

# Regioselective Derivatization of Silylated [20]Silafulleranes

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**ABSTRACT:** Silafulleranes with endohedral Cl<sup>−</sup> ions are a unique, scarcely explored class of structurally well-defined silicon clusters and host-guest complexes. Herein, we report regioselective derivatization reactions on the siladodecahedrane [nBu<sub>4</sub>N][Cl@Si<sub>20</sub>(SiCl<sub>3</sub>)<sub>12</sub>Cl<sub>8</sub>] ([nBu<sub>4</sub>N][1]), which has its cluster surface decorated with 12 SiCl<sub>3</sub> and 8 Cl substituents in perfect *T<sub>h</sub>* symmetry. Room-temperature reaction of [nBu<sub>4</sub>N][1] with excess *i*Bu<sub>2</sub>AlH in *ortho*-difluorobenzene (*o*DFB) furnishes perhydrogenated [nBu<sub>4</sub>N][Cl@Si<sub>20</sub>(SiH<sub>3</sub>)<sub>12</sub>H<sub>8</sub>] ([nBu<sub>4</sub>N][2]) in 50% yield; the non-pyrophoric [2]<sup>−</sup> is the largest structurally authenticated (by XRD) hydridosilane known to-date. A simple switch from pure *o*DFB to an *o*DFB/Et<sub>2</sub>O solvent mixture suppresses core hydrogenation and results in the formation of [nBu<sub>4</sub>N][Cl@Si<sub>20</sub>(SiH<sub>3</sub>)<sub>12</sub>Cl<sub>8</sub>] ([nBu<sub>4</sub>N][3]). In addition to the exhaustive Cl/H exchange at all 44 Si–Cl bonds of [1]<sup>−</sup> and the regioselective 36-fold silyl-group hydrogenation, we achieved the simultaneous introduction of Me substituents at all 8 SiCl vertices along with the conversion of all 12 SiCl<sub>3</sub> to SiH<sub>3</sub> groups by treating [nBu<sub>4</sub>N][1] with Me<sub>2</sub>AlH/Me<sub>3</sub>Al in *o*DFB ([nBu<sub>4</sub>N][Cl@Si<sub>20</sub>(SiH<sub>3</sub>)<sub>12</sub>Me<sub>8</sub>], [nBu<sub>4</sub>N][4]; 73%). Quantum-chemical free-energy calculations find an S<sub>N</sub>2-Si type hydrogenation of the exohedral SiCl<sub>3</sub> moieties in [1]<sup>−</sup> (trigonal-bipyramidal intermediate) slightly preferred over metathesis-like S<sub>N</sub>i-Si substitutions (four-membered transition state). Cage hydrogenation can occur only via S<sub>N</sub>i-Si processes. The experimentally demonstrated influence of an Et<sub>2</sub>O co-solvent, which drastically increases the respective reaction barriers, is attributed to the increased stability of the resulting *i*Bu<sub>2</sub>AlH-OEt<sub>2</sub> adduct and its higher steric bulk compared to free *i*Bu<sub>2</sub>AlH.

## INTRODUCTION

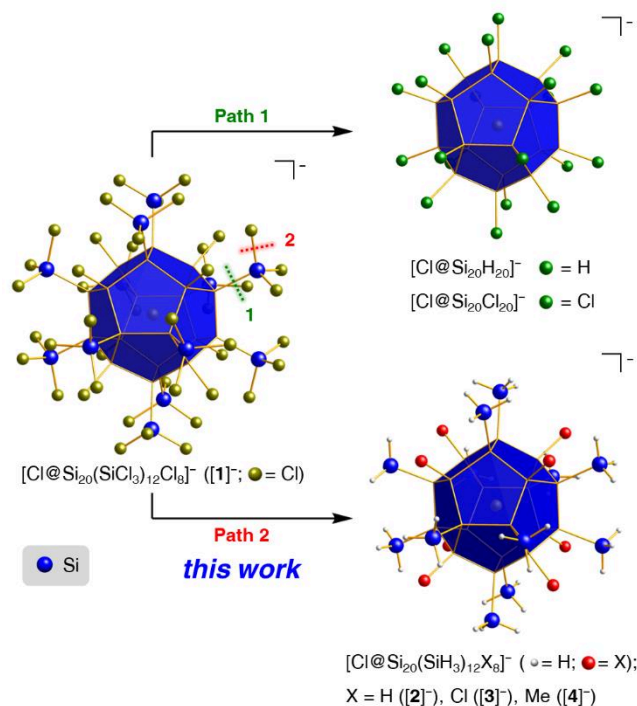
The discovery of the siladodecahedrane [nBu<sub>4</sub>N][Cl@Si<sub>20</sub>(SiCl<sub>3</sub>)<sub>12</sub>Cl<sub>8</sub>] ([nBu<sub>4</sub>N][1]; Figure 1) in 2015 provided the first preparative access to the class of compounds known as silafulleranes,<sup>1</sup> which had already received much attention from the theoretical chemistry community.<sup>2–5</sup> [nBu<sub>4</sub>N][1] is straightforwardly available from Si<sub>2</sub>Cl<sub>6</sub>, [nBu<sub>4</sub>N]Cl, and *n*Bu<sub>3</sub>N in one step and in about 30% yield.<sup>1,6</sup> The anion [1]<sup>−</sup> consists of a dodecahedral Si<sub>20</sub> core carrying 12 SiCl<sub>3</sub> groups and 8 Cl atoms in a perfectly *T<sub>h</sub>*-symmetric pattern and hosting a Cl<sup>−</sup> ion as endohedral guest. This Cl<sup>−</sup> ion likely plays a crucial role as a structure-directing template during the assembly of the silafullerane cluster before it is eventually encapsulated into it. Furthermore, it imparts a negative charge to the cluster, which facilitates the isolation of the salt-like product by crystallization and its analysis by LDI mass spectrometry in the negative-ion mode.<sup>1</sup> The presence of Si–Cl bonds in the substituent sphere of [1]<sup>−</sup> is uncommon in the field of molecular Si and Ge clusters,<sup>7</sup> since most of the saturated clusters reported so far, such as tetrasilatetrahedranes,<sup>8,9</sup> octasilacubanes,<sup>10,11</sup> or decasiladamantane<sup>12,13</sup> and its isomers,<sup>12,14</sup> are decorated with rather inert alkyl, aryl, or

organosilyl groups. Nevertheless, various routes of derivatization have been developed, including reductive<sup>9</sup> or nucleophilic<sup>13</sup> removal of substituents, oxidative cage opening,<sup>15,16</sup> and one-electron reduction of the cluster core.<sup>17</sup> Furthermore, a rich chemistry of unsaturated, so-called “metalloid”<sup>18</sup> Si and Ge clusters<sup>19–24</sup> and completely ligand-free Zintl ions has evolved.<sup>25–31</sup>

Coming back to the silafullerane [nBu<sub>4</sub>N][1], its follow-up chemistry can be developed along two paths (Figure 1): 1) stripping of the 12 SiCl<sub>3</sub> groups to enter the area of Si<sub>20</sub> clusters and 2) derivatization of [1]<sup>−</sup> while preserving its Si<sub>32</sub> framework. Following path 1, our groups have recently synthesized and characterized the parent siladodecahedrane with endohedral Cl<sup>−</sup> ion, [Cl@Si<sub>20</sub>H<sub>20</sub>]<sup>−</sup> (Figure 1),<sup>32</sup> and put an end to previous, exclusively theory-based, discussions on the existence of the *I<sub>h</sub>*-symmetric Si<sub>20</sub>H<sub>20</sub> cage.<sup>3,5</sup> Our synthesis builds upon the protodesilylation of [1]<sup>−</sup> with pinacol and a subsequent Cl/H exchange on the primary product [Cl@Si<sub>20</sub>H<sub>12</sub>Cl<sub>8</sub>]<sup>−</sup> with diisobutylaluminum hydride (*i*Bu<sub>2</sub>AlH). Perchlorination of [Cl@Si<sub>20</sub>H<sub>20</sub>]<sup>−</sup> to afford [Cl@Si<sub>20</sub>Cl<sub>20</sub>]<sup>−</sup> was achieved by treatment with chloromethanes. Due to their highly symmetric environments in the centers of the silafulleranes [1]<sup>−</sup>, [Cl@Si<sub>20</sub>H<sub>12</sub>Cl<sub>8</sub>]<sup>−</sup>, [Cl@Si<sub>20</sub>H<sub>20</sub>]<sup>−</sup>, and [Cl@Si<sub>20</sub>Cl<sub>20</sub>]<sup>−</sup>, the en-

dohedral Cl<sup>-</sup> ions give rise to unusually sharp <sup>35</sup>Cl NMR signals and observable *J*(H,Cl) and *J*(Si,Cl) couplings in the respective NMR spectra. After a thorough quantum-chemical analysis of the shielding components, we found that the chemical shift value  $\delta(^{35}\text{Cl})$  provides a useful analytical probe for evaluating the degree of endohedral Cl<sup>-</sup>→Si<sub>20</sub> charge transfer.<sup>32</sup>

Herein, we are now focusing on path 2 (Scheme 1a) and disclose (i) the perhydrogenation of [1]<sup>-</sup> to furnish [Cl@Si<sub>20</sub>(SiH<sub>3</sub>)<sub>12</sub>H<sub>8</sub>]<sup>-</sup> ([2]<sup>-</sup>), (ii) a regioselective partial Cl/H exchange on [1]<sup>-</sup> to give [Cl@Si<sub>20</sub>(SiH<sub>3</sub>)<sub>12</sub>Cl<sub>8</sub>]<sup>-</sup> ([3]<sup>-</sup>), and (iii) a regioselective three-component reaction to afford [Cl@Si<sub>20</sub>(SiH<sub>3</sub>)<sub>12</sub>Me<sub>8</sub>]<sup>-</sup> ([4]<sup>-</sup>). The new syntheses are complemented by theoretical studies of the underlying reaction mechanisms, the importance of which goes far beyond our specific cluster chemistry, as they improve the understanding of chlorosilane hydrogenation in general.



**Figure 1.** Fundamental approaches to the derivatization of [1]<sup>-</sup> (paths 1 and 2). Path 1: Desilylation allowing the synthesis of Si<sub>20</sub> dodecahedranes. Path 2: Derivatization preserving the original Si<sub>32</sub> framework.

## RESULTS AND DISCUSSION

Hydrosilanes, along with halosilanes and organosilanes, are among the most versatile classes of silicon compounds, but examples of large, non-polymeric representatives are still rare.<sup>33,34</sup> The same is true for selectively mixed-substituted oligosilanes. The synthesis of hydrogenated silafullerenes with molecular weights of around 1000 g mol<sup>-1</sup> is therefore an important objective to get access to the largest structurally well-defined hydrosilanes known to date. The high degree of functionalization of [1]<sup>-</sup> is both a blessing and a calamity. To cope with this ambivalent situation, we set out to develop not only reactions that allow quantitative derivatization of all 44 Si–Cl bonds ([2]<sup>-</sup>), but also protocols that enable substitution of a specific

number of Cl atoms by either functional groups of orthogonal reactivity ([3]<sup>-</sup>) or by inert substituents ([4]<sup>-</sup>).

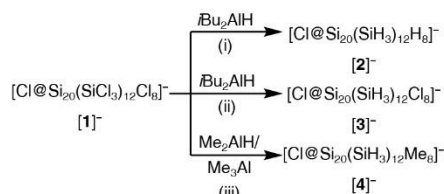
**Syntheses.** In a previous report, we have already disclosed that [2]<sup>-</sup> was formed from [*n*Bu<sub>4</sub>N][1] and Li[AlH<sub>4</sub>] in small amounts, which were, however, sufficient to detect [2]<sup>-</sup> by <sup>29</sup>Si and <sup>1</sup>H/<sup>29</sup>Si-HMBC NMR spectroscopy as well as LDI mass spectrometry.<sup>1</sup> This protocol suffers from a partial degradation of the silafullerene with concomitant formation of pyrophoric SiH<sub>4</sub>, a known problem in the hydrogenation of chlorinated oligosilanes.<sup>33,35</sup> Li[AlH<sub>4</sub>] appears to be nucleophilic enough to cleave not only Si–Cl, but also Si–Si bonds. Moreover, the Li[AlX<sub>4</sub>] (X = H, Cl) byproducts are tedious to remove and therefore impede the purification of [*n*Bu<sub>4</sub>N][2]. We now report that both obstacles can be overcome by using excess diisobutylaluminum hydride (*i*Bu<sub>2</sub>AlH; 100 equiv) as a Lewis-acidic and neutral H-source that substitutes all 44 exohedral Cl atoms of [*n*Bu<sub>4</sub>N][1] with H atoms in the non-donor solvent *ortho*-difluorobenzene (*o*DFB; Scheme 1a). In this way, non-pyrophoric [*n*Bu<sub>4</sub>N][2] was obtained in a typical yield of 50% and in the form of single crystals suitable for X-ray crystallography. The compound is significantly less soluble in *o*DFB than [*n*Bu<sub>4</sub>N][1], but is relatively well soluble in THF without undergoing decomposition. The suitability of *o*DFB for reactions with [*n*Bu<sub>4</sub>N][1] is particularly noteworthy: due to its combination of high dipole moment, non-basicity, high stability towards Lewis acids, and moderate boiling point,<sup>36</sup> it became the solvent of choice for all subsequent transformations.

We next explored the possibility of selectively replacing only the 36 Cl atoms on the sterically exposed SiCl<sub>3</sub> groups of [1]<sup>-</sup> with H atoms to generate the silafullerene [*n*Bu<sub>4</sub>N][3]. An initial reaction of [*n*Bu<sub>4</sub>N][1] with 36 equiv of *i*Bu<sub>2</sub>AlH in *o*DFB again gave solely crystals of [*n*Bu<sub>4</sub>N][2]. The selective synthesis of [*n*Bu<sub>4</sub>N][3] was finally achieved by simply switching from pure *o*DFB as the solvent to an equimolar mixture of *o*DFB and Et<sub>2</sub>O. After precipitation by addition of *n*-hexane and subsequent filtration, [*n*Bu<sub>4</sub>N][3] was isolated as a colorless powder in 40% yield. During the optimization of the synthesis protocol, we obtained X-ray-quality crystals of [*n*Bu<sub>4</sub>N][Cl@Si<sub>20</sub>(SiH<sub>3</sub>)<sub>12</sub>HCl<sub>8</sub>]<sup>-</sup> ([*n*Bu<sub>4</sub>N][3']; cf. the Supporting Information for details). In this compound, one of the 8 cluster-bonded Cl atoms is replaced by an H atom. As long as single crystals of [*n*Bu<sub>4</sub>N][3] are not available, the structure analysis of [*n*Bu<sub>4</sub>N][3'] will serve as a substitute to discuss the main geometric parameters of mixed H/Cl-silafullerenes.

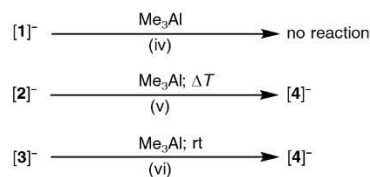
The synthesis protocol for [*n*Bu<sub>4</sub>N][4] was inspired by a serendipitous discovery: Intending to replace *i*Bu<sub>2</sub>AlH with a more easily removable aluminium hydride in the synthesis of [*n*Bu<sub>4</sub>N][2], we treated [*n*Bu<sub>4</sub>N][1] with excess Me<sub>2</sub>AlH. Indeed, we observed the desired quantitative Cl/H exchange at the 12 silyl groups of [1]<sup>-</sup>; at its 8 SiCl moieties, however, not only Cl/H, but also Cl/Me exchange took place without a clear preference. This reaction can be developed into an efficient route to [*n*Bu<sub>4</sub>N][4] if more Me groups are supplied by using 44 equiv of Me<sub>2</sub>AlH along with 30 equiv of Me<sub>3</sub>Al. The product readily crystallizes from the *o*DFB/toluene solvent mixture in 73% yield.<sup>37,38</sup>

**Scheme 1. (a) Syntheses of  $[n\text{Bu}_4\text{N}][2]^-$ – $[n\text{Bu}_4\text{N}][4]^-$ , starting from  $[n\text{Bu}_4\text{N}][1]^-$ . (b) Test reactions to shed light on the substituent-exchange mechanisms. (c) Crystallographically determined structures of the silafullerane salts  $[\text{Et}_4\text{N}][1]^-$ ,<sup>1</sup>  $[n\text{Bu}_4\text{N}][2]^-$ ,  $[n\text{Bu}_4\text{N}][3]^-$ , and  $[n\text{Bu}_4\text{N}][4]^-$  in the solid state (cations are omitted for clarity; in the structure of  $[3]^-$ , H and Cl are equally disordered over the two sites marked with red asterisks).**

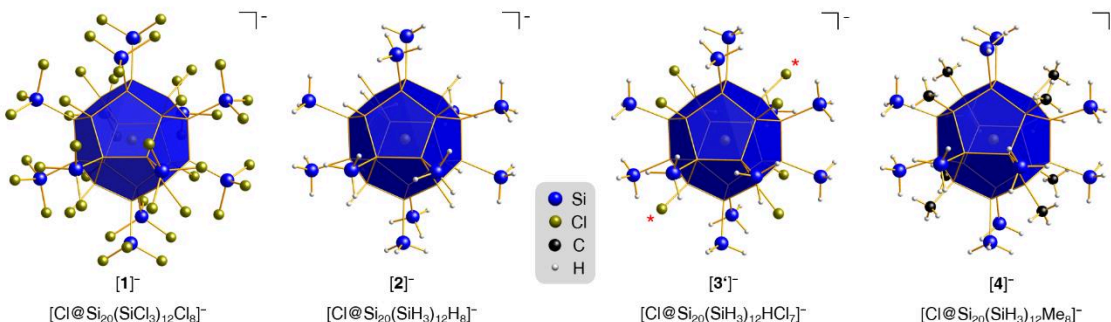
**a) Synthesis protocols:**



**b) Test reactions:**



**c)**



Reagents and conditions: (i) 100 equiv  $t\text{Bu}_2\text{AlH}$ ,  $o\text{DFB}$ , rt, 1 d. Yield: 50%; (ii) 40 equiv  $t\text{Bu}_2\text{AlH}$ ,  $o\text{DFB}/\text{Et}_2\text{O}$  (1:1), rt, 18 h. Yield: 40%. (iii) 44 equiv  $\text{Me}_2\text{AlH}$ , 30 equiv  $\text{Me}_3\text{Al}$ ,  $o\text{DFB}/\text{toluene}$ , rt, 3 d. Yield: 73%. (iv) 120 equiv  $\text{Me}_3\text{Al}$ ,  $o\text{DFB}/\text{toluene}$ , rt, 1 d. (v) 80 equiv  $\text{Me}_3\text{Al}$ ,  $o\text{DFB}/\text{toluene}$ , 100 °C, 21 h. (vi) 80 equiv  $\text{Me}_3\text{Al}$ ,  $o\text{DFB}/\text{toluene}$ , rt, <1 h.

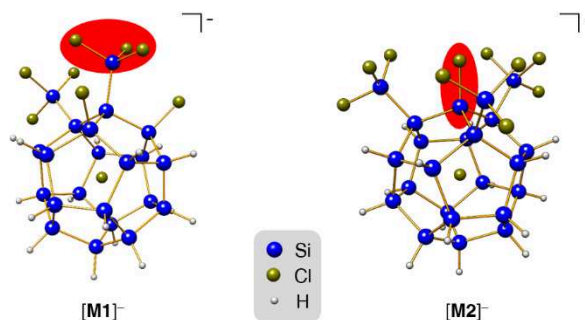
Having optimized the synthesis of  $[n\text{Bu}_4\text{N}][4]^-$ , we subsequently performed several test reactions to shed some light on critical aspects of the underlying three-component reaction. The following results were obtained (Scheme 1b): 1)  $[n\text{Bu}_4\text{N}][1]^-$  is inert toward  $\text{Me}_3\text{Al}$  in the absence of  $\text{Me}_2\text{AlH}$  (room temperature). 2)  $[n\text{Bu}_4\text{N}][2]^-$  undergoes eightfold H/Me exchange at its core when treated with  $\text{Me}_3\text{Al}$  in the absence of  $\text{Me}_2\text{AlH}$  (100 °C).<sup>39</sup> 3)  $[n\text{Bu}_4\text{N}][3]^-$  undergoes eightfold Cl/Me exchange at its core when treated with  $\text{Me}_3\text{Al}$  in the absence of  $\text{Me}_2\text{AlH}$  (room temperature). From these results, the following picture emerges: The aluminium hydride not only serves as H-source for the silyl groups, but also helps to activate the system for Me transfer to the cluster core. A direct mode of action would be the formation of reactive  $(\text{Me}_2\text{AlH})_x(\text{Me}_3\text{Al})_y$  aggregates. A more indirect influence could be primarily based on the initial conversion of  $\text{SiCl}_3$  to  $\text{SiH}_3$ , because (i) pre-coordination of  $\text{Me}_3\text{Al}$  to a silyl-H atom would render Me transfer an intramolecular reaction,<sup>40</sup> and (ii) the lower steric demand and group electronegativity of  $\text{SiH}_3$  vs.  $\text{SiCl}_3$  should facilitate Cl<sup>−</sup> abstraction from the  $\text{Si}_{20}$  core. Moreover, the higher temperature required for reaction 2) as opposed to 3) indicates that core methylation most likely occurs at Si–Cl rather than intermediately formed Si–H bonds. It is probably not a “self-healing” process that corrects “false” core hydrogenation.

To validate the experimental findings and to gain deeper insight into the  $\text{SiCl}_3$  vs. core-SiCl hydrogenation mechanisms, quantum-chemical calculations were conducted. Theoretical considerations regarding the three-component reaction for regioselective hydrogenation/methylation are not discussed as the nature of the actual active H/Me-

transfer reagent(s) is unknown and the number and sizes of potential candidates are prohibitively high.

**Quantum-chemical calculations on the Cl/H-exchange mechanisms.** Free energy calculations were performed at the  $r^2\text{SCAN0-D4}^{41-43}/\text{ma-def2-QZVPP}^{44,45}+\text{COSMO-RS}(\text{CH}_2\text{Cl}_2)^{46,47}+\text{G(mRRHO)}^{48,49}/\text{PBEh-3c}^{50}(\text{SMD}(\text{CH}_2\text{Cl}_2))^{51}$  level using the xtb 6.5.1,<sup>52,53</sup> ORCA 5.0.3<sup>54-56</sup> and TURBOMOLE 7.6.0<sup>57</sup> program packages (cf. the Supporting Information for further details). To keep the computational effort within reasonable limits, we studied substitution reactions at the exohedral  $\text{SiCl}_3$  groups and at the SiCl cluster vertices by using the model systems  $[\text{M1}]^-$  and  $[\text{M2}]^-$ , respectively (Figure 2).

**Computed model systems:**

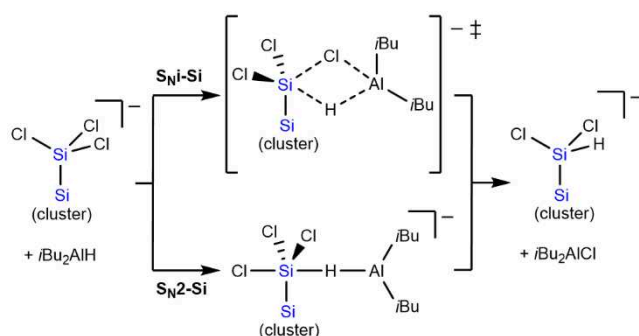


**Figure 2.** Model systems used for the computational studies of substitution reactions at the exohedral  $\text{SiCl}_3$  groups ( $[\text{M1}]^-$ ) and at the SiCl cluster vertices ( $[\text{M2}]^-$ ). The functional groups under investigation are highlighted in red.

In **[M1]**<sup>−</sup>/**[M2]**<sup>−</sup>, we consider one Si–SiCl<sub>3</sub>/Si–Cl moiety and treat only their three adjacent vertices explicitly, while the rest of the cluster is simplified to 16 Si–H vertices.

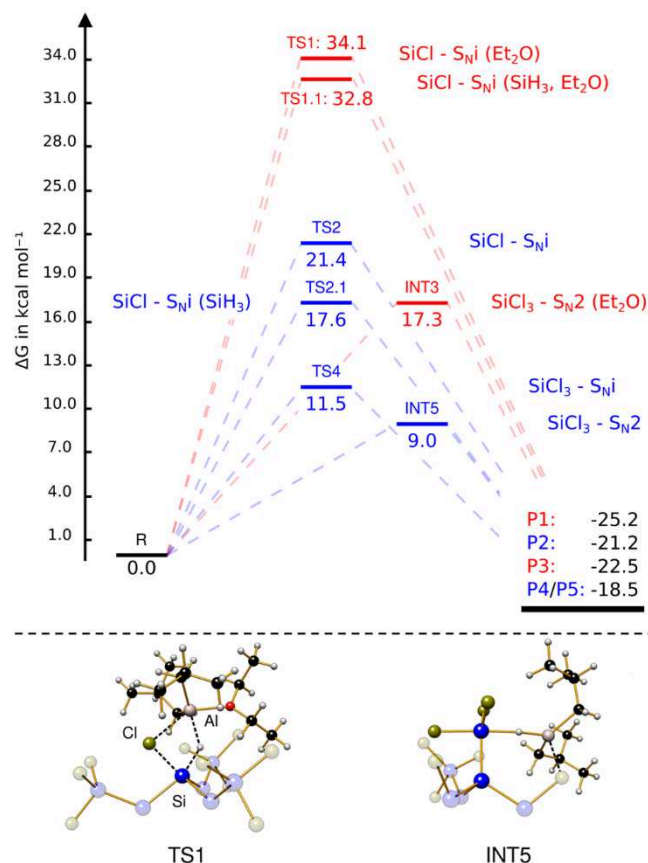
Two possible mechanisms for the hydrogenation of chlorosilanes using *i*Bu<sub>2</sub>AlH are known in the literature.<sup>58–61</sup> In Scheme 2, these are illustrated by the example of an exohedral SiCl<sub>3</sub> group of **[1]**<sup>−</sup>: The so-called "intramolecular nucleophilic substitution mechanism" (S<sub>N</sub>i–Si) involves a four-membered transition state, whereas the S<sub>N</sub>2–Si mechanism includes a trigonal-bipyramidal structure. The latter resembles the transition state of an S<sub>N</sub>2 reaction at a carbon center but is a true intermediate because the silicon atom can become hypercoordinated.

**Scheme 2. Hydrogenation following the S<sub>N</sub>i–Si or S<sub>N</sub>2–Si mechanism at an exohedral SiCl<sub>3</sub> group.**



Since the potential energy curves around these intermediates are very shallow, S<sub>N</sub>2–Si transition states connecting them with reactants and products could not be located. However, exactly because the energy differences between the transition states and the intermediates must be small in the present cases, we can use the intermediates' energies to gain insight into the favored reaction mechanisms even without knowledge of the transition states. While the S<sub>N</sub>i–Si mechanism is geometrically possible at both the SiCl<sub>3</sub> and SiCl functionalities, S<sub>N</sub>2–Si hydrogenation can only take place at SiCl<sub>3</sub> because the backside attack at SiCl is blocked by the cluster core.<sup>62</sup> A comparison of the S<sub>N</sub>i–Si barrier heights already reveals that the barrier for SiCl hydrogenation is almost twice as large as that for SiCl<sub>3</sub> hydrogenation ( $\Delta G^\ddagger(\text{TS2}) = 21.4 \text{ kcal mol}^{-1}$ ,  $\Delta G^\ddagger(\text{TS4}) = 11.5 \text{ kcal mol}^{-1}$ ,  $\Delta\Delta G^\ddagger = 9.9 \text{ kcal mol}^{-1}$ ; Figure 3). The free-energy difference  $\Delta\Delta G^\ddagger$  for Cl/H exchange at the two positions increases even to 12.4 kcal mol<sup>−1</sup>, if we take into account that S<sub>N</sub>2–Si hydrogenation at SiCl<sub>3</sub> is slightly more favorable than S<sub>N</sub>i–Si hydrogenation (cf.  $\Delta G(\text{INT5}) = 9.0 \text{ kcal mol}^{-1}$  vs.  $\Delta G^\ddagger(\text{TS4}) = 11.5 \text{ kcal mol}^{-1}$ ): in the S<sub>N</sub>2 intermediate, *i*Bu<sub>2</sub>AlH is pre-coordinated to the neighboring SiCl vertex and is therefore already in close vicinity to the reacting SiCl<sub>3</sub> group. Most importantly, the barrier height for SiCl hydrogenation decreases from  $\Delta G^\ddagger(\text{TS2}) = 21.4$  to  $\Delta G^\ddagger(\text{TS2.1}) = 17.6 \text{ kcal mol}^{-1}$  once the SiCl<sub>3</sub> groups are fully hydrogenated, which explains why the cluster core is also eventually perhydrogenated to afford **[2]**<sup>−</sup>. Addition of Et<sub>2</sub>O to the reaction mixture leads to the formation of an *i*Bu<sub>2</sub>AlH–OEt<sub>2</sub> adduct, which not only increases the steric demand of the hydrogenation reagent, but also stabilizes the adduct by 16.6 kcal mol<sup>−1</sup> compared to free *i*Bu<sub>2</sub>AlH. As a result, both the SiCl<sub>3</sub> and the SiCl hydrogenation are now associated with a higher energy penalty ( $\Delta G(\text{INT3}) = 17.3 \text{ kcal mol}^{-1}$ ,

$\Delta G^\ddagger(\text{TS1}) = 34.1 \text{ kcal mol}^{-1}$ ,  $\Delta\Delta G^\ddagger = 16.8 \text{ kcal mol}^{-1}$ ), but the  $\Delta\Delta G^\ddagger$  value further increases by 4.4 kcal mol<sup>−1</sup>. While INT3 is still accessible at room temperature, TS1 lies energetically too high to be overcome under these conditions. Even after the exhaustive conversion of SiCl<sub>3</sub> to SiH<sub>3</sub>, hydrogenation at the SiCl vertices still has a barrier of  $\Delta G^\ddagger(\text{TS1.1}) = 32.8 \text{ kcal mol}^{-1}$ , so that this reaction is largely suppressed at room temperature. Taken together, this explains why our synthesis protocol gives essentially pure samples of **[3]**<sup>−</sup> with very little contamination from singly core-hydrogenated **[3']**<sup>−</sup> (Scheme 1c).



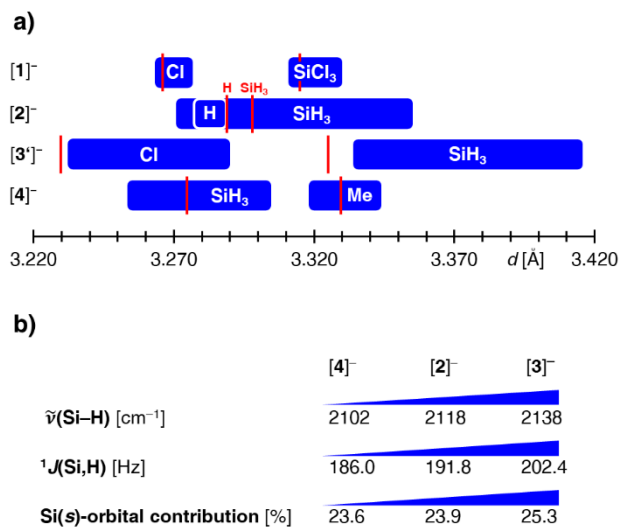
**Figure 3.** Calculated Gibbs free energies  $\Delta G$  for the hydrogenation at the r<sup>2</sup>SCAN0–D4/ma-def2-QZVPP+COSMO–RS(CH<sub>2</sub>Cl<sub>2</sub>)+G(mRRHO)//PBEh–3c(SMD(CH<sub>2</sub>Cl<sub>2</sub>)) level of theory. R represents the separated reactants which are **[M1]**<sup>−</sup> or **[M2]**<sup>−</sup> in combination with the respective nucleophile. P represents the products obtained after a single hydrogenation step via the transition state or intermediate with the same number.

**X-ray Crystal Structure Analyses, IR Spectroscopy, and LDI Mass Spectrometry.** Scheme 1c shows the anion structures of **[nBu<sub>4</sub>N][2]**, **[nBu<sub>4</sub>N][3']**, and **[nBu<sub>4</sub>N][4]** in the solid state (the structure of the known **[1]**<sup>−</sup> was added for completeness). The proposed substitution patterns are fully confirmed. Careful analysis of the residual electron density in the regions near the SiMe and SiH<sub>3</sub> groups of **[4]**<sup>−</sup> (based on high-quality diffraction data obtained with synchrotron radiation) provides no evidence for a possible Me/H crystallographic disorder. All anions lie on inversion centers; Si–H/Cl disorder in **[3']**<sup>−</sup> occurs only at two equivalent positions (marked with red asterisks). The Si–Si bond lengths of the three anions fall in the range 2.3200(5)–



2.381(6) Å.<sup>63</sup> For an assessment of the different propensities of differently substituted SiR cluster vertices to accept charge density from the endohedral Cl<sup>-</sup> ion, the Cl<sup>-</sup>⋯Si distances within each individual cluster are particularly diagnostic (Figure 4a; blue bars: range of experimental values, red lines: computed values). For [2]<sup>-</sup>, the ranges of Cl<sup>-</sup>⋯SiH and Cl<sup>-</sup>⋯SiSiH<sub>3</sub> distances are overlapping. For [3]<sup>-</sup> and [4]<sup>-</sup>, the Cl<sup>-</sup>⋯SiCl<sup>64</sup> and Cl<sup>-</sup>⋯SiMe distances are shorter and longer, respectively, than the corresponding Cl<sup>-</sup>⋯SiSiH<sub>3</sub> distances within the same molecule. This ordering fits to the expected trend in the acceptor-orbital energies according to  $\sigma^*(\text{Si-Me}) > \sigma^*(\text{Si-SiH}_3) \approx \sigma^*(\text{Si-H}) > \sigma^*(\text{Si-Cl})$ .

In the solid-state IR spectra, bands at  $\tilde{\nu}(\text{Si-H}) = 2118 \text{ cm}^{-1}$  ([nBu<sub>4</sub>N][2]; calcd 2160 cm<sup>-1</sup>), 2138 cm<sup>-1</sup> ([nBu<sub>4</sub>N][3]; calcd 2181 cm<sup>-1</sup>), and 2102 cm<sup>-1</sup> ([nBu<sub>4</sub>N][4]; calcd 2149 cm<sup>-1</sup>) are assigned to the Si-H stretching modes of the SiH<sub>3</sub> groups. Only in the case of [nBu<sub>4</sub>N][2], additional, less intense Si-H stretching bands, originating from the SiH vertices, were detected ( $\tilde{\nu}(\text{Si-H}) = 2042 \text{ cm}^{-1}$  and 2026 cm<sup>-1</sup>, calcd 2101 cm<sup>-1</sup>; cf. [nBu<sub>4</sub>N][Cl@Si<sub>20</sub>H<sub>20</sub>]:<sup>32</sup>  $\tilde{\nu}(\text{Si-H}) = 2064 \text{ cm}^{-1}$ ). Since IR wavenumbers correlate directly with the force constants and these, in turn, with the s character of the respective bonds, the experimentally observed trend in the H<sub>2</sub>Si-H stretching modes indicates an increase in the s character in the order [4]<sup>-</sup> < [2]<sup>-</sup> < [3]<sup>-</sup> (Figure 4b). This claim is further supported by a comparison of the corresponding <sup>1</sup>J(Si,H) NMR coupling constants, which also grow larger along the sequence [4]<sup>-</sup> < [2]<sup>-</sup> < [3]<sup>-</sup>, thereby testifying to an increasing Fermi contact interaction. Theoretical validation comes from Bent's rule<sup>65</sup> and a DFT-based natural localized molecular orbital (NLMO) analysis conducted with the NBO 6.0 program,<sup>66,67</sup> which predicts Si(s)-orbital contributions to the H<sub>2</sub>Si-H bonds of 23.6% < 23.9% < 25.3%.



**Figure 4.** (a) Distances Cl<sup>-</sup>⋯SiR between the endohedral Cl<sup>-</sup> ions and the vertices of the Si<sub>20</sub> cages in [1]<sup>-</sup>, [2]<sup>-</sup>, [3]<sup>-</sup>, and [4]<sup>-</sup> (blue bars: experimental ranges within 3σ margins, white font: specification of R; red lines: computed values). (b) Correlations between the experimentally obtained stretching frequencies ( $\tilde{\nu}(\text{Si-H})$ ) and NMR coupling constants (<sup>1</sup>J(Si,H)) with the computed Si(s)-orbital contribution to the H<sub>2</sub>Si-H bonds in [4]<sup>-</sup>, [2]<sup>-</sup>, and [3]<sup>-</sup>.

Laser-desorption ionization (LDI) MS(−) measurements on [nBu<sub>4</sub>N][2]<sup>-</sup>–[nBu<sub>4</sub>N][4]<sup>-</sup> gave the molecular-ion peaks [M]<sup>-</sup> of [2]<sup>-</sup>–[4]<sup>-</sup> with fitting isotope patterns. Similar to [1]<sup>-</sup>, which undergoes gas-phase elimination of SiCl<sub>2</sub> units under LDI-MS conditions,<sup>1</sup> we now see evidence of SiH<sub>2</sub> elimination/insertion (−/+ 30 Da).

**NMR Spectroscopy.** The NMR spectra of [nBu<sub>4</sub>N][2] and [nBu<sub>4</sub>N][4] were recorded in THF-*d*<sub>8</sub>, whereas [nBu<sub>4</sub>N][3] had to be characterized in *o*DFB/C<sub>6</sub>D<sub>12</sub> (5:1 mixture) due to its lability to donor solvents. The SiH<sub>3</sub> and SiH moieties of [nBu<sub>4</sub>N][2] give rise to a singlet at 3.47 ppm (36H) and a 1:1:1:1 quartet at 4.31 ppm (8H; J(H,Cl) = 2.9 Hz), respectively. Upon <sup>35</sup>Cl decoupling, the quartet collapses into a singlet with broadened base (due to unresolved coupling to <sup>37</sup>Cl; S(<sup>35</sup>Cl) = S(<sup>37</sup>Cl) = 3/2, natural abundances: 75.5% and 24.5%<sup>68</sup>).<sup>69</sup> The exclusively peripheral hydrogenation in [3]<sup>-</sup> is evident from the absence of core-SiH resonances. The complete core methylation in [4]<sup>-</sup> is reflected by the SiH<sub>3</sub> vs. core-SiMe integral ratio of 36H vs. 24H.

In its <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum, each of the T<sub>h</sub>-symmetric silafullerenes [2]<sup>-</sup>–[4]<sup>-</sup> shows three resonances for the chemically inequivalent Si<sup>0</sup>, Si<sup>I</sup>, and Si<sup>III</sup> centers. The corresponding chemical shifts agree well with the computed values (Table 1).<sup>70,71</sup>

**Table 1. Experimental (calculated) <sup>29</sup>Si and <sup>35</sup>Cl NMR-spectroscopic parameters of the silafullerenes [nBu<sub>4</sub>N][1]<sup>-</sup>–[nBu<sub>4</sub>N][4]<sup>-</sup>.<sup>[a]</sup> Calculated NMR shifts have been computed at the PBE0<sup>72</sup>(COSMO(CH<sub>2</sub>Cl<sub>2</sub>))<sup>73</sup>/SO-ZORA/TZP<sup>74</sup> level of theory.**

| Compound                | $\delta(^{29}\text{Si})$ |                  |                    | $\delta(^{35}\text{Cl})$        |
|-------------------------|--------------------------|------------------|--------------------|---------------------------------|
|                         | Si <sup>0</sup>          | Si <sup>I</sup>  | Si <sup>III</sup>  |                                 |
| [nBu <sub>4</sub> N][1] | −60.3<br>(−63.5)         | 31.1<br>(31.7)   | 10.3<br>(15.9)     | 274.5<br>(277.6) <sup>[b]</sup> |
| [nBu <sub>4</sub> N][2] | −58.5<br>(−58.3)         | −14.9<br>(−23.9) | −93.7<br>(−98.6)   | 469.0<br>(471.8) <sup>[b]</sup> |
| [nBu <sub>4</sub> N][3] | −73.4<br>(−72.6)         | 51.5<br>(54.3)   | −97.7<br>(−98.5)   | 363.7<br>(360.0) <sup>[b]</sup> |
| [nBu <sub>4</sub> N][4] | −67.2<br>(−67.3)         | 19.1<br>(21.3)   | −100.6<br>(−102.4) | 457.1<br>(455.8) <sup>[b]</sup> |

[a] NMR spectra were recorded in THF-*d*<sub>8</sub> ([nBu<sub>4</sub>N][1],<sup>1,7</sup> [nBu<sub>4</sub>N][2], [nBu<sub>4</sub>N][4]) or *o*DFB/C<sub>6</sub>D<sub>12</sub> (5:1; [nBu<sub>4</sub>N][3]). [b] These values were obtained after scaling according to the following linear equation:  $\delta(^{35}\text{Cl}, \text{scaled}) = 0.8739 \cdot \delta(^{35}\text{Cl}, \text{calcd}) - 8.3536$ .

The endohedral Cl<sup>-</sup> ions within the highly symmetric siladodecahedrane cages of [Cl@Si<sub>20</sub>R<sub>20</sub>]<sup>-</sup> (R = H, Cl) give rise to sharp <sup>35</sup>Cl resonances.<sup>32</sup> Based on a quantum-chemical analysis of the shielding components, we have shown that  $\delta(^{35}\text{Cl})$  is a useful probe of the degree of the Cl<sup>-</sup>→Si<sub>20</sub> host-guest interaction: a downfield shift of the <sup>35</sup>Cl signal is diagnostic for a decreased Cl<sup>-</sup>→Si<sub>20</sub> charge transfer, as illustrated by a comparison of [Cl@Si<sub>20</sub>Cl<sub>20</sub>]<sup>-</sup> (126.0 ppm; more electronegative substituents) and [Cl@Si<sub>20</sub>H<sub>20</sub>]<sup>-</sup> (345.0 ppm; less electronegative substituents).<sup>32</sup> In line with that, the presence of even less electronegative SiH<sub>3</sub> substituents<sup>75</sup> in [2]<sup>-</sup> is accompanied by a further down-

field shift to  $\delta(^{35}\text{Cl}) = 469.0$  (Table 1; cf. also [4]<sup>-</sup>).  $\delta(^{35}\text{Cl}) = 363.7$  of the partly chlorinated [3]<sup>-</sup> lies between the shifts of [2]<sup>-</sup> and exhaustively chlorinated [1]<sup>-</sup> (274.5 ppm).<sup>32</sup> Our measured  $\delta(^{35}\text{Cl})$  values were verified by spin-orbit relativistic DFT calculations,<sup>72–74,76–79</sup> which gave an excellent fit after scaling according to the following linear equation:  $\delta(^{35}\text{Cl}, \text{scaled}) = 0.8739 \cdot \delta(^{35}\text{Cl}, \text{calcd}) - 8.3536$  (cf. the Supporting Information for more details).

As discussed above, our early attempts at the synthesis of  $[\text{nBu}_4\text{N}][\mathbf{4}]$  from  $[\text{nBu}_4\text{N}][\mathbf{1}]$  and  $\text{Me}_2\text{AlH}$  (without  $\text{Me}_3\text{Al}$ ) resulted in a product mixture. In the  $^{35}\text{Cl}\{^1\text{H}\}$  NMR spectrum, this mixture gave rise to a multitude of resonances in the range 469.1–456.8 ppm. Since the two range limits fit to the shift values of  $[\text{nBu}_4\text{N}][\mathbf{2}]$  (8 core-SiH) and  $[\text{nBu}_4\text{N}][\mathbf{4}]$  (8 core-SiMe; Table 1), it is reasonable to assume that the resonances in between belong to mixed-substituted silafullerenes [ $n$  core-SiH + (8- $n$ ) core-SiMe;  $n = 1$ –7]. On the other hand, this conclusion is at odds with previous experience gained from  $[\text{Cl@Si}_{20}(\text{H/Cl})_{20}]^-$  silafullerenes, where any symmetry breaking had resulted in such severely broadened  $^{35}\text{Cl}$  signals that they were no longer detectable. One possible solution of this riddle would be that unsymmetrically distributed core-SiH/SiMe leads to a smaller electric field gradient (EFG) than unsymmetrically distributed core-SiH/SiCl. A smaller EFG should accelerate the relaxation of the  $^{35}\text{Cl}$  quadrupole nucleus to a lesser extent, resulting in a narrower resonance line.

The influence of the substitution pattern on the EFG within a silafullerene cage was investigated by DFT calculations on selected derivatives. To a good approximation, the NMR line width  $\Delta\nu$  is proportional to the square of the largest principal component of the EFG tensor,  $V_{33}^2$  (cf. the Supporting Information for more details).<sup>80–82</sup> For  $T_h$ -symmetric  $[\text{Cl@Si}_{20}\text{H}_{12}\text{Cl}_8]^-$  and [4]<sup>-</sup>, the computed  $V_{33}^2$  values for the endohedral  $\text{Cl}^-$  ion are close to 0<sup>83</sup> (compare the exohedral Cl substituents of  $[\text{Cl@Si}_{20}\text{H}_{12}\text{Cl}_8]^-$  with  $V_{33}^2 = 4.44$  a.u.). For the less symmetric isomer of  $[\text{Cl@Si}_{20}\text{H}_{12}\text{Cl}_8]^-$ , in which one H and one Cl atom have changed places, and for  $[\text{Cl@Si}_{20}\text{H}_{11}\text{Cl}_9]^-$ , in which one H atom is replaced by one Cl atom,  $V_{33}^2$  increases to values in the order of  $1 \times 10^{-2}$  a.u. In stark contrast, hundredfold smaller values  $V_{33}^2 \leq 1 \times 10^{-4}$  a.u. were computed for an isomer of [4]<sup>-</sup>, in which one cage-bonded Me group and one silyl-bonded H atom have changed places, and for  $[\text{Cl@Si}_{20}(\text{SiH}_3)_{12}\text{HMe}_7]^-$ , in which one cage-bonded Me group is replaced by one H atom. Therefore, it should indeed be more likely to detect  $^{35}\text{Cl}$  NMR signals of [4]<sup>-</sup>-type than of  $[\text{Cl@Si}_{20}\text{H}_{12}\text{Cl}_8]^-$ -type compounds with slight deviations from the perfect  $T_h$ -symmetric substitution pattern.

## CONCLUSION

Starting from the perchlorinated silafullerene  $[\text{nBu}_4\text{N}][\text{Cl@Si}_{20}(\text{SiCl}_3)_{12}\text{Cl}_8]$ , we developed facile synthesis routes to the perhydrogenated  $[\text{nBu}_4\text{N}][\text{Cl@Si}_{20}(\text{SiH}_3)_{12}\text{H}_8]$  ( $[\text{nBu}_4\text{N}][\mathbf{2}]$ ;  $i\text{Bu}_2\text{AlH}$  in *o*DFB), the partially hydrogenated  $[\text{nBu}_4\text{N}][\text{Cl@Si}_{20}(\text{SiH}_3)_{12}\text{Cl}_8]$  ( $[\text{nBu}_4\text{N}][\mathbf{3}]$ ;  $i\text{Bu}_2\text{AlH}$  in *o*DFB/ $\text{Et}_2\text{O}$ ), and the regioselectively mixed-substituted  $[\text{nBu}_4\text{N}][\text{Cl@Si}_{20}(\text{SiH}_3)_{12}\text{Me}_8]$  ( $[\text{nBu}_4\text{N}][\mathbf{4}]$ ;  $\text{Me}_2\text{AlH}/\text{Me}_3\text{Al}$  in *o*DFB/toluene, *o*DFB = *ortho*-difluorobenzene). Accord-

ing to quantum-chemical calculations,  $\text{SiCl}_3$  hydrogenation (via an  $\text{S}_{\text{N}}2$ -Si-type scenario) is kinetically more favorable than core-SiCl hydrogenation (via an  $\text{S}_{\text{Ni}}$ -Si-type transition state). This explains why taming the reactivity of  $i\text{Bu}_2\text{AlH}$  through  $\text{Et}_2\text{O}$ -adduct formation suppresses core hydrogenation and ultimately furnishes [3]<sup>-</sup> instead of [2]<sup>-</sup>. Experimentally obtained structural and spectroscopic parameters of [2]<sup>-</sup>–[4]<sup>-</sup> are in very good agreement with computed values. A theoretical assessment of the electric field gradients (EFGs) experienced by the encapsulated  $\text{Cl}^-$  ions of selected silafullerenes helps to understand why the corresponding  $^{35}\text{Cl}$  resonances of [4]<sup>-</sup>-type compounds are detectable even if the strict  $T_h$  symmetry is violated, whereas these signals are broadened beyond detection in comparable symmetry-broken H/Cl-mixed silafullerenes.

As an outlook, the Si–H bonds of [2]<sup>-</sup>–[4]<sup>-</sup> are valuable functional groups for subsequent hydrosilylation<sup>84,85</sup> or dehydrogenative Si–Si coupling reactions.<sup>86,87</sup> Resulting silafullerene oligomers would be nano-sized compounds bridging the gap between small-molecule silanes and extended silicon-based solids.<sup>88–91</sup>

## ASSOCIATED CONTENT

The Supporting Information is available free of charge at <http://pubs.acs.org>.

Experimental and computational details, as well as characterization data (PDF)

Cartesian coordinates of computed molecular structures (ZIP)

X-ray crystallographic data (CIF)

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The authors declare no competing financial interests.

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- (65) According to Bent's rule, the  $\text{H}_3\text{Si}$  group will direct a hybrid orbital with the highest  $p$  character toward the cluster with the highest group electronegativity. Since these group electronegativities follow the order  $[4]^- < [2]^- < [3]^-$ , the  $p$  character of the  $\text{H}_3\text{Si-Si}(\text{cluster})$  bonds and, correspondingly, the  $s$  character of the  $\text{H}_2\text{Si-H}$  bonds should obey the same trend: Bent, H. A. An Appraisal of Valence-bond Structures and Hybridization in Compounds of the First-row Elements. *Chem. Rev.* **1961**, *61*, 275–311. <https://doi.org/10.1021/cr60211a005>
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- (69) Although  $J(\text{H,Cl})$  coupling is only resolved for protons directly bonded to the  $\text{Si}_{20}$  core, we see a weak cross peak between the  $\text{SiH}_3$  and  $^{35}\text{Cl}$  resonances in the  $^1\text{H}^{35}\text{Cl}$ -HMBC spectrum; a more intense cross peak appears between the  $\text{SiH}$  and  $^{35}\text{Cl}$  resonances.
- (70) As a characteristic NMR feature of our silafullerenes, the  $^{29}\text{Si}$  nuclei of the cage vertices ( $\text{Si}^0/\text{Si}^{\text{I}}$ ) are strongly deshielded relative to  $\text{Si}^0/\text{Si}^{\text{I}}$  centers of comparable open-chain oligosilanes; signals from  $\text{Si}^{\text{III}}$  in peripheral  $\text{SiR}_3$  substituents of the same compound classes appear in the same region. Examples: (a)  $[\text{nBu}_4\text{N}][2]$ :  $\delta(^{29}\text{Si}) = -58.5$  ( $\text{Si}^0$ ),  $-14.9$  ( $\text{Si}^{\text{I}}$ ),  $-93.7$  ( $\text{Si}^{\text{III}}$ );  $\text{HSi}(\text{SiH}_3)_3$ :  $\delta(^{29}\text{Si}) = -137.4$  ( $\text{Si}^{\text{I}}$ ),  $-95.7$  ( $\text{Si}^{\text{III}}$ );  $\text{Si}(\text{SiH}_3)_4$ :  $\delta(^{29}\text{Si}) = -165.7$  ( $\text{Si}^0$ ),  $-90.4$  ( $\text{Si}^{\text{III}}$ ).<sup>33</sup> (b)  $[\text{nBu}_4\text{N}][1]$ :  $\delta(^{29}\text{Si}) = 31.1$  ( $\text{Si}^{\text{I}}$ );  $[\text{nBu}_4\text{N}][3]$ :  $\delta(^{29}\text{Si}) = 51.5$  ( $\text{Si}^{\text{I}}$ );  $(\text{Me}_3\text{Si})_3\text{SiCl}$ :  $\delta(^{29}\text{Si}) = -13.3$  ( $\text{Si}^{\text{I}}$ );<sup>92</sup>  $[\text{nBu}_4\text{N}][2]$ :  $\delta(^{29}\text{Si}) = -14.9$  ( $\text{Si}^{\text{I}}$ );  $(\text{Me}_3\text{Si})_3\text{SiH}$ :  $\delta(^{29}\text{Si}) = -115.4$  ( $\text{Si}^{\text{I}}$ );<sup>92</sup>  $[\text{nBu}_4\text{N}][4]$ :  $\delta(^{29}\text{Si}) = 19.1$  ( $\text{Si}^{\text{I}}$ );  $(\text{Me}_3\text{Si})_3\text{SiMe}$ :  $\delta(^{29}\text{Si}) = -87.9$  ( $\text{Si}^{\text{I}}$ ). For  $\delta(^{29}\text{Si})$  of  $(\text{Me}_3\text{Si})_3\text{SiX}$  ( $\text{X} = \text{Cl}, \text{H}, \text{Me}$ ), see: Marsmann, H. C.; Raml, W.; Hengge, E.  $^{29}\text{Si}$ -Kernresonanzmessungen an Polysilanen 2. Isotetrasilane. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35*, 1541–1547. <https://doi.org/10.1515/znbn-1980-1211>
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