Are disilacyclopropylidenes and their carbenoids good precursors for the unknown 1,3-disilaallenes?

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This paper is dedicated to Professor O.M. Nefedov, one of the pioneers of low-valent organic and silicon compounds, on the occasion of his 70th birthday

Abstract

Ring opening of disilacyclopropylidenes provides a possible route to the yet unknown 1,3-disilaallenes. To examine the feasibility of this reaction we studied computationally the potential energy surfaces for the elimination of LiCl from *cyclo*-CSi_2H_4ClLi (and for comparison also for *cyclo*-C_3H_4ClLi), which serve as models for the corresponding substituted systems. On the basis of ab initio molecular orbital calculations at the MP2/6-31G(d)//MP2/6-31G(d) + ZPE level we predict that the activation energy for the conversion of *cyclo*-CSi_2H_4ClLi to 1,3-disilaallene (+ LiCl) is only 6.5 kcal mol^{-1}, making this reaction a promising strategy for the synthesis of 1,3-disilaallenes. This barrier is much smaller than the barrier (42.5 kcal mol^{-1}) for the all carbon analogue, *cyclo*-C_3H_4ClLi. The differences between the silicon and carbon systems are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Disilaallene; Carbenoid; Molecular orbital calculations

1. Introduction

Compounds with multiple bonds to silicon have attracted considerable interest since their first isolation in 1981, due to their unique properties [1]. Despite considerable efforts, so far only one compound type containing a cummulenic double bond to silicon [2], i.e. a 1-silaallene, has been successively synthesized and isolated as a stable compound [3]. The recently isolated 1-silaketenimine is better described as a silylene-isocyanide adduct rather than as a cummulenic double bond [4]. Compounds with Ge=C=C [5a–c] and Sn=Sn=Sn [5d] cummulenic double bonds were also isolated recently. However, 1,3-disilaallenes $R_2Si=C=SiR_2$ are still

unknown experimentally, either as stable species or as reactive intermediates, and furthermore, they have not even been studied computationally. Naturally, there is significant interest in the synthesis and properties of these novel compounds.

The ring opening of cyclopropylidene is a valuable method for the synthesis of allenes [6]. The commonly employed Doering–Moore–Skattebøl method [7], shown in Scheme 1, proceeds via α-halolithio carbenoids, which are generated by the reaction of the easily accessible 1,1-dihalocyclopropanes with alkyl lithium at low temperatures.

Can an analogous reaction sequence, shown in Scheme 2, be used to synthesize the yet unknown 1,3-disilaallenes [8]?
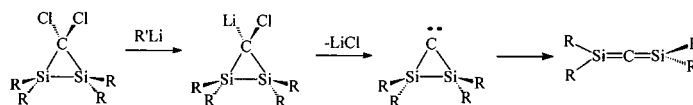
To answer this question we have carried out detailed ab initio molecular orbital calculations of the reactions shown in Scheme 2 (for R = H) and compared them with the analogous all carbon system (R = H) shown in Scheme 1.

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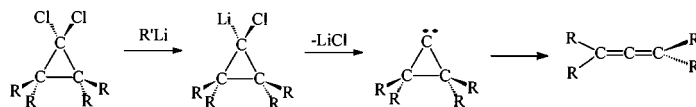
Scheme 1.

Scheme 2.

2. Computational methods

All calculations were performed using standard molecular orbital techniques [9], as implemented in the GAUSSIAN 94 series of programs [10]. All structures were fully optimized by gradient techniques [10] with inclusion of electron correlation using second-order Møller–Plesset perturbation theory (MP2) [11] and the polarized 6-31G(d) basis set [12]. Vibrational frequencies were computed for all structures, in order to characterize them as a minimum (no imaginary frequencies) or transition state, TS (one imaginary frequency). Zero-point energies (ZPEs) were calculated at the same level of theory, i.e. at MP2/6-31G(d). All energies reported in the discussion are calculated (unless stated otherwise) at the MP2/6-31G(d)//MP26-31G(d) level and include unscaled ZPEs. Analysis of the wave function employed Mülliken [13] and the natural bond order (NBO) (i.e. natural population analysis (NPA)) [14] population analyses.

3. Results and discussion

3.1. The potential energy surface for the ring-opening of cyclo-C₃H₄LiCl and cyclo-CSi₂H₄LiCl

First, we discuss the all carbon system, i.e. the elimination of LiCl from the α-halolithio carbenoid cyclo-C_3H_4LiCl (**1**). A schematic presentation of the reaction path leading from **1** to allene, calculated at MP2/6-31G(d)//MP26-31G(d) + ZPE, is shown in Fig. 1 and the calculated absolute and relative energies of the various species are collected in Table 1. The calculations show that elimination of LiCl from **1** produces a carbene–LiCl complex **2**, where the positively charged Li complexes to the lone pair of the carbene. This step is endothermic by 9.5 kcal mol^{-1} and **2** is separated from **1** by an energy barrier of 11.0 kcal mol^{-1} (**TS1/2**). Correspondingly, the barrier for the back-reaction of **2** to **1** is very low, only 1.5 kcal mol^{-1}. Dissociation of the complex **2** to LiCl and cyclopropylidene carbene (**3**) requires a high energy of 26.9 kcal mol^{-1}. The

backwards reaction, i.e. the complexation of LiCl to the carbene **3**, occurs without a barrier. Ring-opening of cyclopropylidene carbene **3b** to give the allene **4** occurs via **TS3/4** with a barrier of only 6.1 kcal mol^{-1}. The ring opening of cyclopropylidene to allene was studied extensively [15] due to the interesting mechanistic aspects of this reaction. In agreement with the previous studies [15], we also find that in **TS3/4** the cyclopropylidene ring opens in conrotatory fashion. The calculated activation energy for the ring-opening of cyclopropylidene to allene ranges from 10.2 kcal mol^{-1} at CISD + Q/DZP//RHF/DZP to 3.1 kcal mol^{-1} at MR-CISD/TZ2P//CASSCF(4,4) [15]. Our MP2/6-31G(d) ZPE value of 6.1 kcal mol^{-1} is in the range of these two values, supporting the reliability of the MP2/6-31G(d) level of theory for this particular problem. The ring opening of cyclopropylidene **3** to the allene **4** is highly exothermic, 68.5 kcal mol^{-1}, in agreement with the previously reported values of 68–69 kcal mol^{-1} [15]. The complexation of LiCl to allene to give **5** is moderately exothermic (14.5 kcal mol^{-1}). Thus, the overall energy required to transform the precursor **1** to allene (and LiCl) via **TS3/4** is quite high, 42.5 kcal mol^{-1}.

Next, we carried out similar calculations for the analogous potential energy surface of cyclo-CSi_2H_2LiCl and the results are summarized in Fig. 2 and in Table 2. The potential energy surface in Fig. 2 is dramatically different from that in Fig. 1. The dominant difference is that the energy barrier required to convert the α-halolithio disilacarbenoid **6** to 1,3-disilaallene is only 6.5 kcal mol^{-1} compared to 42.5 kcal mol^{-1} for the cyclo-C_3H_4LiCl. This shows that the conversion of **6** to 1,3-disilaallene is plausible and that it should occur at considerably milder conditions than for the carbon analogue.

Another important difference between the silicon and the carbon systems is that in contrast to cyclopropylidene **3**, the di-silicon analogue **10** is not a minimum on the potential surface, at all the theoretical levels examined, i.e. at MP2/6-31G(d), HF/6-31G(d) and the density functional theory method B3LYP/6-31G(d) [16]. Thus, elimination of LiCl from the α-halolithio disi-
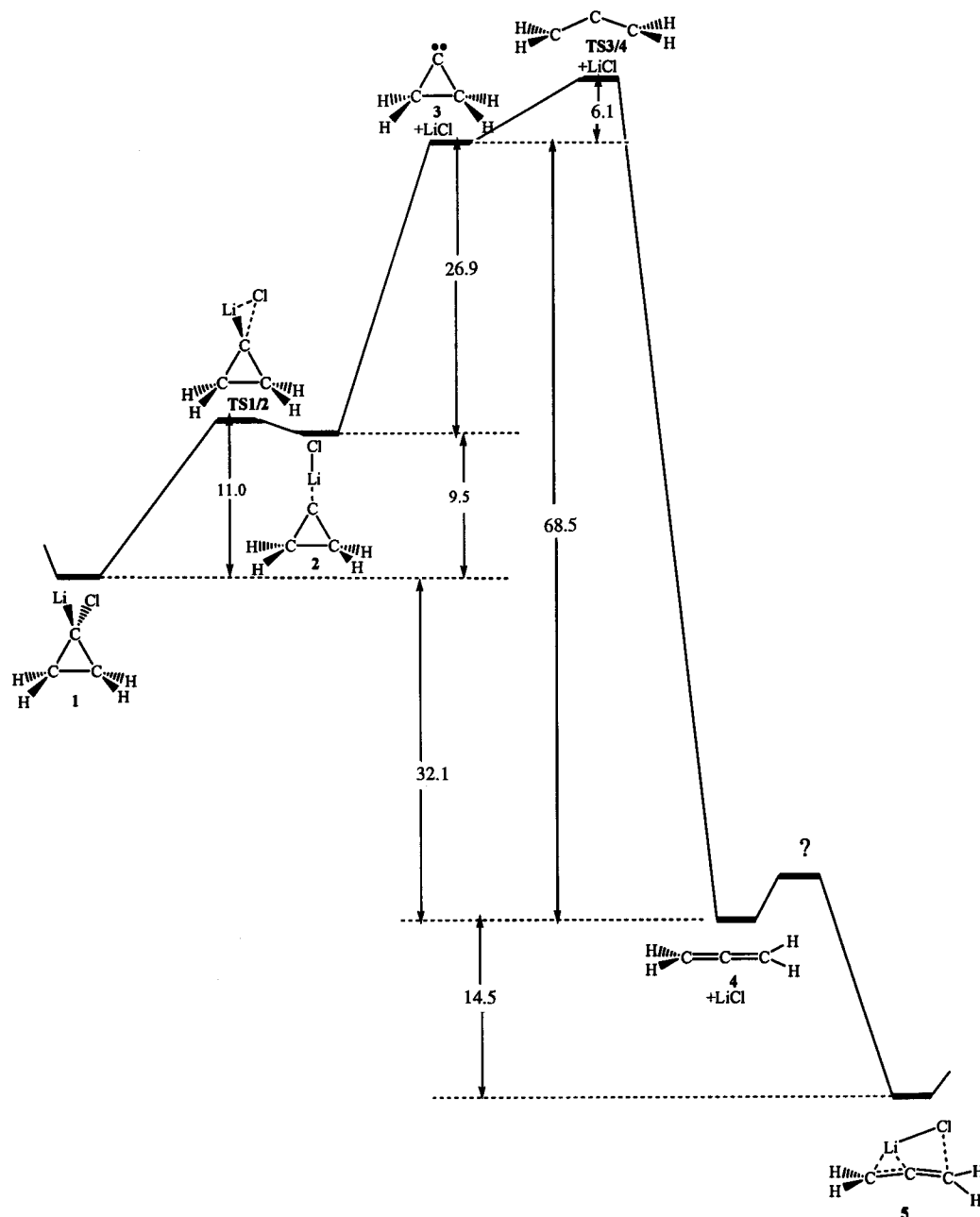
Fig. 1. Calculated reaction path (at MP2/6-31G(d)//MP2/6-31G(d) + ZPE) for the elimination of LiCl from *cyclo*-C_3H_4LiCl. Energies are given in kcal mol^{-1}.

lacarbenoid **6** leads *directly* via a disrotatory ring opening to the 1,3-disilaallene–LiCl complex **7**, which is more stable than **6** by 22.5 kcal mol^{-1}. The calculated barrier for this reaction (via **TS6/7**), which is also the overall barrier for the entire process, is only 6.5 kcal mol^{-1}, indicating that this is a very facile reaction. **7** can dissociate to yield the desired 1,3-disilaallene (**8**), a process which requires 19.6 kcal mol^{-1}. **7** can also easily rearrange (with a barrier of only 0.1 kcal mol^{-1}) via **TS7/9** to form the addition product of LiCl across

one of the C=Si bonds, i.e. **9**. **9** is more stable by 40.3 kcal mol^{-1} than separated 1,3-disilaallene and LiCl.
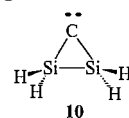
To compare the inherent thermodynamic stabilities of the carbon and silicon systems toward conversion to the corresponding cummulenic system, we have also calculated the energies of isodesmic Eqs. (1) and (2).

Table 1
Calculated absolute, zero-point and relative energies at MP2/6-31G(d)//MP2/6-31G(d) for C_3H_4LiCl isomers

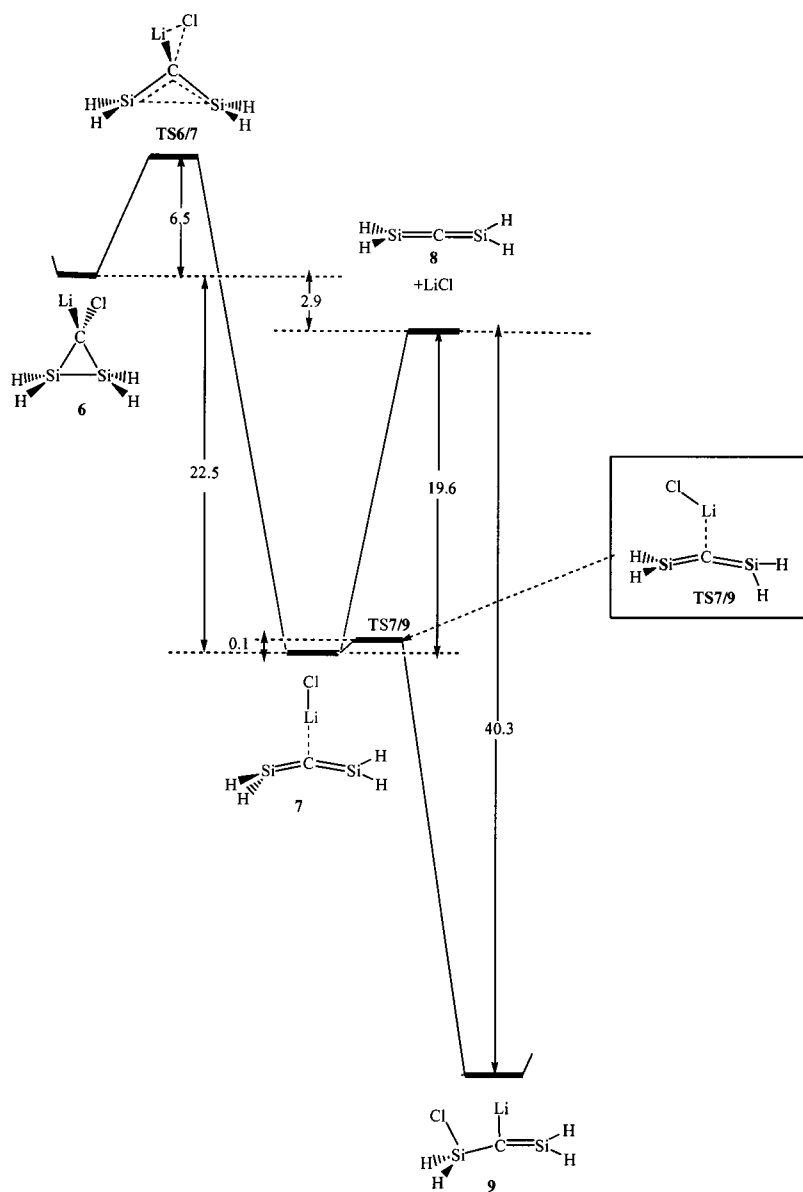| Compound [a]	Absolute energy (Hartree)	Relative energy (kcal mol^{-1})	ZPE (kcal mol^{-1})	Relative energy + ΔZPE (kcal mol^{-1})
1	−583.33370	0.0	39.2	0.0
TS1/2	−583.31249	13.3	36.8	11.0
2	−583.31471	11.9	36.8	9.5
3	−116.12370	40.2 [b]	34.5	36.4 [b]
TS3/4	−116.11330	46.7 [b]	34.1	42.5 [b]
4	−116.23413	−29.1 [b]	35.3	−32.1 [b]
5	−583.40494	−44.7	37.3	−46.6
LiCl	−467.14597		0.9	

[a] See Fig. 1.
[b] Includes the energy of LiCl.

Fig. 2. Calculated reaction path (at MP2/6-31G(d)//MP2/6-31G(d) + ZPE) for the elimination of LiCl from *cyclo*-CSi$_2$H$_4$LiCl. Energies are given in kcal mol^{-1}.

Table 2
Calculated absolute, zero-point and relative energies at MP2/6-31G(d)//MP2/6-31G(d) for CSi_2H_4LiCl isomers

Compound [a]	Absolute energy (Hartree)	Relative energy (kcal mol^{-1})	ZPE (kcal mol^{-1})	Relative energy + ΔZPE (kcal mol^{-1})
6	−1085.32996	0.0	26.5	0.0
TS6/7	−1085.31856	7.2	25.8	6.5
7	−1085.36471	−21.8	25.7	−22.5
8	−618.18548	−0.9 [b]	23.6	−2.9 [b]
TS7/9	−1085.36448	−21.7	25.7	−22.4
9	−1085.39956	−43.7	26.9	−43.2
LiCl	−467.14597		0.9	

[a] See Fig. 2.
[b] Includes the energy of LiCl.

Eq. (1) is endothermic by 1.4 kcal mol^{-1}, while Eq. (2) is endothermic by 21.8 kcal mol^{-1} (both values at MP2/6-31G(d)//MP26-31G(d) + ZPE). Thus, the ring-opening reaction for cyclopropane is thermodynamically more favourable by 20.4 kcal mol^{-1} than the ring-opening of disilacyclopropane. The analogous difference between the corresponding carbenoids **1** and **6** (i.e. for the elimination of LiCl) is somewhat larger, i.e. $32.1 − 2.9 = 29.2$ kcal mol^{-1}.
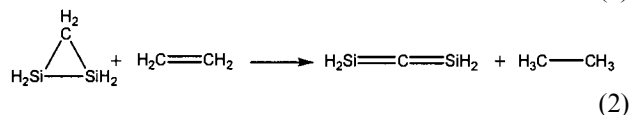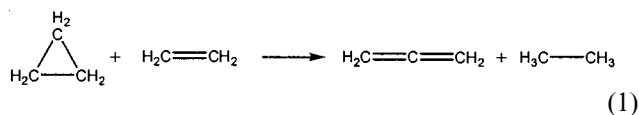
$$(1)$$

$$(2)$$

Fig. 3 shows the calculated geometries of the various species along the reaction shown in Scheme 2 and in Fig. 2. The structure of the transition state for the entire reaction, **TS6/7**, is of particular interest. The following geometric changes are found in **TS6/7**, compared to **6**: the Si–Si bond length is significantly lengthened (by 0.220 Å), while the Si–C bonds are shortened (by 0.057 Å); the C–Cl bond is lengthened dramatically by 0.495 Å, the Li–Cl bond is shortened by 0.123 Å while the C–Li bond is only slightly affected. Thus, **TS6/7** can be described as a 'late' transition state on the path from **6** to **7**. The complex of 1,3-disilaallene with LiCl (**7**) has an interesting structure. The C–Li–Cl bond angle is 180°, the Si–C bonds are elongated (1.701 Å) relative to **8** and the Li–C bond is elongated to 2.199 Å. **TS7/9** is a very early transition state with all geometric parameters (except the C–Li–Cl angle) being very similar to those of **7**. **9**, the addition product of LiCl to **8**, has the expected geometry with one short C=Si bond (1.698 Å), one longer C–Si bond (1.779 Å) and significant interaction between the Li and Cl atoms ($r(Li–Cl) = 2.341$ Å).

On the basis of the calculations for the parent cyclo-CSi_2H_4LiCl system we predict that the synthesis of 1,3-disilaallenes using the silicon analogue of the Doer-

ing–Moore–Skattebøl (DMS) method may indeed be plausible, since the calculations indicate that the activation energy for this reaction is only 6.5 kcal mol^{-1} (Fig. 2). Furthermore, the elimination of LiCl from **6** is favoured by entropy which is not included in the ΔE calculations shown in Fig. 2; i.e. ΔS for the reaction **6 → 8** + LiCl, is 35.8 e.u. and thus at $T = 298$ K the corresponding $T\Delta S$ term is 10.7 kcal mol^{-1}. Thus, while ΔH of the reaction **6 → 8** + LiCl is −2.9 kcal mol^{-1}, ΔE (at $T = 298$ K) for this reaction is −13.4 kcal mol^{-1}. The effect of entropy on **TS6/7** (i.e. on the kinetics of the ring-opening reaction) is small, $\Delta S^{\neq} = 0.2$ e.u., because the transition state does not lead to the elimination of LiCl (which remains bonded to **7**), but only to ring-opening.

One drawback of the DMS reaction is the fact that 1,3-disilaallene reacts with LiCl spontaneously and exothermically to give the LiCl addition product **9**. It is therefore clear that a successful synthesis of 1,3-disilaallene by this method requires the efficient removal of LiCl from the reaction medium.

3.2. Considerations regarding solution phase studies

A word of caution is warranted. The calculations reported here strictly apply only to gas-phase reactions, and in solution other reactions may compete and complicate the situation. However, there are various indications that quantum mechanical calculations do describe the reality in non-polar solvents [17–20]. Thus, previous theoretical studies of reactions of monomeric and dimeric RLi compounds support the conclusion that the solvent effects are not expected to be significant on going from the gas phase to pentane solution [17]. In particular, the formation of strong complexes between the various reaction intermediates and solvent molecules can be excluded [17]. Another factor which may affect the energetics of the reaction is the known tendency of organolithium compounds and of LiCl to form aggregates in non-polar solvents [18]. The calculated dimerization energy of LiCl is indeed substantial, 52.5 kcal mol^{-1} (at MP4SDQ/6-311 + G(d)//MP2/6-31G(d) + ZPE) [19].

Aggregation of LiCl serves as a *driving force* for the desired reaction, because it facilitates the elimination of LiCl from **6**, it reduces the reactivity of LiCl towards the formed 1,3-disilaallene, e.g. to give **9** ((LiCl)$_2$ is expected to be less reactive than LiCl) and it removes LiCl from the reaction mixture, increasing the chances
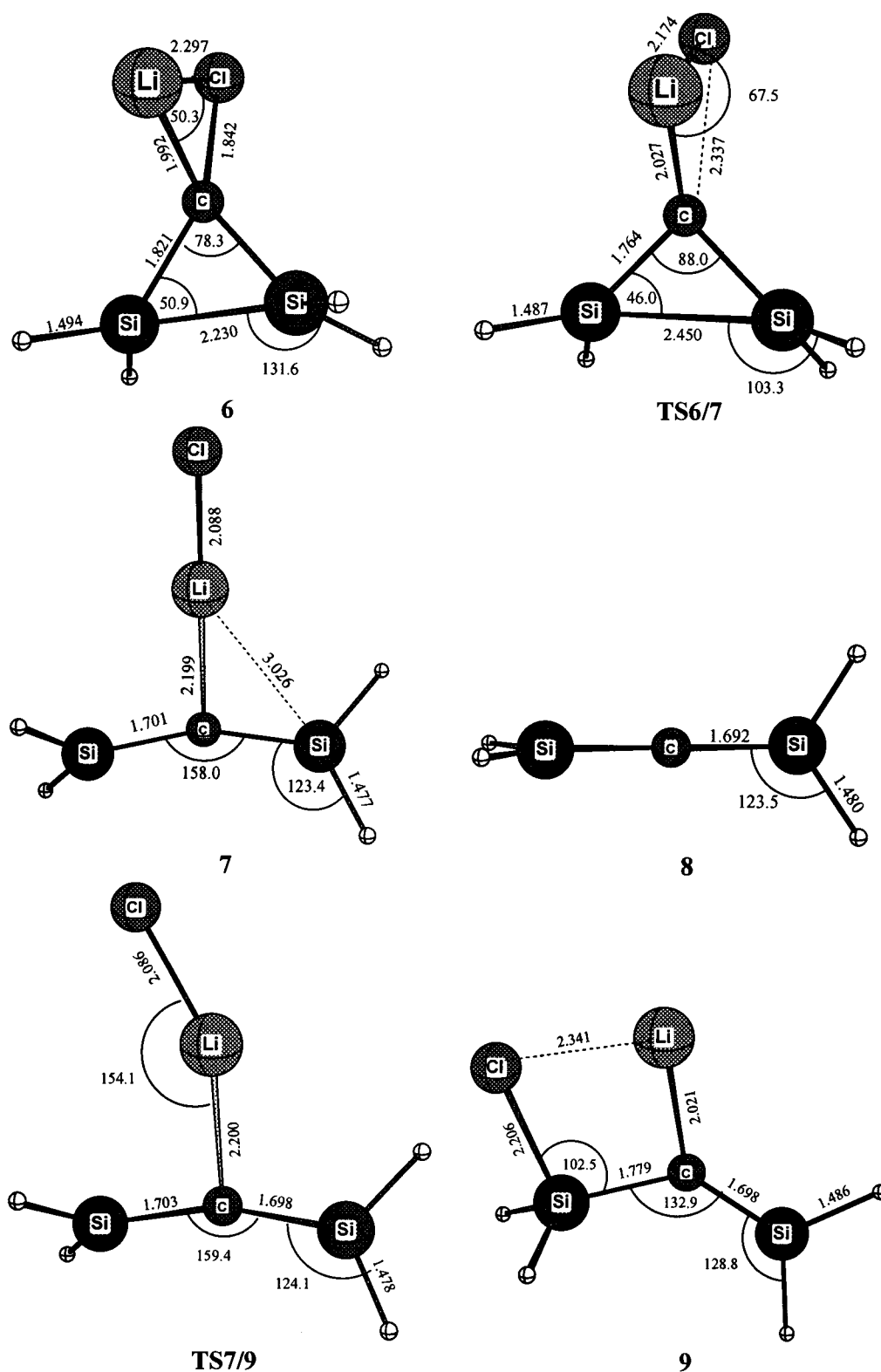

Fig. 3. Calculated structures and selected geometric parameters (at MP2/6-31G(d)) for **6**, **TS6/7**, **7**, **8**, **TS 7/9** and **9**. Bond lengths in Å, bond angles in °.

Mulliken charges   **NPA charges**   **FMO coefficients**

π 0.12   -0.06 π 0.21   -0.19   LUMO   0.59   -0.41

H_2Si══════CH_2 H_2Si══════CH_2 H_2Si══════CH_2

total   0.32   -0.56   total   0.93   -1.14   HOMO   0.40   0.60

π 0.04   -0.03 (0.06)   (0.03) π 0.12   -0.12 (-0.02)   (0.05)   LUMO   0.57   -0.43 (-0.32)   (0.68)

H_2Si══════C══════CH_2 H_2Si══════C══════CH_2 H_2Si══════C══════CH_2

total   0.16   -0.05   -0.37   total   0.85   -0.57   -0.40   HOMO   0.46   0.54 (0.50)   (0.50)

π 0.21   -0.07   0.21 π 0.21   -0.25   0.21   LUMO   0.73   -0.27

H_2Si══════C══════SiH_2 H_2Si══════C══════SiH_2 H_2Si══════C══════SiH_2

total   0.28   -0.28   0.28   total   1.06   -1.39   1.06   HOMO   0.36   0.63

Fig. 4. Calculated (at MP2/6-31G(d)) total and π charges at carbon and silicon (hydrogens not included), using Mülliken population analysis and NPA methods, and normalized square frontier molecular orbital coefficients for $H_2Si=C=SiH_2$ (**8**), $H_2Si=C=CH_2$ and $H_2Si=CH_2$. The values given in parentheses are for the C=C bond of $H_2Si=C=CH_2$.

that the 1,3-disilaallene can be isolated. We have recently used similar theoretical calculations and considerations to analyse and predict the course of a different reaction in which lithium chloride is eliminated, involving the addition of alkyl lithium to alkynes [20].

3.3. 1,3-Disilaallene

The desired 1,3-disilaallene **8** has a classical cummulenic-type structure with D_{2d} symmetry (Fig. 3). The C=Si bond length of 1.692 Å is similar to that (at the same level of theory) in the parent 1-silaallene (1.696 Å) and in 2-silaallene (1.700 Å).

What is the electronic structure of **8**? The calculated (MP2/6-31G(d)) Mülliken and NPA charges, separated into total charges and π-charges, are summarized in Fig. 4. Both methods predict that **8** is more polar than 1-silaallene, regardless of whether total charges or π-charges are considered. Thus, the total Mülliken charges (and π-charges in parentheses) of **8** are: -0.28 (-0.07) electrons on carbon and 0.28 (0.21) electrons on silicon compared to -0.05 (-0.03) electrons on C and 0.16 (0.04) electrons on Si in $H_2C=C=SiH_2$. The total charges calculated using the NPA method are much larger than according to the Mülliken charges (Fig. 4), but the qualitative trend remains the same; i.e. the NPA charges are: in **8** -1.39 (C), 1.06 (Si), and in $H_2C=C=SiH_2$ -0.57 (C), 0.85 (Si). The fact that NPA charges are much higher than Mülliken charges has been documented [21]. Tentatively, a higher polarity suggests a higher reactivity and we thus anticipate that the C=Si bonds of 1,3-disilaallenes are more reactive than the C=Si bond of 1-silaallenes.

The comparison of 1,3-disilaallene and the parent silene $H_2C=SiH_2$ is more problematic because the Mülliken and the NPA charges give different results. Thus, according to the total charges the Mülliken population analysis predicts that the C=Si bonds in **8** are somewhat less polar than in silene $H_2C=SiH_2$, but according to the

π-charges **8** is more polar than $H_2C=SiH_2$. The total NPA charges predict the opposite than the Mülliken total charges, i.e. that **8** has more polar C=Si bonds than the C=Si bond in silene, while the NPA π-charges of **8** and of $H_2C=SiH_2$ are very similar.

The molecular orbitals of **8** are the classical allenic-type orbitals, with two perpendicular π- and π^*-orbitals. However, due to the electronegativity difference between carbon and silicon these orbitals are polarized. The calculated coefficients of the frontier molecular orbitals (FMOs) of **8** (calculated at MP2/6-31G(d)) are summarized in Fig. 4. The FMOs of 1,3-disilaallene are more polarized than those of 1-silaallene; the HOMO (π) coefficients in **8** are 0.36 on Si and 0.63 on C and in 1-silaallene they are 0.46 and 0.54, respectively. The LUMO (π^*) of **8** is more strongly polarized and more heavily concentrated on the silicon atom than in $H_2C=C=SiH_2$. The HOMO of **8** and of $H_2C=SiH_2$ are polarized to a similar degree, while the LUMO of **8** is significantly more polarized than the LUMO of $H_2C=SiH_2$. As both the HOMO and the LUMO of **8** are more polarized than those of $H_2C=C=SiH_2$ (especially the LUMO), 1,3-disilaallene is predicted by FMO theory [22] to be more reactive than $H_2C=C=SiH_2$ towards both nucleophiles (LUMO-controlled) and electrophiles (HOMO-controlled). These predictions are consistent with the conclusions reached from the calculated charges (Fig. 4).

4. Conclusions

On the basis of ab initio calculations we predict that the Doering–Moore–Skattebøl method is an attractive method for the synthesis of the yet unknown 1,3-disilaallenes [8a]. For the parent *cyclo*-CSi_2H_4LiCl (**6**) the activation energy for the DMS-type reaction is only 6.5 kcal mol^{-1} and the reaction proceeds without the intermediacy of the corresponding 1,2-disilacyclopropy-

lidene (**10**), in contrast to the analogous carbon system. Experimentally, it will certainly be advantageous to use bulky substituents at the silicon atoms in order to stabilize kinetically the 1,3-disilaallene when formed. Furthermore, the use of bulky substituents, e.g. R = adamantyl or 2,4,6-tri-*iso*-propylphenyl, would favour the DMS-type reaction because the steric effects associated with these substituents are larger in the precursor disiliranes than in the corresponding 1,3-disilaallenes, making ring-opening energetically more favourable.

Another important clue to the experimentalists from the calculations is the fact that disilacyclopropylidene **10** is *not* a minimum on the potential energy surface and that it spontaneously ring opens to 1,3-disilaallene. This implies that other precursors or methods which produce **10** (e.g. photolysis of suitable precursors) will be well suited for synthesizing 1,3-disilaallenes, circumventing the possible complications resulting from the presence of LiCl or of alkyl lithium reagents which are required to produce the precursor carbenoid (e.g. **6**).

We hope that our calculations will stimulate experiments which will test our computational predictions, hopefully leading to the synthesis of the first 1,3-disilaallene.

5. Supplementary material

Calculated geomeries (in the form of *xyz* coordinates) are available from the authors for all compounds.

Acknowledgements

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