

## Exhaustively Trichlorosilylated C and C Building Blocks: Beyond the Müller-Rochow Direct Process

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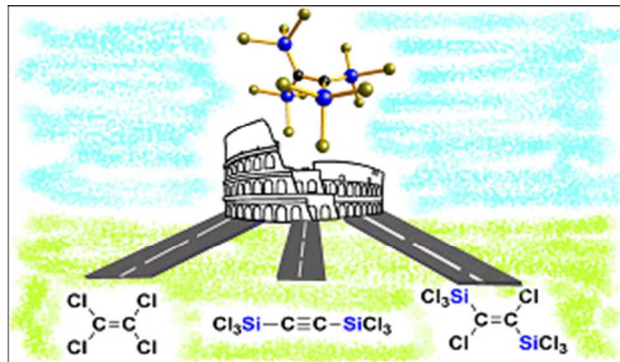
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# Exhaustively Trichlorosilylated C<sub>1</sub> and C<sub>2</sub> Building Blocks: Beyond the Müller-Rochow Direct Process

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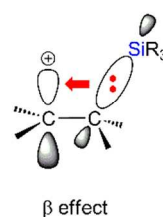
**ABSTRACT:** The Cl<sup>-</sup>-induced heterolysis of the Si–Si bond in Si<sub>2</sub>Cl<sub>6</sub> generates an [SiCl<sub>3</sub>]<sup>-</sup> ion as reactive intermediate. When carried out in the presence of CCl<sub>4</sub> or Cl<sub>2</sub>C=CCl<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> solutions, room temperature or below), the reaction furnishes the mono-carbanion [C(SiCl<sub>3</sub>)<sub>3</sub>]<sup>-</sup> (**[A]**<sup>-</sup>; 92%) or the vicinal dianion [(Cl<sub>3</sub>Si)<sub>2</sub>C–C(SiCl<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> (**[B]**<sup>2-</sup>; 85%) in excellent yields. Starting from **[B]**<sup>2-</sup>, the tetrasilylethane (Cl<sub>3</sub>Si)<sub>2</sub>(H)C–C(H)(SiCl<sub>3</sub>)<sub>2</sub> (**H<sub>2</sub>B**) and the tetrasilylethene (Cl<sub>3</sub>Si)<sub>2</sub>C=C(SiCl<sub>3</sub>)<sub>2</sub> (**B**; 96%) are readily available through protonation (CF<sub>3</sub>SO<sub>3</sub>H) or oxidation (CuCl<sub>2</sub>), respectively. Equimolar mixtures of **H<sub>2</sub>B**/**[B]**<sup>2-</sup> or **B**/**[B]**<sup>2-</sup> quantitatively produce 2 eq of the monoanion [**HB**]<sup>-</sup> or the blue radical anion [**B**]<sup>•-</sup>, respectively. Treatment of **B** with Cl<sup>-</sup> ions in the presence of CuCl<sub>2</sub> furnishes the disilylethyne Cl<sub>3</sub>SiC≡CSiCl<sub>3</sub> (**C**; 80%); in the presence of [HMe<sub>3</sub>N]Cl, the trisilylethene (Cl<sub>3</sub>Si)<sub>2</sub>C=C(H)SiCl<sub>3</sub> (**D**; 72%) is obtained. Alkyne **C** undergoes a [4+2]-cycloaddition reaction with 2,3-dimethyl-1,3-butadiene (CH<sub>2</sub>Cl<sub>2</sub>, 50 °C, 3d) and thus provides access to 1,2-bis(trichlorosilyl)-4,5-dimethylbenzene (**E1**; 80%) after oxidation with DDQ. The corresponding 1,2-bis(trichlorosilyl)-3,4,5,6-tetraphenylbenzene (**E2**; 83%) was prepared from **C** and 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one under CO extrusion at elevated temperatures (CH<sub>2</sub>Cl<sub>2</sub>, 180 °C, 4d). All closed-shell products were characterized by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>29</sup>Si NMR spectroscopy; an EPR spectrum of [*n*Bu<sub>4</sub>N][**B**]<sup>•-</sup> was recorded. The molecular structures of [*n*Bu<sub>4</sub>N][**A**], [*n*Bu<sub>4</sub>N]<sub>2</sub>[**B**], **B**, **E1**, and **E2** were further confirmed by single-crystal X-ray diffraction. Based on detailed experimental investigations, augmented by quantum-chemical calculations, plausible reaction mechanisms for the formation of [**A**]<sup>-</sup>, [**B**]<sup>2-</sup>, **C**, and **D** are postulated.

## INTRODUCTION

Functionalized organosilanes are versatile reagents for organic synthesis and indispensable building blocks for materials science. Their outstanding performance results from a number of unique electronic properties that distinguish silicon from its lighter group homologue carbon: (a) The lower electronegativity of Si (1.7)<sup>1</sup> compared to C (2.5)<sup>1</sup> renders the ionicity of an E–Si bond distinctly different from that of the corresponding E–C bond (E = chemical element). (b) Fragments C–SiR<sub>3</sub> carrying electron-releasing substituents R possess polarizable, energetically high-lying C–Si σ orbitals from which charge density can be transferred to properly aligned empty orbitals. A classic example for such hyperconjugation is seen in the stabilization of carbenium ions by geminal SiR<sub>3</sub> groups (β-silicon effect; Figure 1).<sup>2</sup> (c) Fragments E–SiX<sub>3</sub> carrying electronegative substituents X possess energetically accessible antibonding Si–X σ\* orbitals, which can accept electron density from π-donor atoms E, but also from external

Lewis bases L. The first type of interaction results in a partial E=SiX<sub>3</sub> double-bond character and is also responsible for the marked C–H acidity at the α position to a silyl group (E = C<sup>-</sup>). The second type facilitates the formation of five- and six-coordinate adducts (Figure 1).<sup>3</sup>

R: electron releasing



X: electron withdrawing

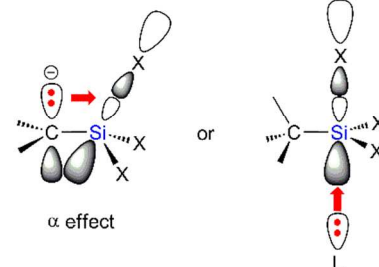


Figure 1. Simplified orbital interactions underlying the  $\beta$ -silicon effect (left), the  $\alpha$ -silicon effect (middle), or dative L–Si  $\sigma$  interactions (right; L = Lewis base).

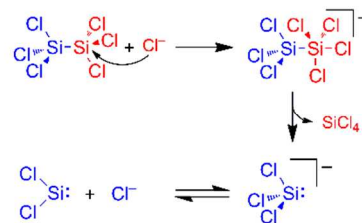
The aptitude of moieties C–SiX<sub>3</sub> to expand their coordination spheres and the more polarized C–Si bonds in adducts [C–SiX<sub>3</sub>L]<sup>n-</sup> (n = 0, 1) are widely exploited in protecting group chemistry,<sup>4</sup> Tamao oxidations,<sup>5–10</sup> and Hiyama-type C–C-coupling reactions.<sup>11–17</sup> The Peterson olefination benefits from both the  $\alpha$  acidity and the Lewis acidity of alkylsilanes.<sup>18</sup> Common to all these examples is that the silyl groups do not appear in the final products, but are split off in the course of the transformations. On the contrary, a number of important functional materials are gaining their useful properties only because the Si atoms remain as essential parts in the molecular scaffolds. Examples are luminescent organosilanes, such as hexaphenylsilole,<sup>19</sup> and silicones, the most abundant class of polymers with inorganic backbones.<sup>3</sup> Hyperconjugative  $n_{\text{O}} \rightarrow \sigma_{\text{SiX}_3}^*$  interactions (cf. the  $\alpha$  effect) are primarily responsible for the increased torsional flexibility and diminished basicity of silicones and thus contribute strongly to their broad application range.<sup>20</sup> Last but not least, organic trichlorosilyl and trialkoxysilyl derivatives represent key starting materials for the preparation of silsesquioxanes and other hybrid organic-inorganic macromolecules, which find applications as surface coatings, catalyst supports, xerogels, ceramic precursors, and optoelectronic materials.<sup>21–28</sup>

The Müller-Rochow Direct Process still constitutes the dominant technology for the preparation of organo(chloro)silanes on an industrial scale. At its most common level, the reaction involves CH<sub>3</sub>Cl and Si(Cu) as starting materials and gives (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> as the major product; the next most abundant species are CH<sub>3</sub>SiCl<sub>3</sub> and (CH<sub>3</sub>)<sub>3</sub>SiCl.<sup>3</sup> For the synthesis of more sophisticated (functionalized) organosilanes, Pt-catalyzed hydrosilylations of olefins and alkynes are extensively applied.<sup>29–33</sup> A third prominent synthesis approach relies on the transformation of SiCl<sub>4</sub> with organolithium or Grignard reagents.<sup>3</sup> However, this method has its limits in terms of functional-group tolerance and selectivity (e.g., multiple vs. single substitutions).<sup>34</sup> Problems also occur in the case of multiply silylated compounds, because the required multiply metallated organic intermediates are often hard to obtain, extremely sensitive, and poorly soluble.<sup>35,36</sup> Alternatively, a polarity-inverted pathway starting from organic halides and nucleophilic silanides is conceivable.

The only systematically investigated silanide-related systems for the preparation of organo(chloro)silanes currently remain the HSiCl<sub>3</sub>/NR<sub>3</sub> combination ('Benkeser reagent'; NR<sub>3</sub> = tertiary amine, typically N(*n*Pr)<sub>3</sub> or N(*n*Bu)<sub>3</sub>, in stoichiometric amounts) and the HSiCl<sub>3</sub>/[R<sub>4</sub>P]Cl pair ([R<sub>4</sub>P]<sup>+</sup> = quaternary phosphonium salt, typically [nBu<sub>4</sub>P]<sup>+</sup>, in catalytic amounts). The Benkeser reagent<sup>37</sup> has been employed to produce organotrichlorosilanes through reductions of carboxyl or carbonyl derivatives,<sup>38–41</sup> hydrosilylations of alkenes or alkynes,<sup>42–44</sup> and the silylation of alkyl halides.<sup>45,46</sup> With respect to the latter transformation, it is important to note that non-activated alkyl halides fail to yield the respective alkyl trichlorosilanes. Suitable substrates are benzyl and allyl halides as well as geminal polyhalogenated hydrocarbons. Thus, mesomeric or inductive electron withdrawal from the reaction center and the efficient stabilization of putative carbanionic

intermediates seem to be prerequisites for a successful halo- or SiCl<sub>3</sub> exchange.<sup>37,45,46</sup> The limitation of the Benkeser reagent to activated alkyl halide starting materials can partly be overcome by employing the HSiCl<sub>3</sub>/[R<sub>4</sub>P]Cl pair, which allows trichlorosilylations also of simple primary alkyl chlorides.<sup>47,48</sup> In terms of the reaction mechanism, already Benkeser postulated the initial formation of [SiCl<sub>3</sub>]<sup>-</sup>/[HR<sub>3</sub>N]<sup>+</sup> ion pairs.<sup>37,49</sup> Depending on the reaction conditions, the chimeric [SiCl<sub>3</sub>]<sup>-</sup> ion behaves either as a silanide nucleophile or as a dichlorosilylene source: i.e., [SiCl<sub>3</sub>]<sup>-</sup>/[HR<sub>3</sub>N]<sup>+</sup> vs. [SiCl<sub>2</sub>]/[HR<sub>3</sub>N]Cl.<sup>50–53</sup> Thus, both nucleophilic pathways and silylene insertion channels have to be regarded as plausible reaction scenarios. Recently, the Si<sub>2</sub>Cl<sub>6</sub>/[R<sub>4</sub>E]Cl combination has been identified as an alternative source of [SiCl<sub>3</sub>]<sup>-</sup> ions (E = N, P; R = Et, *n*-Bu, Ph).<sup>54</sup> Nucleophilic attack of chloride on the disilane results in the heterolytic cleavage of the Si–Si bond with concomitant formation of SiCl<sub>4</sub> and [SiCl<sub>3</sub>]<sup>-</sup> (Scheme 1).<sup>55,56</sup> In the presence of residual Si<sub>2</sub>Cl<sub>6</sub>, the thereby liberated [SiCl<sub>3</sub>]<sup>-</sup> induces the assembly of oligosilane scaffolds, such as perchlorinated cyclohexasilanes or Si<sub>20</sub> dodecahedranes ('silafullerenes').<sup>55,57,58</sup>

### Scheme 1. Generation of [SiCl<sub>3</sub>]<sup>-</sup> and/or [SiCl<sub>2</sub>] from Si<sub>2</sub>Cl<sub>6</sub> in the presence of chloride ions.



Herein, we are expanding the reaction scope of the Si<sub>2</sub>Cl<sub>6</sub>/[nBu<sub>4</sub>N]Cl combination to the synthesis of key organosilane reagents *via* convenient one-pot protocols ([A]<sup>-</sup>–E; Figure 2). The monoanion [A]<sup>-</sup> and vicinal dianion [B]<sup>2-</sup> are archetypal examples of the stabilizing effect of silyl groups on  $\alpha$  carbanions. Moreover, potentially nucleophilic sites coexist with strongly electrophilic sites. Compounds HA and H<sub>2</sub>B, the conjugate acids of [A]<sup>-</sup> and [B]<sup>2-</sup>, are potentially relevant to the preparation of organic-inorganic hybrid materials such as silsesquioxanes and xerogels. The electron-poor unsaturated derivatives B, C, and D should readily undergo substitution reactions at the Si atoms and/or cycloaddition reactions at the unsaturated organic backbones. This provides a broad range of oligo-functionalized precursors to be employed in, e.g., Hiyama-type C–C-coupling protocols (cf. E).<sup>59–61</sup>

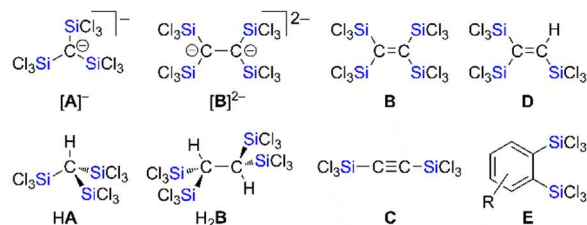


Figure 2. Target compounds of this work: the persilylated mono-carbanion **[A]<sup>-</sup>**, the dicarbanion **[B]<sup>2-</sup>**, and their corresponding acids **HA/H<sub>2</sub>B**; the (per)silylated ethenes **B/D**, ethyne **C**, and benzenes **E**.

## RESULTS AND DISCUSSION

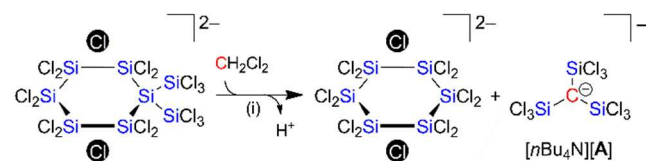
Some of the target compounds compiled in Figure 2 have previously been mentioned in the literature. However, as will be shown below, most of the respective synthesis protocols are at best inconvenient and at worst not practical on a laboratory scale.

In the following, we will first provide a brief literature survey on compounds **[A]<sup>-</sup>**–**E**. Second, we will disclose efficient means to prepare the anions **[A]<sup>-</sup>** and **[B]<sup>2-</sup>** and show that all the other target compounds are readily accessible from these two starting materials. Analytical details and reactivity patterns of **[A]<sup>-</sup>**–**E** will be discussed in the third section. The final paragraph of this publication is devoted to mechanistic considerations.

### Previous Mentions of **[A]<sup>-</sup>**–**E**.

We first observed the tris(trichlorosilyl)methanide salt **[nBu<sub>4</sub>N][A]** in the thermolysate of **[nBu<sub>4</sub>N]<sub>2</sub>[1,1-(Cl<sub>3</sub>Si)<sub>2</sub>Si<sub>6</sub>Cl<sub>10</sub>·2Cl]**, the chloride diadduct of the substituted cyclohexasilane 1,1-(Cl<sub>3</sub>Si)<sub>2</sub>Si<sub>6</sub>Cl<sub>10</sub> (CH<sub>2</sub>Cl<sub>2</sub>, 85 °C; Scheme 2).<sup>55,62</sup> Under the conditions applied, stripping of both SiCl<sub>3</sub> substituents occurred to give the diadduct **[nBu<sub>4</sub>N]<sub>2</sub>[Si<sub>6</sub>Cl<sub>12</sub>·2Cl]** of parent Si<sub>6</sub>Cl<sub>12</sub>.

### Scheme 2. Thermolysis of **[nBu<sub>4</sub>N]<sub>2</sub>[1,1-(Cl<sub>3</sub>Si)<sub>2</sub>Si<sub>6</sub>Cl<sub>10</sub>·2Cl]** in CH<sub>2</sub>Cl<sub>2</sub> to furnish **[nBu<sub>4</sub>N]<sub>2</sub>[Si<sub>6</sub>Cl<sub>12</sub>·2Cl]** and **[nBu<sub>4</sub>N][A]** as part of a complex product mixture.



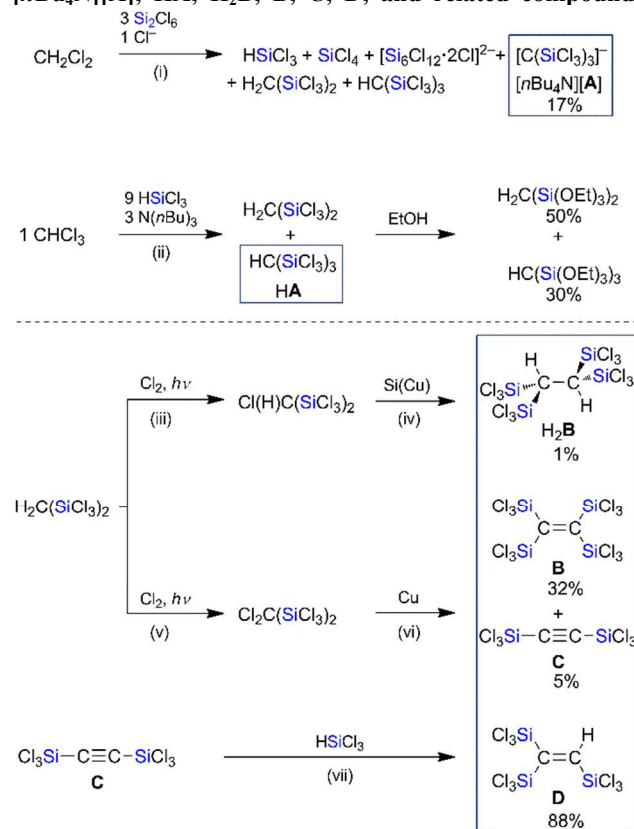
Cation = **[nBu<sub>4</sub>N]<sup>+</sup>** omitted for clarity. (i) CH<sub>2</sub>Cl<sub>2</sub>, 85 °C in a sealed vial, 4 h.

Dichlorosilylenes, formally liberated in the course of the stripping reaction, are found re-inserted into C–Cl and C–H bonds of the solvent, thereby ultimately furnishing **[nBu<sub>4</sub>N][A]** and H<sub>2</sub>C(SiCl<sub>3</sub>)<sub>2</sub>, which was detected as a side product. When Kroke et al. reproduced the synthesis of **[nBu<sub>4</sub>N]<sub>2</sub>[Si<sub>6</sub>Cl<sub>12</sub>·2Cl]**, they succeeded in the isolation of **[nBu<sub>4</sub>N][A]** with 17% yield (Scheme 3, top); they also mentioned that **[nBu<sub>4</sub>N][A]** was formed from a mixture of Si<sub>2</sub>Cl<sub>6</sub>/**[nBu<sub>4</sub>N]Cl** in CHCl<sub>3</sub> (no yield given).<sup>63</sup> In contrast to **[nBu<sub>4</sub>N][A]**, its dianionic homologue **[nBu<sub>4</sub>N]<sub>2</sub>[B]** remained elusive until to-date.

Corriu et al. synthesized preparatively useful amounts of **HA** by treatment of CHCl<sub>3</sub> with excess Benkeser reagent. The chlorosilane **HA** was not isolated, but routinely transformed to HC(Si(OEt)<sub>3</sub>)<sub>3</sub> via ethanolysis (30%; Scheme 3, top).<sup>27,64</sup> Some tetrasilylethane H<sub>2</sub>**B** forms upon reaction of Cl(H)C(SiCl<sub>3</sub>)<sub>2</sub> with Si(Cu) at 300–320 °C in a fixed bed reactor; the synthesis of the precursor molecule, Cl(H)C(SiCl<sub>3</sub>)<sub>2</sub>, requires gas-phase

photochlorination of H<sub>2</sub>C(SiCl<sub>3</sub>)<sub>2</sub> (Scheme 3).<sup>65</sup> The corresponding alkene, (Cl<sub>3</sub>Si)<sub>2</sub>C=C(SiCl<sub>3</sub>)<sub>2</sub> (**B**), and alkyne, Cl<sub>3</sub>SiC≡CSiCl<sub>3</sub> (**C**), are accessible through dechlorinative coupling of Cl<sub>2</sub>C(SiCl<sub>3</sub>)<sub>2</sub> with Cu metal in a stirred bed reactor as parts of a multi-component mixture (Scheme 3, bottom).<sup>66,67</sup> Alternatively, CCl<sub>4</sub> gives some **C** (18%) in the Müller-Rochow Direct Process.<sup>66,68</sup> Catalytic hydrosilylation of **C** has been employed to prepare the 1,1,2-trisilylethane **D** (88%).<sup>69</sup>

### Scheme 3. Selected literature-known synthesis routes to **[nBu<sub>4</sub>N][A]**, **HA**, **H<sub>2</sub>B**, **B**, **C**, **D**, and related compounds.



The cation = **[nBu<sub>4</sub>N]<sup>+</sup>** is omitted for clarity. The yields of **H<sub>2</sub>B**, **B**, and **C** refer to H<sub>2</sub>C(SiCl<sub>3</sub>)<sub>2</sub>. (i) CH<sub>2</sub>Cl<sub>2</sub>, 85 °C in a sealed vial, 24 h; (ii) CH<sub>3</sub>CN, –40 °C to 65 °C, 16 h; (iii) gas phase, high-pressure Hg lamp, 30 h; (iv) Si(Cu), 300–320 °C in a fixed bed reactor, 16 h; (v) CCl<sub>4</sub>, reflux temperature, 64 h; (vi) Cu, room temperature to 380 °C, 2.5 h. (vii) Speier catalyst in *i*PrOH, 90 °C, sealed glass ampoule, 6 d.

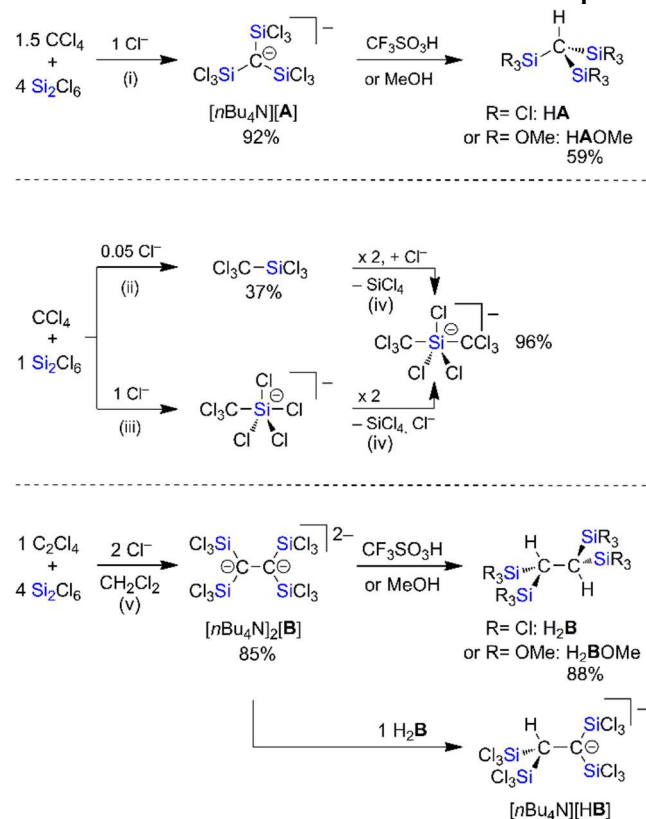
### Syntheses of **[nBu<sub>4</sub>N][A]**–**E**.

We first revisited and expanded the previous studies by our and Kroke's group and systematically screened the behavior of Si<sub>2</sub>Cl<sub>6</sub>/**[nBu<sub>4</sub>N]Cl** toward the entire series of chloromethanes. In brief, C–Si coupling took place with all four substrate molecules: From a solution of CH<sub>3</sub>Cl in CH<sub>2</sub>Cl<sub>2</sub>, we obtained CH<sub>3</sub>SiCl<sub>3</sub>. CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>, employed both as reagents and solvents, furnished **[nBu<sub>4</sub>N][A]** in yields of 34% (sealed glass ampoule, 120 °C, 30 h) and 78% (reflux temperature, 2 h), respectively (cf. the SI for more details). Almost quantitative yields of **[nBu<sub>4</sub>N][A]** were harvested from 4:1:1.5 mixtures of Si<sub>2</sub>Cl<sub>6</sub>, **[nBu<sub>4</sub>N]Cl**, and CCl<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> (Scheme 4, top).<sup>70</sup> This new protocol opens a time- and cost-efficient access route to



preparatively useful quantities of  $[n\text{Bu}_4\text{N}][\text{A}]$ , it does not require elevated temperatures, the exothermic reaction occurs instantaneously, and workup is facile.

**Scheme 4. Reactions of  $\text{CCl}_4$  and  $\text{C}_2\text{Cl}_4$  with  $\text{Si}_2\text{Cl}_6/[n\text{Bu}_4\text{N}]\text{Cl}$ , resulting in the formation of C–Si-bonded species.**



The cation =  $[n\text{Bu}_4\text{N}]^+$  is omitted for clarity. Synthesis of HA/HAOMe or  $\text{H}_2\text{B}/\text{H}_2\text{BOMe}$  via protonation/methanolysis of  $[n\text{Bu}_4\text{N}][\text{A}]$  or  $[n\text{Bu}_4\text{N}]_2[\text{B}]$ ; synthesis of  $[n\text{Bu}_4\text{N}][\text{HB}]$  through proton transfer between  $\text{H}_2\text{B}$  and  $[n\text{Bu}_4\text{N}]_2[\text{B}]$ . (i)  $\text{CH}_2\text{Cl}_2$ , 0 °C to room temperature, 1 h; (ii)  $\text{CCl}_4$ , room temperature, 24 h; (iii)  $\text{CCl}_4$ , room temperature, 1 h; (iv)  $\text{CH}_2\text{Cl}_2$ , room temperature, 1 h; (v)  $\text{CH}_2\text{Cl}_2$ , –10 °C to room temperature, 12 h.

$\text{CCl}_4$  possesses the highest reactivity among the four chloromethanes. Competing solvent activation does therefore not occur even under conditions of high dilution, which is of crucial importance in the present context: Contrary to the cases of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , no  $[n\text{Bu}_4\text{N}][\text{A}]$  formed when  $\text{Si}_2\text{Cl}_6$  was added to  $[n\text{Bu}_4\text{N}]\text{Cl}$  in excess neat  $\text{CCl}_4$  (Scheme 4, middle). Depending on the relative amounts of the chloride salt, we either obtained the perchlorinated methylsilane  $\text{Cl}_3\text{C-SiCl}_3$  (catalytic  $[n\text{Bu}_4\text{N}]\text{Cl}$ ; 95% conversion, 37% yield) or its  $[\text{CCl}_3]^-$  adduct  $[n\text{Bu}_4\text{N}][\text{Cl}_3\text{C-SiCl}_3-\text{CCl}_3]$  after recrystallization from  $\text{CH}_2\text{Cl}_2$  (1 eq  $[n\text{Bu}_4\text{N}]\text{Cl}$ , 96% yield; relative to  $\text{Si}_2\text{Cl}_6$ ).  $\text{Cl}_3\text{C-SiCl}_3$  is usually prepared *via* the potentially hazardous photochlorination of  $\text{H}_3\text{C-SiCl}_3$ ,<sup>69</sup> whereas  $[n\text{Bu}_4\text{N}][\text{Cl}_3\text{C-SiCl}_3-\text{CCl}_3]$  is so far unknown. Our current working hypothesis assumes that a primary  $\text{Cl}^-$  adduct  $[n\text{Bu}_4\text{N}][\text{Cl}_3\text{C-SiCl}_4]$  acts as a  $\text{Cl}_3\text{C}$ -transfer reagent along the way from  $\text{Cl}_3\text{C-SiCl}_3$  to  $[n\text{Bu}_4\text{N}][\text{Cl}_3\text{C-SiCl}_3-\text{CCl}_3]$ . In the

non-polar solvent  $\text{CCl}_4$ , the ionic species  $[n\text{Bu}_4\text{N}][\text{Cl}_3\text{C-SiCl}_4]$  and  $[n\text{Bu}_4\text{N}][\text{Cl}_3\text{C-SiCl}_3-\text{CCl}_3]$  precipitate immediately and can thus no longer participate in further reactions. The chemical constitution of  $[n\text{Bu}_4\text{N}][\text{Cl}_3\text{C-SiCl}_4]$  was confirmed by X-ray crystallography, however, the poor crystal quality precludes publication of the data (cf. the SI for more information). We finally emphasize a conceptual relationship between  $[\text{Cl}_3\text{C-SiCl}_3-\text{CCl}_3]^-$  and the previously published anion  $[\text{Cl}_3\text{Si-SiCl}_3-\text{SiCl}_3]^-$ , which has been interpreted as the  $[\text{SiCl}_3]^-$  adduct of  $\text{Si}_2\text{Cl}_6$ .<sup>55,62</sup>

The fact that the reaction of  $\text{CCl}_4$  with  $\text{Si}_2\text{Cl}_6/[n\text{Bu}_4\text{N}]\text{Cl}$  made three important organosilane building blocks readily available, prompted us to study next the synthetic potential of the higher homologue  $\text{C}_2\text{Cl}_4$ . Treatment of this compound with 1 eq of  $\text{Si}_2\text{Cl}_6$  and catalytic amounts of  $[n\text{Bu}_4\text{N}]\text{Cl}$  at room temperature in  $\text{CD}_2\text{Cl}_2$  led to clean dechlorination with formation of tetrachloroethene ( $\text{C}_2\text{Cl}_4$ ; see the SI for more details and Ref[37] for a related transformation).  $\text{C}_2\text{Cl}_4$  was therefore employed as starting material in all further reactions with  $\text{Si}_2\text{Cl}_6/[n\text{Bu}_4\text{N}]\text{Cl}$  (Scheme 4, bottom), which always furnished at least some  $[n\text{Bu}_4\text{N}]_2[\text{B}]$ , irrespective of the stoichiometric ratios employed. The optimized protocol for the synthesis of  $[n\text{Bu}_4\text{N}]_2[\text{B}]$  requires  $\text{Si}_2\text{Cl}_6$  (4 eq), which is added at –10 °C to a solution of  $[n\text{Bu}_4\text{N}]\text{Cl}$  (2 eq) and  $\text{C}_2\text{Cl}_4$  (1 eq) in  $\text{CH}_2\text{Cl}_2$ .<sup>70</sup> After warming to room temperature, colorless crystals of  $[n\text{Bu}_4\text{N}]_2[\text{B}]$  can be isolated from the deep blue reaction mixture in yields of 85%.

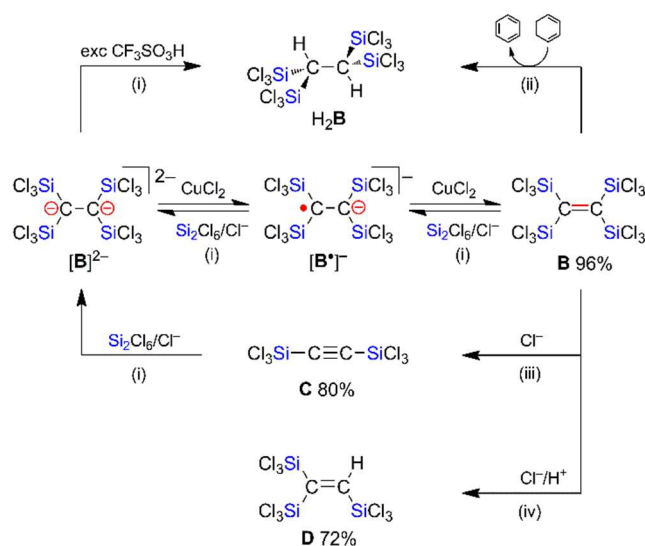
As first reactivity tests, we treated  $[n\text{Bu}_4\text{N}][\text{A}]$  and  $[n\text{Bu}_4\text{N}]_2[\text{B}]$  with anhydrous  $\text{MeOH}/\text{NMe}_2\text{Et}$  and obtained HAOMe<sup>64</sup> and  $\text{H}_2\text{BOMe}$  in yields of 59% and 88%, respectively. By the same token, protonation with  $\text{CF}_3\text{SO}_3\text{H}$  selectively furnished HA<sup>71</sup> and  $\text{H}_2\text{B}$ ,<sup>65</sup> respectively. Both protonation reactions can also be conducted with ethereal  $\text{HCl}$ , but care must be taken to avoid partial desilylation by nucleophilic attack of  $\text{Cl}^-$ . The monoprotonated species  $[n\text{Bu}_4\text{N}][\text{HB}]$  is accessible by adjusting the amount of acid employed or by simple mixing of  $[n\text{Bu}_4\text{N}]_2[\text{B}]$  and  $\text{H}_2\text{B}$  in equimolar quantities (Scheme 4, bottom).

Equimolar mixtures of  $[n\text{Bu}_4\text{N}]_2[\text{B}]$  and  $\text{B}$  undergo a disproportionation reaction to furnish the blue-colored monoradical  $[n\text{Bu}_4\text{N}][\text{B}^\bullet]$ . The two-electron oxidation of  $[n\text{Bu}_4\text{N}]_2[\text{B}]$  was carried out with 2 eq of  $\text{CuCl}_2$  under heterogeneous conditions and affords the tetrasilylene  $\text{B}$  in yields of 96% (Scheme 5).

The targeted cleavage of C–Si bonds by halide ions (mainly  $\text{F}^-$  and  $\text{Cl}^-$ ) is broadly exploited in organic synthesis, particularly in protecting group chemistry.<sup>4</sup> We now found that  $\text{B}$  formally eliminates  $\text{Si}_2\text{Cl}_6$  upon addition of  $[n\text{Bu}_4\text{N}]\text{Cl}$  (1 eq) to provide the bis(trichlorosilyl)ethyne  $\text{C}$  (Scheme 5). During workup,  $\text{C}$  (41%) was separated from the byproduct  $[n\text{Bu}_4\text{N}]_2[\text{B}]$  (43%) through extraction into *n*-pentane. Based on the observation that the byproduct  $[n\text{Bu}_4\text{N}]_2[\text{B}]$  can be recycled through *in situ* oxidation with  $\text{CuCl}_2$ , we developed an optimized one-pot protocol to prepare  $\text{C}$  from  $\text{Si}_2\text{Cl}_6$  (4 eq),  $[n\text{Bu}_4\text{N}]\text{Cl}$  (4 eq),  $\text{C}_2\text{Cl}_4$  (1 eq), and  $\text{CuCl}_2$  (4 eq) in a yield of 80%. The alkyne content of the *n*-pentane stock solution was determined by quenching an aliquot with  $\text{MeOH}$  and titration of the produced  $\text{HCl}$ . Even though fractional distillation of the extract affords  $\text{C}$  as a colorless oil, the effort is lowered and

yield losses are avoided, if the *n*-pentane extract is used directly for further transformations.

**Scheme 5: Transformations of  $[n\text{Bu}_4\text{N}]_2[\text{B}]$  to give  $\text{H}_2\text{B}$ ,  $[n\text{Bu}_4\text{N}][\text{B}^-]$ , **B**, or **C**.**



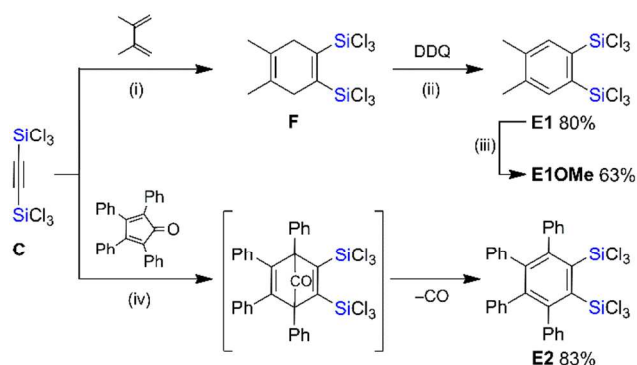
The cation  $[n\text{Bu}_4\text{N}]^+$  is omitted for clarity. (i)  $\text{CD}_2\text{Cl}_2$ , room temperature, 1 h; (ii)  $\text{C}_6\text{D}_6$ , 120–150 °C in a sealed NMR tube, 8 d; (iii) 2 eq  $\text{CuCl}_2$ ,  $\text{CH}_2\text{Cl}_2$ , room temperature, 1 h; (iv) 1 eq  $[\text{HMe}_3\text{N}]\text{Cl}$ , 10 mol%  $[n\text{Bu}_4\text{N}]\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ , room temperature, 3 d.

A mono-desilylation of **B** to afford the 1,1,2-tris(trichlorosilyl)ethene **D** (72%) is achievable at room temperature in  $\text{CH}_2\text{Cl}_2$  using  $[\text{HMe}_3\text{N}]\text{Cl}$  (1 eq) as a mild  $\text{H}^+$  source and a catalytic amount of  $[n\text{Bu}_4\text{N}]\text{Cl}$ .<sup>72</sup>

The unsaturated compounds **B–D** constitute highly promising reagents for the construction of oligosilylated organic scaffolds, but their limited availability has largely prevented such developments in the past. As two of very few examples, **C** can readily be permethylated and permethoxylated;<sup>68</sup> **D** enters into a stereo- and regioselective  $[2\sigma + 2\sigma + 2\pi]$ -cycloaddition with quadricyclane to give a corresponding norbornene derivative, which is a useful monomer for the synthesis of membrane polymers with high gas permeability.<sup>61</sup> It is important to note in this context that the reactivities of a number of silylated olefins increase in the order  $\text{Cl}_3\text{Si}(\text{H})\text{C}=\text{CH}_2 < \text{trans-Cl}_3\text{Si}(\text{H})\text{C}=\text{C}(\text{H})\text{SiCl}_3 < \text{D}$  and decrease once electron-withdrawing chlorine atoms are replaced by electron-donating methyl groups. Upon reaction with cyclopentadiene, **D** forms *exo*- and *endo*-norbornenes, albeit only in a dynamic equilibrium with the starting materials.<sup>61</sup> Alkyne **C** and cyclopentadiene provide 2,3-bis(trichlorosilyl)norbornadiene-2,5 in yields of 83%.<sup>73</sup> To push the synthetic utility of **C** to its limits, we considered the preparation of 1,2-bis(trichlorosilyl)benzenes for the following reasons: (a) Already 1,2-bis(trimethylsilyl)benzenes are not trivial to make, mainly due to steric congestion.<sup>35</sup> (b) The only

published synthesis of 1,2-bis(trichlorosilyl)benzene starts from 1,2-dichlorobenzene and  $\text{HSiCl}_3$  and requires irradiation of the reaction mixture with  $\gamma$  rays at temperatures of 300 °C.<sup>74</sup> An exploratory NMR experiment was conducted with **C** and an approximate twofold excess of 2,3-dimethyl-1,3-butadiene in  $\text{CD}_2\text{Cl}_2$ . After heating to 50 °C for 3 d in a flame-sealed tube, NMR spectroscopy and GC/MS confirmed the quantitative consumption of **C** and the concomitant formation of 1,2-bis(trichlorosilyl)-4,5-dimethylcyclohexa-1,4-diene **F** as the exclusive product (Scheme 6). Repeating the synthesis of **F** on a preparative scale with subsequent oxidation using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature resulted in the quantitative conversion to the 1,2-disilylbenzene derivative **E1** (80% yield with respect to **C**; for more information see the SI). In this way we achieved the synthesis of **E1** in an overall yield of 52%.<sup>75</sup> Treatment of 1,2-disilylbenzene **E1** with 6 eq of MeOH in the presence of  $\text{NMe}_2\text{Et}$  resulted in the formation of the permethoxylated derivative **E1OMe** (62% yield). To examine the scope of the Diels-Alder reactions of **C**, also 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one was used as diene: Heating a  $\text{CH}_2\text{Cl}_2$  solution of both compounds at 180 °C for 4 d in a sealed glass ampoule furnished **E2** as the only reaction product (83% yield; Scheme 6). NMR spectroscopic monitoring of the reaction progress showed no resonances assignable to a cyclohexadiene intermediate. Thus, the electrocyclic reaction between **C** and the ketone appears to be rate limiting, while CO liberation with formation of the aromatic system occurs instantaneously under the conditions applied. Importantly, unwanted desilylation reactions are not an issue, in spite of the high temperatures required for the cycloaddition reactions and the pronounced steric repulsion between the two  $\text{SiCl}_3$  substituents in **E1** and **E2**.

**Scheme 6. Synthesis of cyclohexa-1,4-diene **F** from **C** and 2,3-dimethyl-1,3-butadiene; subsequent oxidation of **F** with DDQ to furnish the benzene derivative **E1**. Synthesis of the benzene derivative **E2** from **C** and 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one.**



(i)  $\text{CH}_2\text{Cl}_2$ , 50 °C, 3 d, sealed glass ampoule; (ii)  $\text{CH}_2\text{Cl}_2$ , room temperature, 12 h; (iii)  $\text{CH}_2\text{Cl}_2$ , MeOH/ $\text{NMe}_2\text{Et}$  (6 eq), 0 °C to room temperature, 1 h; (iv)  $\text{CH}_2\text{Cl}_2$ , 180 °C, 4 d, sealed glass ampoule

### Characterization of the New Organotrichlorosilanes.

*NMR Spectroscopy.* Plots of the  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{29}\text{Si}$  NMR spectra of all organosilanes covered in this publication, together with a discussion of key NMR features, are provided in the SI. Whenever literature data are available, our results are in full agreement with the previously reported chemical shift values.

*X-ray Crystallography and Corresponding Quantum-Chemical Calculations.* Crystals of  $[\text{nBu}_4\text{N}][\text{A}]$  and  $[\text{nBu}_4\text{N}]_2[\text{B}]$  suitable for X-ray analysis were grown from  $\text{CH}_2\text{Cl}_2$  (Figure 3a,b).<sup>76</sup> The monoanion  $[\text{A}]^-$  possesses a  $C_3$  axis,  $[\text{B}]^{2-}$  has no symmetry element. Both compounds contain essentially planar carbanion centers (bond-angle sums =  $358.5^\circ$ - $359.9^\circ$ ). The two halves of  $[\text{B}]^{2-}$  are mutually orthogonal, thereby minimizing the electrostatic repulsion between the vicinal, carbon-based lone-pair electrons (dihedral angle  $\text{Si}(1)\text{C}(1)\text{Si}(2)//\text{Si}(3)\text{C}(2)\text{Si}(4)$  =  $85.85(6)^\circ$ ). Nevertheless, the  $\text{C}(1)\text{--C}(2)$  bond is elongated from 1.47 Å, the expected value for a single bond between  $\text{sp}^2$ -hybridized carbon atoms,<sup>77</sup> to 1.532(5) Å, a value typically observed for single bonds between  $\text{sp}^3$ -hybridized carbon atoms. The  $\text{C--Si}$  bond length of  $[\text{A}]^-$  amounts to 1.768(1) Å and the corresponding bonds of  $[\text{B}]^{2-}$  are even slightly shorter (1.744(4) Å - 1.764(4) Å).

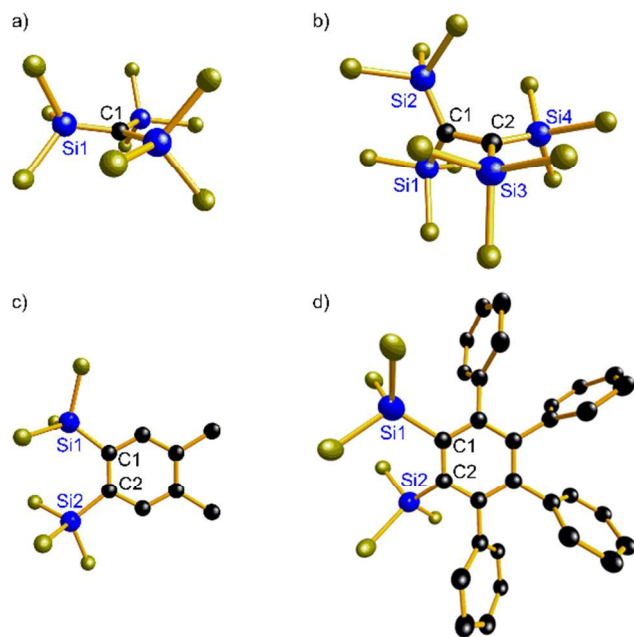


Figure 3. Molecular structures of (a)  $[\text{nBu}_4\text{N}][\text{A}]$ , (b)  $[\text{nBu}_4\text{N}]_2[\text{B}]$ , (c) **E1**, and (d) **E2** in the solid state;  $[\text{nBu}_4\text{N}]^+$  ions and H atoms omitted for clarity.

In comparison, the neutral olefin **B** features  $\text{C--Si}$  bond lengths in the range 1.910(3) Å - 1.917(3) Å.<sup>78</sup> The significantly smaller values found for  $[\text{A}]^-$  and  $[\text{B}]^{2-}$  are partly due to Coulomb attraction between the anionic carbon atoms and the positively polarized Si atoms, but also symptomatic of partial  $\text{C=Si}$  double-bond character as a result of  $\pi$  donation from the carbanion lone pairs into energetically low-lying substituent group orbitals (cf. the  $\alpha$  effect; a structural comparison of  $[\text{B}]^{2-}$  with its  $\text{SiMe}_3$ -substituted congener is provided in the SI).<sup>79</sup>

Further insight into the electronic structures of  $[\text{B}]^{2-}$  and **B** was gained from quantum-chemical calculations. First, we note a pleasingly good agreement between the computed and crystallographically determined geometric parameters of both compounds (Table 1).

**Table 1.** Selected structural parameters of compounds **B**,  $[\text{B}]^+$ , and  $[\text{B}]^{2-}$ . The final calculated geometries were obtained at the PBE0-D3(BJ)(CPCM( $\text{CH}_2\text{Cl}_2$ ))/ma-def2-TZVP level of theory.<sup>80-85</sup>

com- pound	C(1)–C(2) [Å]		C–Si (av) [Å]		Si(1)C(1)Si(2)//Si(3) C(2)Si(4) [°]	
	X-ray	calcd	X-ray	calcd	X-ray	calcd
<b>B</b>	1.368(4)	1.355	1.914	1.905	28.1(2)	27.8
$[\text{B}]^+$	-/-	1.438	-/-	1.824	-/-	44.9
$[\text{B}]^{2-}$	1.532(5)	1.502	1.753	1.757	85.85(6)	83.4

Natural Bonding Orbital (NBO)<sup>86</sup> analyses and Wiberg bond indices (WBI)<sup>87</sup> reveal a well-defined  $\text{C=C}$  double bond for **B** (WBI = 1.90) and a  $\text{C--C}$  single bond for  $[\text{B}]^{2-}$  (WBI = 1.00) with two equally occupied ( $\text{occ} = 1.61$ ) p-type electron lone pairs located at the carbon atoms. The lowered occupation of the lone pairs of  $[\text{B}]^{2-}$ , a reduced p character of the hybrid orbital at silicon (Si:  $\text{sp}^{1.45}$ , C:  $\text{sp}^{2.13}$ ), and the Natural Population Analysis (NPA)<sup>86</sup> charges ( $12 \times \text{Cl} = -4.77 \text{ e}$ ,  $4 \times \text{Si} = +5.80 \text{ e}$ ,  $2 \times \text{C} = -3.02 \text{ e}$ ) indicate efficient delocalization of electron density toward the  $\text{SiCl}_3$  groups via  $\text{C--Si}$   $\pi$  interactions (cf. the  $\alpha$  effect; Figure 1). This charge delocalization likely contributes to the stability of  $[\text{nBu}_4\text{N}]_2[\text{B}]$ , which shows no tendency for polymerization despite the presence of formally nucleophilic carbanions and electrophilic  $\text{SiCl}_3$  moieties in the same molecule (similar arguments hold for  $[\text{nBu}_4\text{N}][\text{A}]$ ).

For E-type compounds, two possibilities exist to reduce unfavorable interactions between the adjacent  $\text{SiCl}_3$  groups: The molecule could widen the bond angles  $\text{Si}(1)\text{--C}(1)\text{--C}(2)$  and  $\text{Si}(2)\text{--C}(2)\text{--C}(1)$  and/or bend both substituents in opposite directions out of the benzene plane. In the solid-state structure of **E1** (Figure 3c), the  $\text{Si--C--C}$  bond angles are expanded to  $127.6(1)^\circ$  and  $128.5(1)^\circ$ , while the  $\text{Si}(1)\text{--C}(1)\text{--C}(2)\text{--Si}(2)$  torsion remains negligible ( $-1.1(2)^\circ$ ). Bond-angle expansion is not an option for **E2** (Figure 3d), because the  $\text{SiCl}_3$  groups would inevitably collide with the *ortho*-phenyl rings. Thus,  $\text{Si}(1)\text{--C}(1)\text{--C}(2) = 121.5(1)^\circ$  and  $\text{Si}(2)\text{--C}(2)\text{--C}(1) = 122.7(1)^\circ$  are still close to  $120^\circ$ , while the  $\text{Si--C--Si}$  torsion angle assumes an appreciable value of  $46.6(2)^\circ$ . Similar features as in the cases of **E1** and **E2** are evident in the solid-state structures of 1,2-bis(trimethylsilyl)-4,5-dichlorobenzene<sup>35</sup> and hexakis(trimethylsilyl)benzene<sup>88</sup>, respectively (cf. the SI for more details).

*Redox Properties of B and Corresponding Quantum-Chemical Calculations.* Our syntheses of the radical species  $[\text{nBu}_4\text{N}][\text{B}^{\cdot-}]$  and the dianion salt  $[\text{nBu}_4\text{N}]_2[\text{B}]$  prove that **B** is capable of accepting not only one but even two electrons



without decomposition. Accordingly, the cyclic voltammogram (CV) of **B** in CH<sub>2</sub>Cl<sub>2</sub> with [nBu<sub>4</sub>N][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as supporting electrolyte revealed two reversible redox transitions at half wave potentials of  $E_{1/2} = -0.73$  V and  $-0.98$  V (vs. FcH/FcH<sup>+</sup>).<sup>89</sup> We finally note that **B** is not inert toward [nBu<sub>4</sub>N][PF<sub>6</sub>] in THF or CH<sub>2</sub>Cl<sub>2</sub>, but rather abstracts F<sup>-</sup> ions from the commonly used supporting electrolyte, which underscores a strong Lewis acidity of the alkene (cf. the SI for more details).

The neutral compound **B** and its doubly reduced form [nBu<sub>4</sub>N]<sub>2</sub>[**B**] are colorless in solution and the solid state. Solutions of the monoradical [nBu<sub>4</sub>N][**B**<sup>•-</sup>] in CH<sub>2</sub>Cl<sub>2</sub> show a deep blue color and a concomitant broad absorption band in the UV/vis spectrum ( $\lambda_{\max} = 650$  nm). For comparison, the methylated monoanion radical [(Me<sub>3</sub>Si)<sub>2</sub>C=C(SiMe<sub>3</sub>)<sub>2</sub>]<sup>-•</sup> gives a dark green solution (THF;  $\lambda_{\max} = 697$  nm).<sup>90</sup>

The colors of the chlorinated vs. methylated species likely depend on electronic substituent effects and/or the torsion about the central C–C bond. To evaluate the relative weights of both influence factors, we performed quantum-chemical calculations on the neutral olefins **B** and (Me<sub>3</sub>Si)<sub>2</sub>C=C(SiMe<sub>3</sub>)<sub>2</sub>, because here, contrary to the cases of the corresponding reduced forms, ion pairing does not have to be taken into account as a third important parameter. We come to the conclusions that twisting of the molecular scaffolds influences the absorption bands of **B** and (Me<sub>3</sub>Si)<sub>2</sub>C=C(SiMe<sub>3</sub>)<sub>2</sub> to similar extents such that the difference between their calculated  $\lambda_{\max}^c$  values is largely independent of the C–C-torsion angle. At any given torsion angle, differences in the absorption maxima of both olefins result from electronic substituent effects, such as the different  $\pi$ -acceptor strengths of SiCl<sub>3</sub> and SiMe<sub>3</sub> groups (cf. the SI for more information).

With a C–C bond length of 1.438 Å and a dihedral angle of 44.9°, the calculated key structural parameters of the monoradical anion [**B**<sup>•-</sup>] are intermediate between those of **B** and [**B**]<sup>2-</sup> (Table 1). The progressively more pronounced twist helps to avoid an unfavorable orbital overlap in the course of the step-wise population of the anti-bonding  $\pi^*$  molecular orbital (LUMO) of **B** (Figure 4).

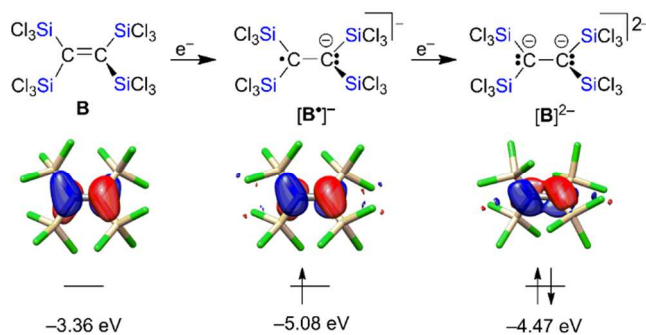


Figure 4. Selected Kohn-Sham molecular orbitals and their energy eigenvalues [eV] of compounds **B**, [**B**<sup>•-</sup>] and [**B**]<sup>2-</sup> at the PBE0-D3(BJ)(CPCM(CH<sub>2</sub>Cl<sub>2</sub>))/ma-def2-TZVP level of theory. Isosurface value = 0.05 e-bohr<sup>-3</sup>.

TD-DFT calculations show that the intense blue color of [**B**<sup>•-</sup>] in solution arises from a  $\pi \rightarrow \pi^*$  transition into the singly occupied molecular orbital of [**B**<sup>•-</sup>].

EPR spectra were recorded at room temperature on solutions of [nBu<sub>4</sub>N][**B**<sup>•-</sup>] in CH<sub>2</sub>Cl<sub>2</sub> (0.75 mM). The radical gives rise to a multi-line signal with partly overlapping <sup>35/37</sup>Cl couplings and obscured <sup>29</sup>Si coupling. A simulation of the experimentally obtained spectrum with hyperfine coupling constants of  $a(^{29}\text{Si}) = 4.4$  G and  $a(^{35}\text{Cl}) = 1.27$  G gave an excellent match (Figure 5). Moreover, the values obtained are in good agreement with calculated coupling constants obtained at the B3LYP(CPCM(CH<sub>2</sub>Cl<sub>2</sub>))/IGLO-III//PBE0-D3(BJ)(CPCM(CH<sub>2</sub>Cl<sub>2</sub>))/ma-def2-TZVP<sup>86,91</sup> level of theory ( $a(^{29}\text{Si}) = -3.3$  G and  $a(^{35}\text{Cl}) = 1.29$  G; cf. the SI for more information). For comparison, the SiMe<sub>3</sub>-substituted radical [(Me<sub>3</sub>Si)<sub>2</sub>C=C(SiMe<sub>3</sub>)<sub>2</sub>]<sup>-•</sup> is characterized by an  $a(^{29}\text{Si})$  value of 4.65 G.<sup>92</sup> The significant spin density  $\rho_s$  on each Si atom of [nBu<sub>4</sub>N][**B**<sup>•-</sup>] ( $\rho_s(\text{Si}) = 8\%$ ,  $\rho_{s,\text{tot}}(4\text{Si}) = 32\%$ ;  $\rho_s(\text{C}) = 30\%$ ,  $\rho_{s,\text{tot}}(2\text{C}) = 60\%$ ) indicates a delocalization of the odd electron over all four C–Si bonds. The  $a(^{29}\text{Si})$  value thus seems to be governed mainly by electronic substituent effects, which influence the C–Si bonding interactions.<sup>93</sup>

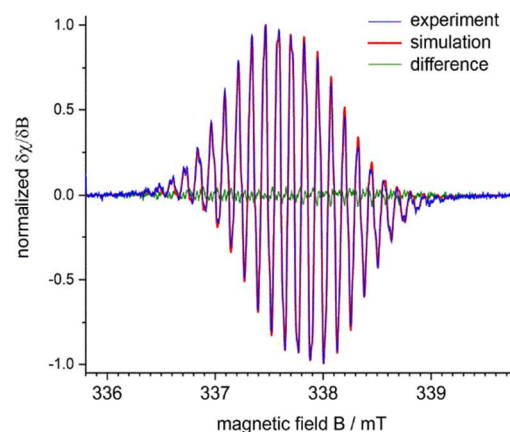


Figure 5. Optimized EPR spectrum of [nBu<sub>4</sub>N][**B**<sup>•-</sup>] (blue; 0.75 mM in CH<sub>2</sub>Cl<sub>2</sub>, room temperature); fit results: g value = 2.0026,  $a(^{29}\text{Si}) = 4.4$  G and  $a(^{35}\text{Cl}) = 1.27$  G, line width(G) = 0.118 G and line width(L) = 0.188 G.

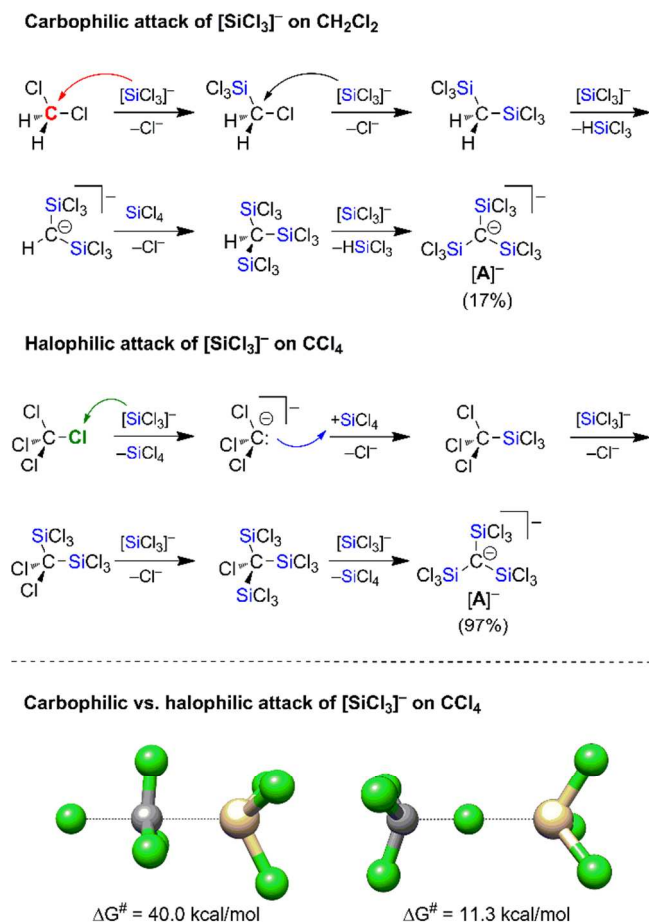
## Mechanistic Considerations.

Our mechanistic proposals are based on the view that the chloride-induced disproportionation of Si<sub>2</sub>Cl<sub>6</sub> generates [SiCl<sub>3</sub>]<sup>-</sup> ions as the primary reactive species (Scheme 1). The [SiCl<sub>3</sub>]<sup>-</sup> intermediate can principally react further in three different ways: (1) A redox reaction may occur during which a single electron is transferred from the anion to the organic substrate R–Cl. (2) [SiCl<sub>3</sub>]<sup>-</sup> may dissociate to liberate [SiCl<sub>2</sub>], which can subsequently insert into the R–Cl bond. (3) If [SiCl<sub>3</sub>]<sup>-</sup> reacts as a nucleophile, it could attack either at the carbon atoms or at the chlorine atoms with concomitant formation of SiCl<sub>4</sub> and [R]<sup>-</sup>. The carbanion would subsequently

have to bite back into  $\text{SiCl}_4$  (or  $\text{Si}_2\text{Cl}_6$ ) to establish a C– $\text{SiCl}_3$  bond.<sup>46</sup>

**Reaction of  $[\text{SiCl}_3]^-$  with  $\text{CCl}_4$ .** With regard to the reaction of  $\text{Si}_2\text{Cl}_6/[\text{nBu}_4\text{N}]\text{Cl}$  with  $\text{CH}_2\text{Cl}_2$ , Kroke et al. suggested a sequential nucleophilic substitution reaction at the carbon atom (but did not exclude the possibility of a dichlorosilylene pathway). The resulting  $\text{H}_2\text{C}(\text{SiCl}_3)_2$  undergoes *in situ* deprotonation by a third molecule of  $[\text{SiCl}_3]^-$  to furnish  $[\text{HC}(\text{SiCl}_3)_2]^-$ . This ionic intermediate subsequently attacks  $\text{SiCl}_4$  (or residual  $\text{Si}_2\text{Cl}_6$ ) and forms  $\text{HC}(\text{SiCl}_3)_3$ . A second deprotonation step finally produces  $[\text{nBu}_4\text{N}][\text{A}]$  (Scheme 7 top).<sup>63</sup> The reaction of  $\text{Si}_2\text{Cl}_6/[\text{nBu}_4\text{N}]\text{Cl}$  with  $\text{CCl}_4$  in  $\text{CH}_2\text{Cl}_2$  proceeds so fast that the detection of intermediates by *in situ* NMR monitoring becomes impossible. The conversion is also highly selective, and we did not observe any side products (only the byproduct  $\text{SiCl}_4$ ) that could shed light on mechanistic details.

**Scheme 7. Proposed reaction mechanisms for the formation of  $[\text{nBu}_4\text{N}][\text{A}]$  from  $[\text{SiCl}_3]^-$  and  $\text{CH}_2\text{Cl}_2$  (Ref[63]) or  $\text{CCl}_4$  (this work, top). Comparison of the transition states of the carbophilic vs. halophilic attack of  $[\text{SiCl}_3]^-$  on  $\text{CCl}_4$  (bottom).**



Cation =  $[\text{nBu}_4\text{N}]^+$  omitted for clarity. Calculated transition states for the carbophilic (left) and halophilic (right) attack of  $[\text{SiCl}_3]^-$  on  $\text{CCl}_4$  at the B2-PLYP-D3(BJ,ATM)+COSMO-

$\text{RS}(\text{CH}_2\text{Cl}_2)/\text{def2-QZVP//PBE0-D3(BJ)}(\text{COSMO}(\text{CH}_2\text{Cl}_2))/\text{def2-TZVPD}$  level of theory.<sup>81–84,94–98</sup>

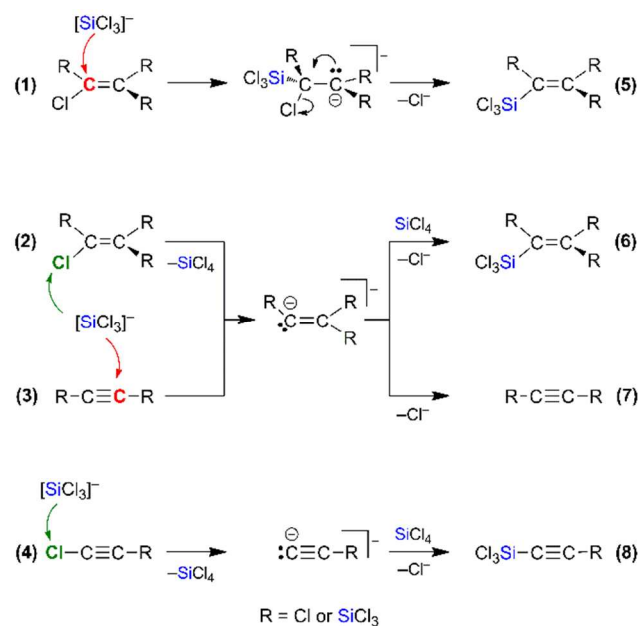
Yet, for the following reasons our current working hypothesis assumes an initial nucleophilic attack of  $[\text{SiCl}_3]^-$  on one of the Cl atoms of  $\text{CCl}_4$ , followed by a rebound reaction of the thus generated  $[\text{CCl}_3]^-$  ion:<sup>46,99,100</sup> (1) The carbon center of  $\text{CCl}_4$  is sterically more shielded than that of  $\text{CH}_2\text{Cl}_2$ . (2)  $[\text{CCl}_3]^-$  ions are good leaving groups compared to corresponding  $[\text{H}_2\text{CCl}]^-$  ions, as evidenced by the haloform reaction<sup>101</sup> and the fact that  $\text{Me}_3\text{SiCCl}_3$  is readily desilylated with  $[\text{nBu}_4\text{N}]\text{F}$ , whereas  $\text{Me}_3\text{SiCH}_2\text{Cl}$  is not.<sup>102</sup> (3) Within the series of chloromethanes  $\text{CCl}_n\text{H}_{4-n}$  ( $n = 1-4$ ), the NBO charges at the Cl atoms continuously become less negative as  $n$  increases; for  $n > 2$  the Cl sites are even positivated.<sup>103</sup>  $\text{CCl}_4$  was recognized as a typical halogen-bond donor due to positive surface potentials of up to  $17 \text{ kcal mol}^{-1}$  at the end regions of the Cl atoms ( $\sigma$ -holes).<sup>104,105</sup> (4) In neat  $\text{CCl}_4$ , the  $\text{Si}_2\text{Cl}_6/[\text{nBu}_4\text{N}]\text{Cl}$  system forms the  $[\text{CCl}_3]^-$  adduct  $[\text{nBu}_4\text{N}][\text{Cl}_3\text{C}-\text{SiCl}_3-\text{CCl}_3]$  (see above). (5) Phosphines are isoelectronic to the  $[\text{SiCl}_3]^-$  ion and nucleophilic displacement on halogen atoms of halocarbons is a central concept of phosphine chemistry (cf. the Appel and Corey-Fuchs reactions).<sup>45,106,107</sup> Moreover, our group recently succeeded in the activation of  $\text{CX}_4$  ( $X = \text{Cl}, \text{Br}$ ) by the geminal frustrated Lewis pair  $(\text{Fxy})_2\text{B}-\text{CH}_2-\text{PtBu}_2$  to furnish  $(\text{Fxy})_2\text{B}(\text{CX}_3)-\text{CH}_2-\text{P}(\text{X})\text{tBu}_2$  ( $\text{Fxy} = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3$ ).<sup>108</sup> To further substantiate our working hypothesis, we calculated the transition states of the carbophilic ( $\Delta G^\ddagger = 40.0 \text{ kcal/mol}$ ) vs. halophilic ( $\Delta G^\ddagger = 11.3 \text{ kcal/mol}$ ) attack of  $[\text{SiCl}_3]^-$  on  $\text{CCl}_4$  and found the latter to be energetically favorable by  $28.7 \text{ kcal/mol}$  (cf. Scheme 7, bottom).

In contrast to the mechanism that is likely operative in the formation of  $[\text{nBu}_4\text{N}][\text{A}]$  from  $\text{Si}_2\text{Cl}_6/[\text{nBu}_4\text{N}]\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$ , we thus propose the following scenario for  $\text{CCl}_4$  as the carbon source (Scheme 7, top):  $[\text{SiCl}_3]^-$  abstracts a  $\text{Cl}^+$  cation from  $\text{CCl}_4$  to form  $\text{SiCl}_4$  and  $[\text{CCl}_3]^-$ , which then react further to furnish  $\text{Cl}_3\text{C}-\text{SiCl}_3$  and  $\text{Cl}^-$  (nucleophilic attack of  $[\text{CCl}_3]^-$  on residual  $\text{Si}_2\text{Cl}_6$  would provide the same product, together with  $[\text{SiCl}_3]^-$ ). If this sequence is repeated twice, we obtain the trisilylmethane  $\text{ClC}(\text{SiCl}_3)_3$ , which, upon losing a last  $\text{Cl}^+$  cation to  $[\text{SiCl}_3]^-$ , is transformed to  $[\text{A}]^-$ . In line with the required stoichiometry, all steps are catalytic in  $[\text{nBu}_4\text{N}]\text{Cl}$ , apart from the final one, which consumes one equivalent of  $\text{Cl}^-$ .<sup>70</sup> The carbon centers of the neutral intermediates become sterically less and less accessible as the reaction proceeds, while the charge of the carbanionic intermediates becomes more and more delocalized due to the  $\alpha$  effects of an increasing number of  $\text{SiCl}_3$  substituents (Figure 1). Even with some excess of  $\text{CCl}_4$ , we never observed partially silylated chloromethanes and therefore conclude that the first Cl-atom substitution is rate determining. For steric reasons, also this observation points toward  $[\text{SiCl}_3]^-$  attack on Cl and not the central C atom.

All four involved reaction steps are mechanistically related to each other, which renders the proposed scenario simple and conceptually appealing. Nevertheless, the involvement of  $[\text{SiCl}_2]$  cannot be excluded, but the non-donor solvent ( $\text{CH}_2\text{Cl}_2$ ) and the non-coordinating  $[\text{nBu}_4\text{N}]^+$  counter ion employed are not expected to promote  $[\text{SiCl}_3]^-$  dissociation. By the same token, the putative intermediate  $[\text{nBu}_4\text{N}][\text{CCl}_3]$  should have a longer lifetime than alkali metal carbenoids

$M[CCl_3]$  ( $M^+$  = alkali metal cation), because the thermodynamic driving force for  $MCl$  elimination with concomitant  $[CCl_2]$  formation is lacking.<sup>102,109,110</sup> We therefore consider not only  $[SiCl_3]^-$  but also  $[CCl_2]$ -based pathways less likely than the alternative ionic mechanisms. In view of the proven sensitivity of  $Cl_3C-SiCl_3$  toward  $Cl^-$  ions (Scheme 4), we finally note that five-coordinate anions such as  $[Cl_3C-SiCl_4]^-$  and  $[Cl_3C-Cl_3Si-CCl_3]^-$  not only occur as transient intermediates, but can also serve as  $[CCl_3]^-$ -transfer reagents (cf. Scheme 4).

**Scheme 8: Conceivable elementary reactions underlying the formation of  $[nBu_4N]_2[B]$ .**



Note: In the cases of paths (2)→(7) and (3)→(7), at least one of the substituents R in the starting material and the vinyl-anion intermediate must be Cl; in the cases of paths (3)→(6) and (3)→(7), at least one of the substituents R in the vinyl-anion intermediate and the products must be  $SiCl_3$ . Residual  $Si_2Cl_6$  should be capable of taking the role of  $SiCl_4$  as a source of  $SiCl_3$  substituents by releasing  $[SiCl_3]^-$  in place of  $Cl^-$ ; the overall balance would remain the same. Cations =  $[nBu_4N]^+$  omitted for clarity.

**Reactions of  $[SiCl_3]^-$  with  $C_2Cl_6$  and  $C_2Cl_4$ .** As mentioned above, treatment of  $C_2Cl_6$  with 1 eq of  $Si_2Cl_6$  and catalytic amounts of  $[nBu_4N]Cl$  quantitatively generates tetrachloroethene,  $C_2Cl_4$ . For similar reasons as outlined above,  $C_2Cl_6$ , the higher homologue of  $CCl_4$ , likely reacts with  $[SiCl_3]^-$  through initial  $Cl^-$ -cation abstraction. The resulting  $[C_2Cl_5]^-$  anion eliminates  $Cl^-$  to furnish  $C_2Cl_4$ .<sup>37</sup> We have also confirmed that the synthesis of  $[nBu_4N]_2[B]$  can equally well (and more cost-efficiently) be performed using  $Si_2Cl_6/[nBu_4N]Cl$  and  $C_2Cl_4$

rather than  $C_2Cl_6$ . Any further considerations will thus be focused on  $C_2Cl_4$  as starting material.

It is possible to construct reasonable mechanistic scenarios by combining the limited set of substance classes and elementary reactions outlined in Scheme 8.

**Addition-elimination, (1)→(5):** Carbophilic attack of  $[SiCl_3]^-$  on chloroethenes will produce alkyl anions,<sup>111</sup> which eliminate  $Cl^-$  to generate (trichlorosilyl)ethenes. A corresponding sequence has been postulated for the stereospecific reaction of  $C_2Cl_4$  with sodium *p*-toluenethiolate (NaSTol), resulting in the formation of  $TolS(Cl)C=CCl_2$  and ultimately *trans*- $TolS(Cl)C=C(Cl)STol$ .<sup>112</sup>

**Elimination-addition, (2)→(6), or elimination-elimination, (2)→(7):** Halophilic attack of  $[SiCl_3]^-$  on chloroethenes will produce vinyl anions, which can bite back into  $SiCl_4$  to generate (trichlorosilyl)ethenes. Provided that the vinyl anion bears at least one chlorine substituent, an alternative sequence leads to alkynes *via* release of  $Cl^-$ .<sup>113</sup> Cl atoms in *trans*- $\beta$  (highest rates), *cis*- $\beta$ , or even  $\alpha$  positions to the electron lone pair are suitable leaving groups.<sup>114-116</sup> Reaction scenarios related to (2)→(6) and (2)→(7) have been investigated in detail using  $Li(Cl)C=CCl_2$  as the example. At  $-110^\circ C$ , the half-life time of the compound is  $t_{1/2} = 70-80$  min.<sup>115</sup> In our case,  $Cl^-$  elimination from  $[nBu_4N][(Cl)C=CCl_2]$  should require longer times, similar to the example of  $[nBu_4N][CCl_3]$  vs.  $M[CCl_3]$  discussed above.<sup>102,117,118</sup>

**Addition-addition, (3)→(6), or addition-elimination, (3)→(7):** Carbophilic attack of  $[SiCl_3]^-$  on alkynes formed *via* path (2)→(7) will again generate intermediate vinyl anions, which can undergo the same follow-up reactions as discussed above. Comparable reactions have been described in the context of frustrated Lewis-pair chemistry. As an example,  $PPh_3$  and  $B(C_6F_5)_3$  add to  $PhC\equiv CH$  to afford the zwitterionic species  $Ph(PPh_3)C=C(H)B(C_6F_5)_3$ .<sup>119</sup>  $[SiCl_3]^-$  should be a stronger nucleophile than  $PPh_3$  and the Lewis acidic  $SiCl_4$  may take the role of  $B(C_6F_5)_3$  in  $C\equiv C$  triple-bond activation.

**Elimination-addition, (4)→(8):** Similar to the cases of chloroethenes,  $[SiCl_3]^-$  can accept  $Cl^+$  cations from chloroethynes to generate acetylides, which will re-attack  $SiCl_4$  to afford (trichlorosilyl)ethynes. As a related example, disilylethynes are readily available upon treatment of  $R_3SiCl$  with a mixture of trichloroethene and *n*-BuLi (3 eq) in THF at  $-78^\circ C$ .<sup>120-122</sup> The reaction proceeds *via* LiCl elimination with intermediate formation of dichloroethyne, which undergoes Cl/Li-exchange to form dilithioacetylide.<sup>123</sup>

One should note that all these elementary steps are competing with each other and that their relative importance can change as the reaction proceeds and the nature of the substituents R changes (i.e. Cl vs.  $SiCl_3$ ). For example, an alkyl-anion intermediate (cf. (1)→(5)) will become increasingly more stable as Cl atoms are replaced by  $SiCl_3$  groups ( $\alpha$  effect; Figure 1). The following insights provided by the literature and by our own control experiments are helpful to arrive at a more focused picture:

a) The dianion salt  $[nBu_4N]_2[B]$  also forms cleanly if the  $Cl^-$ -induced disproportionation of  $Si_2Cl_6$  is carried out in  $C_2Cl_4$  as the solvent (containing a small volume of  $CH_2Cl_2$  to dissolve  $[nBu_4N]Cl$ ). This indicates that the first step of the reaction cascade is rate determining.



b) The phosphorus congener of  $[\text{SiCl}_3]^-$ ,  $\text{Li}[\text{PPh}_2]$ , and  $\text{C}_2\text{Cl}_4$  furnish the tetrasubstituted ethene  $(\text{Ph}_2\text{P})_2\text{C}=\text{C}(\text{PPh}_2)_2$  at  $-78^\circ\text{C}$ , whereas under ambient conditions the ethyne  $\text{Ph}_2\text{P}=\text{C}\equiv\text{C}\text{PPh}_2$  is obtained.<sup>124</sup> It has been suggested that initial substitution leads to the intermediate  $\text{Cl}_2\text{C}=\text{C}(\text{Cl})\text{PPh}_2$ , which upon warming in the presence of excess  $\text{Li}[\text{PPh}_2]$  provides  $\text{Ph}_2\text{P}=\text{C}\equiv\text{C}\text{PPh}_2$ ,  $\text{LiCl}$ , and  $\text{ClPPh}_2$  (product of a halophilic attack).

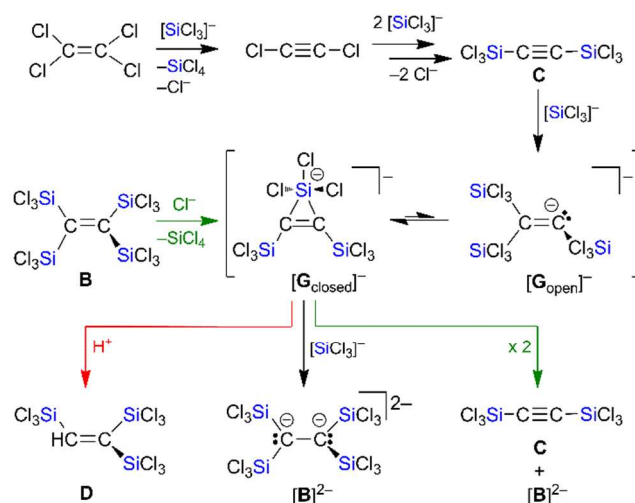
c) The elementary reactions compiled in Scheme 8 lead either to (trichlorosilyl)ethenes or -ethynes. We therefore selected *trans*- $\text{Cl}_3\text{Si}(\text{Cl})\text{C}=\text{C}(\text{Cl})\text{SiCl}_3$ ,<sup>69</sup> and  $\text{Cl}_3\text{SiC}\equiv\text{CSiCl}_3$  as archetypal members of both compound classes and treated them with  $\text{Si}_2\text{Cl}_6/\text{Cl}^-$  (3 eq;  $\text{CD}_2\text{Cl}_2$ ). In both cases, we obtained  $[\text{nBu}_4\text{N}]_2[\mathbf{B}]$  as the major product. In this respect, the overall behavior is similar to that of the  $\text{Cl}_2\text{C}=\text{CCl}_2/\text{Si}_2\text{Cl}_6/\text{Cl}^-$  mixture. However, the reaction of *trans*- $\text{Cl}_3\text{Si}(\text{Cl})\text{C}=\text{C}(\text{Cl})\text{SiCl}_3$  is significantly slower than the reactions of  $\text{Cl}_3\text{SiC}\equiv\text{CSiCl}_3$  or  $\text{Cl}_2\text{C}=\text{CCl}_2$  (cf. the SI for more information). Only in the case of *trans*- $\text{Cl}_3\text{Si}(\text{Cl})\text{C}=\text{C}(\text{Cl})\text{SiCl}_3$ , the  $^{29}\text{Si}$  NMR-spectroscopic monitoring of the reaction mixture revealed significant amounts of cyclohexasilane-chloride diadducts, such as  $[1,1-(\text{Cl}_3\text{Si})_2\text{Si}_6\text{Cl}_{10}\cdot 2\text{Cl}]^{2-}$  (cf. Scheme 2). These species are common products of the  $\text{Si}_2\text{Cl}_6/\text{Cl}^-$  system if other reaction partners are absent, which underlines the reluctance of *trans*- $\text{Cl}_3\text{Si}(\text{Cl})\text{C}=\text{C}(\text{Cl})\text{SiCl}_3$  to take part in further transformations under the conditions applied. Moreover, small quantities of  $\text{Cl}_3\text{SiC}\equiv\text{CSiCl}_3$  were detectable in the same sample, thereby indicating that *trans*- $\text{Cl}_3\text{Si}(\text{Cl})\text{C}=\text{C}(\text{Cl})\text{SiCl}_3$  is slowly dechlorinated to  $\text{Cl}_3\text{SiC}\equiv\text{CSiCl}_3$  and that the observed formation of  $[\text{nBu}_4\text{N}]_2[\mathbf{B}]$  may ultimately start from the formed ethyne.

Based on these observations, *trans*- $\text{Cl}_3\text{Si}(\text{Cl})\text{C}=\text{C}(\text{Cl})\text{SiCl}_3$  cannot be excluded as a reaction intermediate, but the major pathways likely proceed *via* ethyne species. It is important to note in this context that the reactivity of  $\text{ClC}\equiv\text{CCl}$  toward  $\text{Si}_2\text{Cl}_6/\text{Cl}^-$  is not directly assessable, because this highly unstable ethyne can only be handled in ethereal solvents, which are not compatible with  $\text{Si}_2\text{Cl}_6$ .<sup>113</sup>

Before this background, we can combine the limited set of substrate classes and elementary reactions outlined in Scheme 8<sup>111</sup> and arrive at a plausible mechanistic scenario, which straightforwardly accounts for all the reactions and  $\text{C}_2$ -products discussed so far (Scheme 9): The rate-determining first step likely involves a halophilic attack of  $[\text{SiCl}_3]^-$  on  $\text{C}_2\text{Cl}_4$ , followed by  $\text{Cl}^-$  elimination to give small local concentrations of  $\text{ClC}\equiv\text{CCl}$  (cf. path (2) $\rightarrow$ (7) in Scheme 8). The highly reactive alkyne is immediately transformed further to afford the more stable disilylalkyne  $\text{Cl}_3\text{SiC}\equiv\text{CSiCl}_3$  (*via* path (3) $\rightarrow$ (7) and/or (4) $\rightarrow$ (8)). A carbophilic attack of  $[\text{SiCl}_3]^-$  on the electron-poor intermediate  $\text{Cl}_3\text{SiC}\equiv\text{CSiCl}_3$  leads to the vinyl anion  $[\text{Cl}_3\text{SiC}=\text{C}(\text{SiCl}_3)_2]^-$  ( $[\mathbf{G}_{\text{open}}]^-$ ), which stabilizes itself through intramolecular adduct formation resulting in the  $\text{Si}_2$ -ring compound  $[\mathbf{G}_{\text{closed}}]^-$  with pentacoordinate Si atom. If  $[\text{SiCl}_3]^-$  ions are in sufficient supply, attack on  $[\mathbf{G}_{\text{closed}}]^-$  induces ring opening with formation of the dianion  $[\mathbf{B}]^{2-}$  (black path). If  $[\text{SiCl}_3]^-$  ions are lacking, one  $[\mathbf{G}]^-$  anion can transfer an  $[\text{SiCl}_3]^-$  fragment to another  $[\mathbf{G}]^-$  anion, which is equivalent to a disproportionation reaction and affords equimolar quantities of  $\mathbf{C}$  and  $[\mathbf{B}]^{2-}$  (green path). Since this is precisely the product distribution we observe (together with 1 eq of  $\text{SiCl}_4$ )

when we treat olefin  $\mathbf{B}$  with 1 eq of  $[\text{nBu}_4\text{N}]\text{Cl}$  in the absence of  $\text{CuCl}_2$ ,  $[\mathbf{G}_{\text{closed}}]^-$  likely also constitutes the key intermediate in the conversion of  $\mathbf{B}$  to  $\mathbf{C}$ . This assumption is further supported by the fact that the corresponding protonation product,  $\mathbf{D}$ , quantitatively forms upon addition of  $[\text{nBu}_4\text{N}]\text{Cl}$  to  $\mathbf{B}$  in the presence of  $[\text{HMe}_3\text{N}]\text{Cl}$  as a mild proton source (red path)

### Scheme 9: Proposed mechanism for the reactions underlying the formation of all $\text{C}_2$ -species covered in this work.



Black path: Formation of  $[\mathbf{B}]^{2-}$  from  $\text{Si}_2\text{Cl}_6/[\text{nBu}_4\text{N}]\text{Cl}/\text{C}_2\text{Cl}_4$  mixtures; green path: formation of  $\mathbf{C}$  through treatment of  $\mathbf{B}$  with  $[\text{nBu}_4\text{N}]\text{Cl}$ ; red path: formation of  $\mathbf{D}$  through treatment of  $\mathbf{B}$  with  $[\text{nBu}_4\text{N}]\text{Cl}$  in the presence of  $[\text{HMe}_3\text{N}]\text{Cl}$ ; cations =  $[\text{nBu}_4\text{N}]^+$  omitted for clarity.

The vinyl anion  $[\mathbf{G}]^-$  is a crucial species in our mechanistic scenario and the crossing point of several reaction paths. Yet, despite many attempts, we have so far not succeeded in its isolation, let alone structural characterization. We therefore investigated the structure and reactivity of  $[\mathbf{G}]^-$  by means of quantum-chemical calculations at B2-PLYP-D3(BJ, ATM)+COSMO-RS( $\text{CH}_2\text{Cl}_2$ )/def2-QZVP//PBE0-D3(BJ)(COSMO( $\text{CH}_2\text{Cl}_2$ ))/def2-TZVPD level of theory.<sup>81-84,94-98</sup> We indeed found two minimum structures, the open-chain structure  $[\mathbf{G}_{\text{open}}]^-$  and the cyclic structure  $[\mathbf{G}_{\text{closed}}]^-$ , the former being less stable by  $\Delta G = 4.2$  kcal/mol (Figure 6). Given the low energy barriers of the transition state  $\text{TS}_1$  in both directions,  $[\mathbf{G}_{\text{open}}]^-$  and  $[\mathbf{G}_{\text{closed}}]^-$  should be interconvertible at room temperature. In line with that, the lengths of the  $\text{C}=\text{C}$  double bonds in  $[\mathbf{G}_{\text{open}}]^-$  (1.336 Å) and  $[\mathbf{G}_{\text{closed}}]^-$  (1.349 Å) are very similar; the  $\text{C}-\text{C}-\text{Si}$  bond angle about the carbanion



$[\mathbf{G}_{\text{open}}]^-$  amounts to  $143.8^\circ$  and is thus significantly wider than the ideal angle of  $120^\circ$  for an  $sp^2$ -hybridized C atom.

The proposed attack of  $[\text{SiCl}_3]^-$  on  $[\mathbf{G}_{\text{closed}}]^-$  requires only little activation energy ( $\text{TS}_2 = 10.5$  kcal/mol), even though the electrostatic repulsion of two negative charges has to be overcome. As to be expected from the high yields of  $[\mathbf{B}]^{2-}$ , its formation is strongly exergonic ( $\Delta G = -27.1$  kcal/mol).

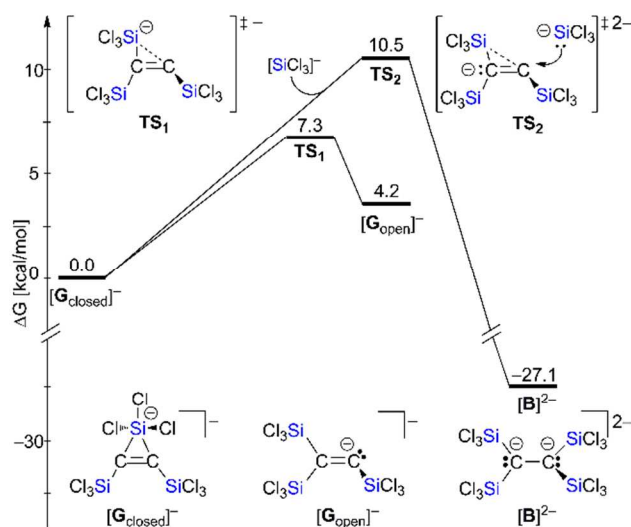


Figure 6. Relative Gibbs free energy diagram for the formation of  $[\mathbf{B}]^{2-}$  from  $[\mathbf{G}_{\text{closed}}]^-$  at the B2-PLYP-D3(BJ, ATM)+COSMORS( $\text{CH}_2\text{Cl}_2$ )/def2-QZVP//PBE0-D3(BJ)(COSMO( $\text{CH}_2\text{Cl}_2$ ))/def2-TZVPD level of theory.<sup>81–84,94–98</sup> All energies are given in kcal/mol relative to  $[\mathbf{G}_{\text{closed}}]^-$ .

Schemes 8 and 9 provide plausible explanations of how the unique vicinal dianion  $[\mathbf{B}]^{2-}$  may form through the  $\text{Cl}^-$ -induced disproportionation of  $\text{Si}_2\text{Cl}_6$  in the presence of  $\text{C}_2\text{Cl}_4$ . However, they do not account for all available experimental evidence and the detailed picture is likely more complex:

(a) The reproducible appearance of the blue radical  $[\mathbf{B}^\cdot]^-$  in almost all reaction mixtures indicates that single-electron-transfer (SET) processes are operative in addition to the proposed closed-shell pathways.

(b) The nature of  $[\text{SiCl}_3]^-$  as  $\text{Cl}^-$  adduct of  $[\text{SiCl}_2]$  (Scheme 1) opens a possibility for silylene-type reactions. For example, [2+1] cycloaddition between the disilylethyne **C** and  $[\text{SiCl}_2]$  would lead to a silacyclopropene,<sup>125</sup> which could subsequently engage in a  $\text{Cl}^-$  association/dissociation equilibrium with  $[\mathbf{G}_{\text{closed}}]^-$ .<sup>126</sup>

(c) The tetrasilylethene **B** is readily reduced to  $[\mathbf{B}]^{2-}$  by means of  $\text{Si}_2\text{Cl}_6/\text{Cl}^-$  in  $\text{CH}_2\text{Cl}_2$  and can thus not be ruled out as a potential synthesis intermediate of  $[\mathbf{B}]^{2-}$ .

Fortunately, “all roads lead to Rome” and all the conceivable reaction pathways ultimately join to provide excellent yields of  $[\mathbf{B}]^{2-}$ .

## CONCLUSION

We have developed convenient protocols for the synthesis of multiply  $\text{SiCl}_3$ -substituted organic scaffolds, starting from

$\text{Cl}_2\text{C}=\text{CCl}_2$ , a stable, non-flammable compound, so cheap that it is widely used in dry cleaning.<sup>127</sup> Upon reaction with the  $\text{Si}_2\text{Cl}_6/\text{Cl}^-$  system,  $\text{Cl}_2\text{C}=\text{CCl}_2$  furnishes the vicinal dianion  $[(\text{Cl}_3\text{Si})_2\text{C}=\text{C}(\text{SiCl}_3)_2]^{2-}$  ( $[\mathbf{B}]^{2-}$ ) in excellent yields. One-step transformations of  $[\mathbf{B}]^{2-}$  lead to the tetrasilylethane  $(\text{Cl}_3\text{Si})_2(\text{H})\text{C}=\text{C}(\text{H})(\text{SiCl}_3)_2$  ( $\text{H}_2\mathbf{B}$ ), the tetrasilylethene  $(\text{Cl}_3\text{Si})_2\text{C}=\text{C}(\text{SiCl}_3)_2$  (**B**), the trisilylethene  $(\text{Cl}_3\text{Si})_2\text{C}=\text{C}(\text{H})(\text{SiCl}_3)$  (**D**), or the disilylethyne  $\text{Cl}_3\text{SiC}\equiv\text{CSiCl}_3$  (**C**). By virtue of their  $\text{SiCl}_3$  groups, all these products are useful building blocks for silicones and silsesquioxanes. Moreover, the unsaturated  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$  bonds of **B/D** and **C** offer ample opportunities for further functionalization, e.g., through hydrosilylation or cycloaddition reactions. We have already used the latter, followed by a final aromatization step, to prepare previously unknown 1,2-bis(trichlorosilyl)benzenes (**E**) from **C** and a selection of butadienes. The potential of **E**-type compounds as ditopic, chelating Lewis acids or Hiyama-coupling reagents is currently being explored in our laboratories.

The reaction cascade leading to the key product  $[\mathbf{B}]^{2-}$  likely starts with the halophilic attack of  $[\text{SiCl}_3]^-$  on  $\text{Cl}_2\text{C}=\text{CCl}_2$  and continues with the intermediate formation of **C**, which is then subject to a carbophilic attack of  $[\text{SiCl}_3]^-$  to give the vinyl anion  $[(\text{Cl}_3\text{Si})_2\text{C}=\text{CSiCl}_3]^-$  ( $[\mathbf{G}]^-$ ). According to quantum-chemical calculations,  $[\mathbf{G}]^-$  readily adds a second  $[\text{SiCl}_3]^-$  ion to afford  $[\mathbf{B}]^{2-}$ . The vinyl anion  $[\mathbf{G}]^-$  also forms during the synthesis of **C** via the  $\text{Cl}^-$ -induced elimination of  $\text{SiCl}_4$  from **B**. In the absence of other reaction partners,  $[\mathbf{G}]^-$  disproportionates and thereby furnishes equimolar amounts of **C** and  $[\mathbf{B}]^{2-}$ . Added  $\text{CuCl}_2$  oxidizes  $[\mathbf{B}]^{2-}$  *in situ* and continuously regenerates the starting material **B**, which substantially improves the yields of **C**. This last example underscores the benefit gained from our mechanistic insights, even though the full scenario is probably more complex and includes  $[\text{SiCl}_2]$  chemistry as well as single-electron-transfer processes (cf. the appearance of the blue radical  $[\mathbf{B}^\cdot]^-$  during the synthesis of  $[\mathbf{B}]^{2-}$ ). Fortunately, most of these pathways are apparently funneling into the same channel such that  $[\mathbf{B}]^{2-}$  is formed with remarkably high selectivity.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental details and characterization data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (70) Even though our proposed mechanisms ideally requires a 4:1:1 stoichiometry of Si<sub>2</sub>Cl<sub>6</sub>, [nBu<sub>4</sub>N]Cl, and CCl<sub>4</sub> for [nBu<sub>4</sub>N][A] (4 Si<sub>2</sub>Cl<sub>6</sub> + [nBu<sub>4</sub>N]Cl + CCl<sub>4</sub> → [nBu<sub>4</sub>N][A] + 5 SiCl<sub>4</sub>), and a 5:2:1 stoichiometry of Si<sub>2</sub>Cl<sub>6</sub>, [nBu<sub>4</sub>N]Cl, and C<sub>2</sub>Cl<sub>4</sub> in the case of [nBu<sub>4</sub>N]<sub>2</sub>[B] (5 Si<sub>2</sub>Cl<sub>6</sub> + 2 [nBu<sub>4</sub>N]Cl + C<sub>2</sub>Cl<sub>4</sub> → [nBu<sub>4</sub>N]<sub>2</sub>[B] + 6 SiCl<sub>4</sub>). We empirically found that a 4:1:1.5 stoichiometry for [nBu<sub>4</sub>N][A] and a 4:2:1 stoichiometry for [nBu<sub>4</sub>N]<sub>2</sub>[B] is advantageous to suppress side-product formation (mainly oligosilanes).
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