.

<sup>§</sup> National Academy of Sciences of Ukraine.

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Chart 1



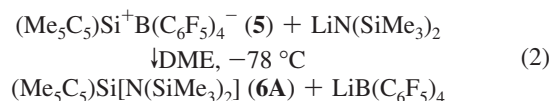
The first example of a reversible disilene cleavage has been reported by R. Okasaki, N. Tokitoh and co-workers.<sup>16</sup> The sterically congested disilene **1B** in its E- or Z-form is characterized by a long Si=Si distance of 2.228 Å (in the E-form) and dissociates under rather mild conditions (60–90 °C) into the reactive, and thus unisolable, silylene **1A** as proven by several trapping experiments. A relatively facile thermal dissociation has been observed by S. Tsutsui, K. Sakamoto and co-workers<sup>17</sup> for the disilene **2B** (Si=Si distance of 2.262 Å); the presence of the highly reactive silylene **2A** in equilibrium with **2B** was revealed once again by trapping experiments. M. Kira and co-workers<sup>18</sup> have presented convincing spectroscopic evidence that the diaminosilylene **3A** is rather stable in solution at room temperature and is in equilibrium with its dimer **3B** at low

temperatures. Concentration of a solution of **3A** leads to decomposition. The Si=Si distance in **3B** has been calculated to be 2.472 Å and, thus, is substantially longer than a regular Si=Si bond (2.142 Å in Me<sub>2</sub>Si=SiMe<sub>2</sub>).<sup>19</sup> A more complicated reaction sequence has been reported by Y. Apeloig, R. West and co-workers<sup>20</sup> in which a reversible transformation between the stable disilene **4B** (its Si=Si bond length of 2.289 Å is the longest yet proved experimentally) and four molecules of the stable silylene Si(NRCH<sub>2</sub>)<sub>2</sub> is observed via the silylene **4A** as reactive intermediate.

Here we describe the unique situation where both the silylene and the corresponding disilene are stable and isolable compounds under normal conditions of temperature and pressure, and a quantitative mutual transformation can be easily realized simply by phase transfer from solution (**A** present) to the solid state (**B** present) and vice versa, accompanied by slight temperature changes. This unusual process is explained mainly by steric strain in the solid disilene (molecular jack in the box) and flexibility in bonding modes ( $\sigma$  or  $\pi$ ) of a silicon-bound pentamethylcyclopentadienyl (Cp\*) substituent. The intermediate R<sub>2</sub>Si compound is not a silylene in the true sense of the word, but a higher coordinated silicon(II) species, which rearranges to a true silylene during the dimerization process. The R<sub>2</sub>Si=SiR<sub>2</sub> compound possesses, like a classical disilene, a short Si=Si double bond. Experimental observations are rationalized by theoretical calculations.

## Results

**Synthesis and Characterization.** Reaction of ( $\eta^5$ -pentamethylcyclopentadienyl)silicon(II) tetrakis(pentafluorophenyl)borate (**5**)<sup>21</sup> with lithium bis(trimethylsilyl)amide performed at –78 °C in dimethoxyethane (DME) solvent afforded [bis(trimethylsilyl)amino][pentamethylcyclopentadienyl]silicon(II) (**6A**) (eq 2). After exchange of DME by hexane, filtration of the lithium salt, and evaporation of the solvent, compound **6A** was obtained in the form of a colorless viscous oil in nearly quantitative yield, together with very small amounts of an unknown impurity. Purification of the extremely air- and moisture-sensitive compound **6A** was performed via conversion to the crystalline dimer **6B** and then reconversion to **6A**, as described in more detail in the next chapter. Attempts to crystallize the oily liquid **6A** were unsuccessful.



Compound **6A** is extremely difficult to handle. Nevertheless, **6A** could be characterized by mass and NMR spectroscopic studies and by the formation of a cycloaddition product (vide infra). A mass spectroscopic investigation gave the exact molecular mass of 323.19173 Da for the cation **6A**<sup>+</sup> with the correct isotopic pattern. The <sup>1</sup>H NMR spectrum of **6A**, measured in C<sub>6</sub>D<sub>6</sub> at room temperature, shows a singlet for the protons of the trimethylsilyl groups and another singlet for the methyl protons of the Cp\* ligand. The latter becomes only slightly broadened at –50 °C, typical for the presence of a fluxional

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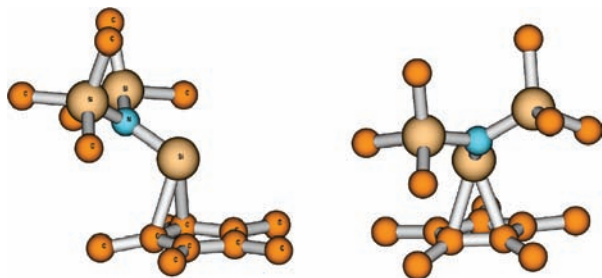


Figure 1. MOLDEN plots of the calculated structure of **6A**.

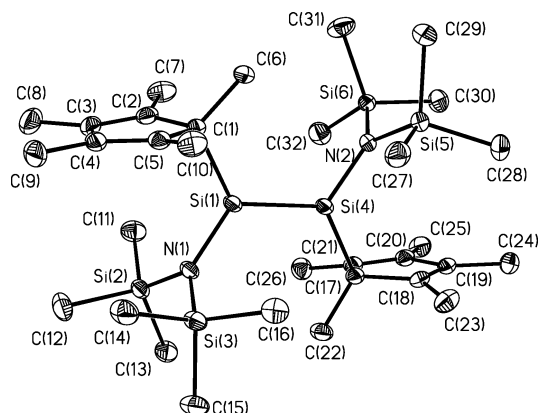


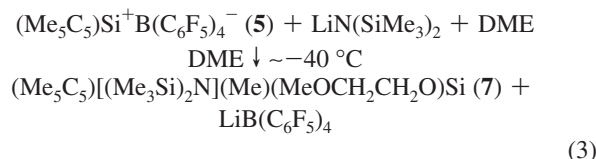
Figure 2. Molecular structure of **6B**; the ellipsoids are at the 50% level.

$\pi$ -bonded cyclopentadienyl system (calculations *vide infra*). Similarly, the  $^{13}\text{C}$  NMR spectrum (in  $\text{C}_6\text{D}_6$ ) shows one set of signals each for the carbon atoms of the trimethylsilyl groups, for the  $\text{Cp}^*$  methyl groups, and for the  $\text{Cp}^*$  ring carbon atoms, with only slight broadening of the signals for the  $\text{Cp}^*$  ligand on cooling. In the  $^{29}\text{Si}$  NMR spectrum, resonances are observed for the tetravalent silicon of the trimethylsilyl groups at  $\delta = -3.9$  (1.8;  $-2.4$ ) ppm and for the divalent silicon at  $\delta = -10.1$  (24.9) ppm. Computed values for the chemical shifts (B3LYP/TZVP) are added in parentheses; they suggest a slight non-equivalence of the trimethylsilyl groups. Chemical shift values at the RI-BP86/TZVP level are fairly close and listed in the Supporting Information (Table S4).

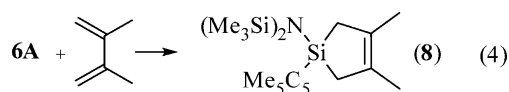
To obtain more detailed information on the molecular structure of **6A**, theoretical calculations were performed at two different levels of density functional theory: (a) RI-BP86/TZVP and (b) B3LYP/TZVP. Further computational details are given in the Computational Section and as Supporting Information. In Figure 1, a ball and stick model of the calculated monomeric structure **6A** is presented from two perspectives; important bond lengths and angles are collected in Table 1, and the numbering scheme for **6A** is given in Figure 3. The  $\eta^2$ -bonding of the  $\text{Cp}^*$  ligand to the divalent silicon atom is documented by comparable Si(1)C(1) and Si(1)C(2) bond lengths (2.27 Å) and by an angle of  $81.7^\circ$  between the Si(1)C(1)C(2) plane and the  $\text{C}_5$  perimeter. According to the calculation the  $\text{Cp}^*$  group can easily adopt haptotropic shifts (see Supporting Information, Figure S3). The Si–C bond lengths in **6A** are in the range of the bond lengths found for the  $\eta^3$ -bonding in the  $\text{Cp}^*(\text{aryl})$  silicon(II) compound  $(\text{Me}_5\text{C}_5)[2,6-(\text{Trip})_2\text{H}_3\text{C}_6]\text{Si}^{13}$  (2.27, 2.10, 2.28 Å) (Trip = 2,4,6-*i*Prop $_3\text{C}_6\text{H}_2$ ). These are smaller than those found for the  $\eta^{2/3}$ -bonding in decamethylsilicocene,  $(\text{Me}_5\text{C}_5)_2\text{Si}$ , (2.32 – 2.53 Å),<sup>2</sup> but are greater than that in the  $\eta^2$ -bonded half-sandwich cation  $\text{Me}_5\text{C}_5\text{Si}^+$  (2.14–2.16 Å) in **5**.<sup>21</sup> It is important to note that

only the  $\text{Cp}^*$  ligand, and not the bis(trimethylsilyl)amino group, is in the right orientation for a  $\pi$ -interaction with the vacant p-orbital at silicon. The measured NMR spectroscopic data of **6A** are in accord with the calculated structure.

When the reaction of **5** with the lithium amide in DME is performed not at  $-78^\circ\text{C}$  but, instead, at temperatures of approximately  $-40^\circ\text{C}$ , the only product is the silicon(IV) compound **7** (eq 3), which can be described as the formal oxidative addition product in the reaction of **6A** with DME. Compound **7** was unambiguously characterized by NMR spectroscopic data (see Experimental Section). It is notable that **6A** does not react with DME to give the oxidative addition product **7**. Thus, compound **7** must have resulted from a so far unknown intermediate formed under the reaction conditions.



Compound **6A** behaves like a typical silylene in the reaction with 2,3-dimethylbutadiene. Thus, the cycloaddition product 1-bis(trimethylsilyl)amino-1-pentamethylcyclopentadienyl-3,4-dimethyl-1-silacyclopentene-3 (**8**) was isolated after addition of the alkene to a hexane solution of **6A** and evaporation of the solvent (eq 4).



A rather unusual behavior was observed in experiments to crystallize **6A** from a hexane solution. After cooling the solution to approximately  $-10^\circ\text{C}$ , it took several days or even weeks before the formation of a crystalline compound was observed. Interestingly, air- and moisture-sensitive deep-yellow crystals separated from a nearly colorless solution. An X-ray structure analysis showed these crystals to consist of the disilene *E*-[( $\text{Me}_3\text{Si}$ ) $_2\text{N}$ ]( $\eta^1$ - $\text{Me}_5\text{C}_5$ )Si=Si( $\eta^1$ - $\text{C}_5\text{Me}_5$ )[N( $\text{SiMe}_3$ ) $_2$ ] (**6B**), the formal trans-dimer of **6A**. Comparable behavior was observed when crystallization experiments with **6A** were performed in a THF or toluene solution. The formation of **6B** directly from the reaction of **5** with lithium amide has already been described in an earlier communication.<sup>21</sup>

The molecular structure of **6B** is presented in Figure 2 where selected bond lengths and bond angles are given in Table 1; further structural parameters are given as Supporting Information (Tables S1, S2). Noteworthy features of the structure of **6B** are (a) a short Si=Si double bond (2.17 Å); (b) trans-orientated  $\sigma$ -bound  $\text{Cp}^*$  and bis(trimethylsilyl)amino substituents, both in an arrangement that does not allow appreciable  $\pi$ -interaction to the silicon atoms of the disilene unit; and (c) trans-bent angles (fold angle, out-of-plane angle, defined as the angle between the Si–Si vector and the  $\text{SiL}_2$  plane) of  $9.0^\circ$  and  $6.9^\circ$ . The geometrical parameters of the atoms in **6B** indicate a rigid structure in the solid state. Thus, sigmatropic rearrangements within the  $\text{Cp}^*$  fragments as well as rotations of the trimethylsilyl groups in the silylamino substituents cannot take place. As a consequence of the presence of a short Si=Si double bond, there is some strain within and between the substituents, which causes deviations in bond lengths and bond angles with rather short nonbonding contacts. Specifically, the N(1)Si(1)C(1) angle

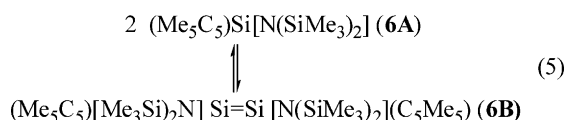
**Table 1.** Calculated and Experimental Bond Lengths (Å) and Bond Angles (deg) in **6A**, **6B**, **9**, **10**, and **11**; Values Are Obtained at the RI-BP86/TZVP (B3LYP/TZVP) Level

	<b>6A</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>6B</b> calcd <b>6B</b> exptl <b>6B/2 = 11*</b>
Si1–C1	2.275 (2.281)	2.186	2.189	2.295 (2.354)	2.006(2.000) [1.9451(12)]
Si1–C2	2.275 (2.261)	2.184	2.289	2.220 (2.176)	–
Si1–N	1.829 (1.818)	1.768	1.804	1.794 (1.784)	1.787(1.779) [1.7476(10)]
Si2–N	1.795 (1.788)	–	1.802	1.797 (1.791)	1.806(1.800) [1.7663(11)]
Si3–N	1.788 (1.782)	–	1.811	1.791 (1.785)	1.805(1.798) [1.7683(11)]
C1–C2	1.448 (1.444)	1.452	1.447	1.468 (1.468)	1.506(1.512) [1.5031(17)]
C2–C3	1.447 (1.443)	1.427	1.419	1.445 (1.450)	1.369(1.355) [1.3529(19)]
C3–C4	1.406 (1.398)	1.406	1.408	1.406 (1.390)	1.471(1.473) [1.4679(19)]
∠ Si1/C1C2/C4	81.7 (83.1)	90.1	87.1	106.2 (106.9)	–
∠ Si2/N/Si3	119.8 (119.7)	111.3	119.3	121.4 (120.8)	118.2(117.7) [119.17(6)]
∠ N/Si1/C1(C2)	109.5 (109.9)	93.0	103.7	115.1 (114.9)	116.2(116.2) [116.36(5)]
Si1–Si1'					2.252(2.212) [2.1683(5)]

(116.4°) is smaller and the Si(1)C(1)C(6) angle (112.7°) is greater than expected for an sp<sup>2</sup> and an sp<sup>3</sup> hybridized atom, and an elongation is observed for the Si(1)C(1) bond (1.94 Å). The nonbonding distances C(6)C(31), C(6)C(32), and C(2)C(11), C(3)C(11) are shorter than expected for van der Waals contacts. A van der Waals model of **6B** showing the compressed structure and the efficient packing of the substituents is given as Supporting Information (Figure S1).

Once again, a rather unusual behavior was observed for disilene **6B** in experiments requiring the dissolution of the compound in organic solvents such as hexane, THF-*d*<sub>8</sub>, or benzene-*d*<sub>6</sub>. After several minutes and vigorous shaking, or after ultrasound treatment, colorless instead of expected deep yellow solutions had formed. These solutions contain the silicon(II) compound **6A**, as demonstrated by the observation of the typical NMR data and by the isolation of pure **6A** as a colorless oil after solvent evaporation. The experiments described above were repeated several times with the same sample.

It is concluded from the experimental data that the disilene **6B** is stable only in the solid state of matter, whereas the silicon(II) compound **6A** is stable in solution and the liquid state. The observed transformations are reversible, as described in eq 5.



A mass spectrometric investigation of the disilene **6B** by the EI method afforded the fragment *m/z* = 323 as the ion with the highest mass. This observation indicates the dissociation of **6B** (molecular mass 646 Da) into two molecules of **6A** (molecular mass 323 Da). Thus, the process described in eq 5 might also be valid for the transition from the solid state into the gas phase.

**Quantum Chemical Calculations.** As has been skillfully discussed by Kira,<sup>14a</sup> the stability of disilenes, i.e., their bond dissociation energy (BDE), depends essentially on the π-bond energy gained in the individual monomeric silicon(II) compounds (silylenes) upon dissociation. The theoretical underpinning for these facts relies on the Carter–Goddard–Malrieu–

Trinquier (CGMT) model.<sup>22,23</sup> In silicon(II) compounds with amino and cyclopentadienyl substituents, both groups principally stabilize the ground-state structure by π-interaction with the vacant 3p-orbital at silicon. The amino group can choose a conformation in which electron density is transferred from the nitrogen lone pair to the silicon atom. This bonding situation has already been theoretically discussed for several diaminosilylenes and their dimerization products.<sup>19,24</sup> On the other hand the cyclopentadienyl group can occupy several hapticities (η<sup>2</sup>–η<sup>5</sup>) in which a π-interaction with the silicon atom is possible.<sup>25</sup>

To put the discussion of bonding in amino(cyclopentadienyl) silicon(II) compounds, and in corresponding disilenes, on firmer ground, we performed quantum chemical calculations (RI-BP86 and B3LYP, at times with the TZVP basis set; see Computational Section) on several molecular structures, which are portrayed in Figure 3. Further details of the computational results are given as Supporting Information. The most relevant bonding parameters obtained from the energy optimization are summarized in Table 1.

The structure of the parent, sterically unhindered, silicon(II) compound substituted by an amino and a cyclopentadienyl group is given in **9**. The cyclopentadienyl group adopts a η<sup>2</sup>-configuration with equal bonds from two adjacent ring carbons to the divalent silicon atom (see Table 1). The amino group adopts a conformation in which electron density is transferred from the nitrogen lone pair to the silicon atom. As regards the mutual orientation of the amino and the Cp substituent in relation to the silicon atom, an *exo*-conformation can be assigned to this species. Compound **9** possesses a highly fluxional structure

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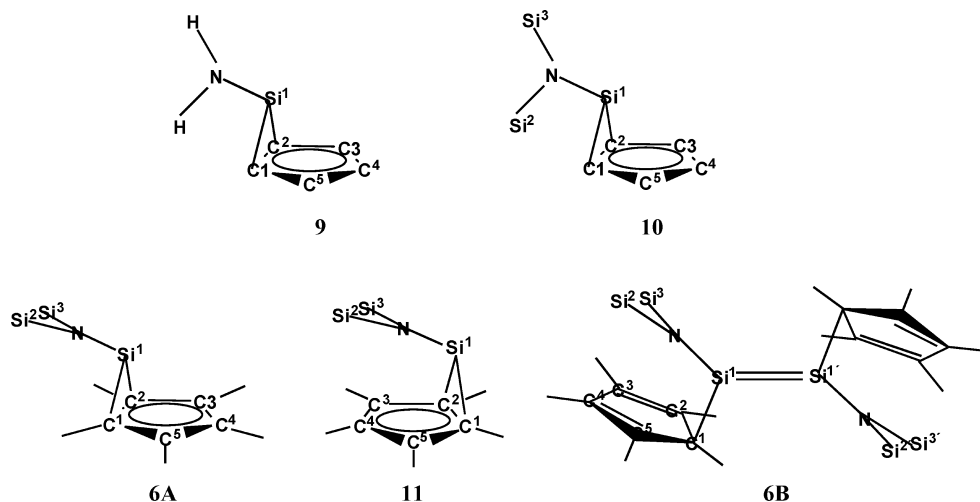


Figure 3. Representation of calculated structures.

with a fairly low energy barrier for a walk rearrangement over the Cp unit.<sup>26,27</sup> Structural details for isomers of **9** are presented in Figure S2 in the Supporting Information. The replacement of the hydrogen atoms at the amino substituent by trimethylsilyl groups, as in **10**, does not change the structure observed in **9**. However, increasing the steric demand of the  $\eta^2$ -Cp ligand by substitution with methyl groups (Cp\*) induces steric hindrance such that conformation **6A** is preferred. In this situation, the  $\pi$ -backbonding to silicon is restricted to the Cp\* ligand. Compound **11** represents an isomer of **6A** with a  $\eta^2$ -bound Cp\* substituent in an *endo*-conformation which is regarded as a reactive intermediate on the way to the formation of the disilene **6B**. The species **11\*** corresponds to a silylene in the “frozen” disilene geometry. It is formed by stretching of the Si=Si bond while keeping the residual structure within the geometrical arrangement of the disilene. The calculated bond lengths, bond angles, and the nonbonding distances C(6)C(31), C(6)C(32), and C(2)C(11), C(3)C(11) for the disilene **6B** in the gas phase are comparable to those values obtained for the solid state from an X-ray structure analysis (see Table 1). Furthermore, the calculated total energies for the solid-state and the gas-phase structure are nearly identical (vide infra). The observation of comparable data for the solid state and the gas-phase structure of **6B** excludes the presence of structure-determining intermolecular crystal forces in the solid state.

Further calculations (RI-BP86/TZVP) show that the  $\pi$ -contribution of a  $\eta^2$ -Cp group is a little stronger than that of a NH<sub>2</sub> group [the reaction (H<sub>2</sub>N)SiH + (H<sub>5</sub>C<sub>5</sub>)SiH<sub>3</sub> = (H<sub>2</sub>N)SiH<sub>3</sub> + (H<sub>5</sub>C<sub>5</sub>)SiH is exothermic by 5.2 kcal/mol]. It is concluded from these calculations that a  $\eta^2$ -Cp\* group is a better  $\pi$ -donor to a divalent silicon atom than a bis(trimethylsilyl)amino group.

For a better understanding of the factors responsible for the observed reversible transformation process according to eq 6, the (electronic) energies for the dissociation of **6B** into two species **6A** and **11** were calculated (Table 2). The table also lists the accompanying changes in the entropies (at 25 °C), obtained by statistical thermodynamical treatment for the gas phase. Since the sterically encumbered **6B** suffers from strong van der Waals contacts (see also Figure S1), we included in our density functional calculations additional corrections for the

Table 2.  $\Delta E$  (Relative Electronic Energy) and  $\Delta S \times 298$  K values ( $T = 298$  K,  $p = 0.1$  MPa) for the Transformations According to Eq 6 (RI-BP86+disp)<sup>a</sup>

	6A	11	11*	6B
$\Delta E$	23.2	39.9	59.5	0
$\Delta S \times 298$ K	10.4	14.8		0

<sup>a</sup> All given values in kcal/mol. Full details of the data are supplied in Tables S10 and S11.

dispersion energies; in other words this refers to an account for the different van der Waals contacts in the investigated species. The responses of different density functionals on the equilibria of the investigated species are summarized in Table S10 and S11. Structures **11** and **6A** are interconnected by a haptotropic rearrangement with a small energy barrier, although **6A** is more stable than **11** by 8.4 kcal/mol. Snapshots of the relaxed surface scan for the reaction of **11** to **6A** are presented in Figure S3. A possible structure **11\***, obtained by dissociation of the disilene **6B** and keeping the remaining geometry frozen, is not stable; it relaxes upon energy optimization into **11**.



The calculations indicate that the Si=Si bond stretching in **6B** to two silylenes **11** is sizable endothermically and the energy-rich species **11\*** is not involved in the transformation process. The entropy part  $T \times \Delta S$  (see Table 2) plays an important role for the transformation process. At low temperature, the formation of the disilene **6B** is favored. At higher temperature, the formation of **6A** is facilitated. In other words, Si=Si double bond formation is favored on the basis of the electronic energies but is at the same time antagonistic to the entropy contributions. These become more prominent with increasing temperature. Thus, the small energy differences  $\Delta E$  between **6A**, **11**, and **6B** allow the transformation process to be influenced in the normal temperature region. These conclusions are obtained from a thermodynamic gas-phase consideration of the equilibria (eq 6); they do not account for possible solvation energies stabilizing the individual species.

Quantum chemical calculations also indicate that the sigma-tropic shifts in **6A** are fast at room temperature, in accord with the NMR spectroscopic data. The activation energy of 2.3 kcal/mol for this degenerate process can be extracted from the energy profile of the transformation of **11** into **6A** (Figure S3).

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The silylene character of a silicon(II) compound is determined by the corresponding singlet–triplet (S–T) energy separation.<sup>22–24</sup> Our calculations indicate a relatively small singlet–triplet (S–T) energy separation of 27.7 kcal/mol for **11** and with 39.6 kcal/mol a more sizable quantity for **6A** (see Tables S12, S13, Supporting Information). This result reveals a “stronger” silylene character for **11** than for **6A**. Optimized geometries of the singlet and triplet species are given in Tables S5–S8 (Supporting Information); absolute energies (in a.u.) and relative energy differences are presented in Tables S9–S11.

Finally, the <sup>29</sup>Si NMR shift values for **6A**, **6B**, and **11** have been calculated with two density functionals (B3LYP/TZVP and RI-BP86/TZVP level; see Table S4). The values for the central silicon atoms in **6A** (24.9 and 3.9 ppm) and **11** (455.9 and 416.3 ppm) conform with the different silylene characters of these compounds. The values for the silicon atoms in the disilene unit of **6B** (127.8, 129.7 ppm and 131.2, 136.9 ppm) differ from the experimental data of the disilenes *cis*- (49.4 ppm) and *trans*-Mes\*N(SiMe<sub>3</sub>)<sub>2</sub>Si=Si(N(SiMe<sub>3</sub>)Mes\* (61.9 ppm),<sup>28</sup> in which Cp\* ligands are replaced by Mes\* groups.

## Conclusion

In this paper we have described the synthesis of the silicon(II) compound ( $\eta^2$ -Me<sub>5</sub>C<sub>5</sub>)(Me<sub>3</sub>Si)<sub>2</sub>N]Si (**6A**) and the phase-dependent reversible transformation of this species into the disilene ( $\eta^1$ -Me<sub>5</sub>C<sub>5</sub>)(Me<sub>3</sub>Si)<sub>2</sub>N]Si=Si[N(SiMe<sub>3</sub>)<sub>2</sub>]-( $\eta^1$ -C<sub>5</sub>Me<sub>5</sub>) (**6B**). Compound **6A** is stable in the gas phase, in the liquid state, and in solution; compound **6B** is stable only in the solid state.

To describe the formation of a disilene from two silylenes, the CGMT model is generally accepted.<sup>22</sup> According to this model, the structure of a R<sub>2</sub>Si=SiR<sub>2</sub> dimer depends on the electronic situation in the corresponding R<sub>2</sub>Si monomers. A silylene with a low singlet–triplet energy difference  $\Delta E_{ST}$  gives rise to the formation of a planar or slightly trans-bent disilene with a short Si=Si double bond. A silylene featuring a high  $\Delta E_{ST}$  value gives rise to the formation of a more pronounced trans-bent disilene with a comparatively weak Si=Si bond. In the case of the presence of a lone pair at an electronegative substituent R (R = F, NR<sub>2</sub>), the formation of a dimer formed by R-bridged monomers in a three-center, two-electron bond is a structural alternative.<sup>24</sup> Finally, some silylenes,<sup>4–8</sup> and also some higher coordinated silicon(II) compounds,<sup>9–13</sup> do not show any tendency for disilene formation for electronic as well as for steric reasons. The consequences of stereoelectronic effects of amino groups in silylenes on the  $\Delta E_{ST}$  value and the structure of the corresponding dimer have already been discussed in detail in the literature.<sup>24,29</sup>

In the case described here, we have the novel situation that a Cp\* group changes its electronic properties in the silylene–disilene transformation process. In compound **6A**, which is not a silylene in the true sense of the word but a higher coordinated silicon(II) species, the Cp\* group is  $\eta^2$ -bonded to the silicon atom. In compound **11**, the Cp\* group is still  $\eta^2$ -bonded, but on the way to the disilene **6B** a haptotropic shift takes place now allowing the formation of a disilene displaying a short Si=Si double bond. The other substituent, the bis(trimethylsilyl)amino group, is

stereoelectronically inactive: its conformation is the same in **6A**, **11**, and **6B** and does not allow efficient electron back-donation.<sup>30</sup>

The observed phase-dependent reversible transformation can be explained on the basis of some experimental data of **6B** and our results from quantum chemical calculations. Steric and stereoelectronic effects of the substituents in **6A**, **6B**, and the reactive species involved in the transformation process play an important role. The structural parameters for the disilene **6B** reveal the presence of a slightly compressed structure containing rigid  $\eta^1$ -Cp\* and bis(trimethylsilyl)amino substituents. This molecule represents to some extent an energy storage reservoir in the solid state, which, upon dissolution, is able to cause the cleavage of the Si=Si bond. The resulting two silylenes (**11**) instantaneously relax to form the stable silicon(II) compound **6A** by a haptotropic shift of the Cp\* group from an  $\eta^1$  to an  $\eta^2$  bonding. The calculations reveal that the R<sub>2</sub>Si=SiR<sub>2</sub> to R<sub>2</sub>Si transformation is endothermic but is counteracted by entropy effects which facilitate dissociation. The reverse process requires some cooling of the solution containing **6A**. The observed rather slow crystallization of **6B** may be caused by the necessary conformational changes of the Cp\* groups and the formation of a slightly compressed molecule. The small energy differences between the compounds **6A** and **6B** on the one hand, and between the transient silylene **11** and the stable species **6A/6B** on the other, allow the observation of reversible transformations in a region near room temperature.

Our findings in the system **6A/6B** are not totally unexpected. The groups of Rankin, Cowley, Lappert, and Power have recently published a lucid study<sup>31</sup> on the spontaneous, but not reversible, generation of persistent pnictinyl radicals from bulky dipnictines; the latter are regarded as examples of a molecular “jack in the box”. In our case, the disilene **6B** might play the role of a molecular “jack in the box”.

Similar transformations have been described for the germylene and the stannylene of the type El(CHSiMe<sub>3</sub>)<sub>2</sub> (El = Ge, Sn), including a phase-dependent process for the germanium compound.<sup>32</sup> However, in these situations, the formed dimers formed are only loosely held together by weak El–El bonds, consistent with the CGMT model and with the presence of substituents which are not variable in their stereoelectronic effects. In our case, the formation of a dimer with a strong El=El double bond is due to the stereoelectronic variability of the pentamethylcyclopentadienyl substituent.

## Computational Section

All calculations were performed with the Turbomole-5.7.1, Turbomole-6.0,<sup>33</sup> and Gaussian G03 (see Supporting Information) sets of program systems. Throughout density functional theory was employed. The calculations were done at the RI-BP86 and B3LYP

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(VWN(V)) correlation energy functional) levels of sophistication. For the BP86 function the resolution of the identity approximation<sup>34</sup> was employed (see also the Turbomole instruction manual). As a basis set we always used the TZVP basis set of Ahlrichs et al.,<sup>35</sup> which is known to provide a very good bonding description for higher main group elements. For the calculations with the Turbomole program, a grids size of 4 and an SCF convergence criterium of  $10^{-7}$  were used. The vibrational analyses for the characterization of the various structures and the calculation of the thermodynamic data were performed on the basis of numerical differentiation.

## Experimental Section

All manipulations were carried out under an inert atmosphere of argon by standard Schlenk techniques. High resolution NMR data were collected on a Bruker DRX 500 and a Bruker Avance 600 instrument. Mass spectra were recorded on a VG AutoSpec instrument.

**[Bis(trimethylsilyl)amino](pentamethylcyclopentadienyl)silicon(II) (6A) and E-1,2-Di[bis(trimethylsilyl)amino]-1,2-di(pentamethylcyclopentadienyl)disilene (6B)**, 350  $\mu\text{L}$  of a solution of lithium bis(trimethylsilyl)amide in *n*-hexane (1.0 M) were dissolved in 2 mL of dimethoxyethane and cooled to  $-78^\circ\text{C}$ . To this solution, 309 mg (0.37 mmol) of **5** dissolved in 1 mL of dimethoxyethane were added dropwise. Thereafter, the mixture was stirred for 2 h and then slowly warmed to  $-40^\circ\text{C}$ . The cooling bath was removed, and all volatile components were distilled off in vacuo. The pale yellow residue was extracted twice with 5 mL of *n*-hexane. After removing the solvent in vacuo, there remained 110 mg of a viscous, nearly colorless and extremely air- and moisture-sensitive oil, which contained compound **6A** (95% according to  $^1\text{H}$  NMR data) and traces of impurities. The oily residue was dissolved in 3 mL of *n*-hexane and stored for  $\sim 10$  days at  $-30^\circ\text{C}$ . During this time, 30 mg of compound **6B** had formed as slightly air- and moisture-sensitive, deep yellow crystals (in 25% yield, referred to the amount of **6A**). In repeating experiments, the formation of **6B** sometimes required even several weeks; the yield was in the range of 20–50%.

Compound **6B**:  $\text{C}_{32}\text{H}_{66}\text{N}_2\text{Si}_6$  calcd  $m/z$  646.384;  $\text{C}_{\text{calcd}}$  59.46%,  $\text{H}_{\text{calcd}}$  10.28%,  $\text{N}_{\text{calcd}}$  4.33%;  $\text{C}_{\text{found}}$  59.17%,  $\text{H}_{\text{found}}$  10.01%,  $\text{N}_{\text{found}}$  4.10%. MS (EI,  $m/z$ ): 323 ( $\text{M}^+$ ), 278 ( $\text{M}^+ - 3\text{Me}$ ), 205 ( $\text{M}^+ - \text{SiMe}_3 - 3\text{Me}$ ), 188 ( $\text{M}^+ - \text{C}_5\text{Me}_5$ ), 135 ( $\text{Me}_5\text{C}_5^+$ ); MS data are comparable to those obtained for **6A**. For X-ray structural data, see literature<sup>21</sup> and Supporting Information.

Pure **6A** (according to  $^1\text{H}$  NMR data) could be obtained quantitatively as a colorless viscous oil by dissolving 30 mg of **6B** in 2 mL of benzene under ultrasound treatment and by subsequent evaporation of the solvent in vacuo.

Compound **6A**:  $^1\text{H}$  NMR (600.13 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  [ppm]): 0.23 (s, 18H,  $\text{Me}_3\text{Si}$ ), 1.90 (s, 15H,  $\text{Me}_5\text{C}_5$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.92 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  [ppm]): 5.2 ( $\text{Me}_3\text{Si}$ ), 10.9 ( $\text{Me}_5\text{C}_5$ ), 120.4 ( $\text{Me}_5\text{C}_5$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119.20 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  [ppm]):  $-10.2$  ( $(\text{Me}_5\text{C}_5)\text{Si}$ ),  $-3.9$  ( $\text{Me}_3\text{Si}$ ); MS (EI,  $m/z$ ): 323 ( $\text{M}^+$ ), 278 ( $\text{M}^+ - 3\text{Me}$ ), 220 ( $\text{M}^+ - \text{SiMe}_3 - \text{CH}_3 - \text{CH}_2$ ), 205 ( $\text{M}^+ - \text{SiMe}_3 - 3\text{Me}$ ), 188 ( $\text{M}^+ -$

$\text{C}_5\text{Me}_5$ ), 135 ( $\text{Me}_5\text{C}_5^+$ ). Exact mass for  $\text{C}_{16}\text{H}_{33}\text{NSi}_3$  calcd  $m/z$  = 323.19208, found  $m/z$  = 323.19173 (by exact ion mass determination). Satisfactory elemental analyses of **6A** could not be obtained due to its extreme air and moisture sensitivity.

**[Bis(trimethylsilyl)amino](pentamethylcyclopentadienyl)[(2-methoxyethoxy)(methyl)silane (7)**. Synthetic procedure similar to the preparation of compound **6A**. The lithium bis(trimethylsilyl)amide solution in *n*-hexane was cooled to  $-40^\circ\text{C}$ . After addition of the DME solution of **5**, the reaction mixture was maintained at  $-40^\circ\text{C}$  for 2 h. Workup which was analogous to the isolation of **6A** led in quantitative yield to compound **7** as a colorless oily liquid.

Compound **7**:  $^1\text{H}$  NMR (600.13 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  [ppm]):  $-0.09$  (s, 3H,  $\text{SiMe}$ ), 0.31 (s, 18H,  $\text{SiMe}_3$ ), 1.33, 1.81, 1.97, 2.04 (15H,  $\text{Me}_5\text{C}_5$ ), 3.13 (s, 3H,  $\text{OCH}_3$ ), 3.33 (s, 2H,  $\text{CH}_2\text{O}$ ), 3.67 (s, 2H,  $\text{SiOCH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.92 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  [ppm]):  $-2.0$  ( $\text{SiMe}$ ), 5.3 ( $\text{Me}_3\text{Si}$ ), 16.0, 11.3, 11.4, 12.3, 13.5 ( $\text{Me}_5\text{C}_5$ ), 57.0, 135.5, 136.3, 137.6, 140.7 ( $\text{C}_5\text{Me}_5$ ), 57.0 ( $\text{MeOCH}_2\text{CH}_2\text{O}$ ), 61.9, 73.8 ( $\text{OCH}_2\text{CH}_2\text{O}$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119.20 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  [ppm]):  $-8.4$  ( $\text{SiC}_5\text{Me}_5$ ), 2.2 ( $\text{SiMe}_3$ );  $\text{C}_{20}\text{H}_{43}\text{O}_2\text{NSi}_3$  calcd  $m/z$  413.822;  $\text{C}_{\text{calcd}}$  58.05%,  $\text{H}_{\text{calcd}}$  10.47%,  $\text{N}_{\text{calcd}}$  3.38%;  $\text{C}_{\text{found}}$  57.72%,  $\text{H}_{\text{found}}$  10.11%,  $\text{N}_{\text{found}}$  3.17%; MS (EI,  $m/z$ ): 413 ( $\text{M}^+$ ), 338 ( $\text{M}^+ - \text{OCH}_2\text{CH}_2\text{OME}$ ), 278 ( $\text{M}^+ - \text{Me}_5\text{C}_5$ ).

**1-Pentamethylcyclopentadienyl(1-bis(trimethylsilyl)amino)-3,4-dimethyl-1-silacyclopent-3-ene (8)**, 300 mg (0.93 mmol) of **6A** were dissolved in 5 mL of toluene. At room temperature, 13  $\mu\text{L}$  (1.15 mmol) of 2,3-dimethylbutadiene were added and the mixture was heated to  $60^\circ\text{C}$  for 1 h. After the mixture cooled to room temperature, all volatile components were removed in vacuo. Compound **8** was obtained as a pale yellow oil in quantitative yield.

Compound **8**:  $^1\text{H}$  NMR (600.13 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  [ppm]): 0.27 (s, 18H,  $\text{NSiMe}_3$ ), 1.18 (d,  $^2J$  (H,H) = 17.4 Hz, 2H,  $\text{CH}_2$ ), 1.31 (s, 3H,  $\text{Me}_5\text{C}_5$ ), 1.46 (d,  $^2J$  (H,H) = 17.4 Hz, 2H,  $\text{CH}_2$ ), 1.64 (s, 6H,  $\text{C}-\text{CH}_3$ ), 1.82 (s, 12H,  $\text{Me}_5\text{C}_5$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.92 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  [ppm]): 0.3 ( $\text{NSiMe}_3$ ), 11.1, 11.2, 16.1 ( $\text{Me}_5\text{C}_5$ ), 19.0 ( $\text{C}-\text{CH}_3$ ), 28.4 ( $\text{Si}-\text{CH}_2$ ), 56.8 ( $\text{Me}_5\text{C}_5$ ), 130.3 ( $\text{C}-\text{CH}_3$ ), 135.4, 139.0 ( $\text{Me}_5\text{C}_5$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119.20 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  [ppm]): 3.5 ( $\text{NSiMe}_3$ ), 11.9 ( $\text{Me}_5\text{C}_5\text{Si}$ ); MS (EI,  $m/z$ ): 403 ( $\text{M}^+$ ), 268 ( $\text{M}^+ - \text{Me}_5\text{C}_5$ ); Exact mass for  $\text{C}_{22}\text{H}_{43}\text{NSi}_3$  calcd  $m/z$  405.27033, found 405.27014 (by exact ion mass determination).

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**Supporting Information Available:** Crystal structure data (CIF file) of **6B**; van der Waals model of **6B**; quantum chemical calculations for **6A**, **6B**, **11**, and **11\*** [optimized geometry, absolute energy (in a.u.), relative energy differences, S–T energy differences]; activation energy calculation for the sigmatropic rearrangements in **6A**; snapshots of the relaxed surface scan of **11** to **6A**;  $^{29}\text{Si}$  NMR shifts of **6A**, **6B**, and **11**; calculations for the parent amino(Cp)silicon(II) compound **9a** and for the isomers **9b–9d**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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