# **Inorganic Chemistry**



[Et₄N]

### Trapping Experiments on a Trichlorosilanide Anion: a Key Intermediate of Halogenosilane Chemistry

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Supporting Information

ABSTRACT: Treatment of Si<sub>2</sub>Cl<sub>6</sub> with [Et<sub>4</sub>N][BCl<sub>4</sub>] in CH<sub>2</sub>Cl<sub>2</sub> furnished Cl<sub>3</sub>Si–SiCl<sub>3</sub> + Bl<sub>3</sub> + [Et<sub>4</sub>N]Cl CH<sub>2</sub>Cl<sub>2</sub> [Et<sub>4</sub>N][l<sub>3</sub>Si–Bl<sub>3</sub>] the known products of a chloride-induced disproportionation reaction of the disilane, such as SiCl<sub>4</sub>, [Si(SiCl<sub>3</sub>)<sub>3</sub>]<sup>-</sup>, and [Si<sub>6</sub>Cl<sub>12</sub>·2Cl]<sup>2-</sup>. No Si-B-bonded products were detectable. In contrast, the addition of  $Si_2Cl_6$  to  $[Et_4N][BI_3Cl]$ afforded the Si-B adduct [Et<sub>4</sub>N][I<sub>3</sub>SiBI<sub>3</sub>]. Thus, a quantitative Cl/I exchange at the silicon atom accompanies the trihalogenosilanide formation.  $[Et_4N][I_3SiBI_3]$  was also accessible from a mixture of  $Si_2I_{6}$ ,  $[Et_4N]I_1$ , and  $BI_3$ .

According to X-ray crystallography, the anion  $[I_3SiBI_3]^-$  adopts a staggered conformation with an Si–B bond length of 1.977(6) Å. Quantum-chemical calculations revealed a polar covalent Si–B bond with significant contributions from intramolecular I…I dispersion interactions.

#### INTRODUCTION

Perchlorinated oligosilanes (PCSs) are valuable precursors for the deposition of silicon thin films. The PCS sample is either thermolyzed directly to give elemental silicon in a disproportionation reaction<sup>1</sup> or converted to the corresponding perhydrogenated oligosilanes prior to thermolysis.<sup>2,3</sup>

Apart from these industrial applications, PCSs are also attractive in their own right because they exhibit rich molecular chemistry, which often proceeds via intriguing intermediates to finally furnish products with sophisticated structural frameworks. The underlying mechanistic pathways are characterized by the tendency of covalent Si-Si bonds to undergo rearrangement reactions, a dynamic behavior that can be triggered deliberately by the addition of Lewis bases. As one of the first examples, Urry and co-workers reported that hexachlorodisilane (Si<sub>2</sub>Cl<sub>6</sub>) undergoes quantitative transformation to perchlorinated neopentasilane Si(SiCl<sub>3</sub>)<sub>4</sub> and SiCl<sub>4</sub> upon the catalytic action of various trialkylamines  $(R_3N)$ .<sup>4–9</sup>

Recent experimental and quantum-chemical studies have shown that dichlorosilylene adducts R<sub>3</sub>N-SiCl<sub>2</sub> play a decisive role in the course of this reaction.<sup>10-13</sup> Certain diarylmethanones can also liberate dichlorosilylenes from Si<sub>2</sub>Cl<sub>6</sub>, albeit only at elevated temperatures. Under these conditions, the resulting ketone-SiCl<sub>2</sub> adducts ultimately lead to the reductive coupling of carbonyl compounds to afford tetraarylethylenes (sila-McMurry reaction).<sup>14</sup> Reduction reactions have also successfully been performed on organic nitro compounds, phosphine oxides, and sulfoxides by means of Si<sub>2</sub>Cl<sub>6</sub> or HSiCl<sub>3</sub>/  $R_3N$ .<sup>15–21</sup> In most cases, donor-stabilized SiCl<sub>2</sub> has been proposed as the key intermediate.

One of the simplest Lewis bases that can be employed for the disproportionation of Si<sub>2</sub>Cl<sub>6</sub> is the chloride ion. Depending on the reaction temperatures and the molar ratios of the starting materials, treatment of the disilane with soluble chloride salts [R<sub>4</sub>N]Cl in CH<sub>2</sub>Cl<sub>2</sub> leads either to open-chain oligosilanechloride adducts, such as  $[Si_3Cl_9]^-$  and the branched  $[Si_6Cl_{15}]^-$ , or to chloride-complexed cyclohexasilanes, such as  $[Si_6Cl_{12}]$ .  $2Cl^{2-}$  (Figure 1).<sup>22</sup> The propensity of the underlying PCSs to coordinate additional chloride ions not only testifies to the high Lewis acidity of these species but also facilitates their isolation and crystallographic characterization. In the case of the cyclohexasilane diadduct, the two chloride ions can be conveniently abstracted using AlCl<sub>3</sub>, which opens up a facile route for preparing Si<sub>6</sub>Cl<sub>12</sub> on a larger scale.<sup>23</sup> In addition to chainlike and cyclic PCSs, monodisperse silicon cluster compounds are also readily accessible: Our group has recently prepared the first Si<sub>20</sub> dodecahedrane ("silafullerane") from Si<sub>2</sub>Cl<sub>6</sub>, [nBu<sub>4</sub>N]Cl, and nBu<sub>3</sub>N through a one-step self-assembly protocol in 27% yield (Figure 1).<sup>24</sup> Each silafullerane cage hosts an endohedral chloride ion and thereby acquires a negative charge. Moreover, the clusters are decorated regioselectively with 12 SiCl<sub>3</sub> substituents, which may serve as anchor groups to link individual silafulleranes together.

A quantum-chemical assessment of the chloride-induced disproportionation of Si<sub>2</sub>Cl<sub>6</sub> indicates an initial nucleophilic attack of the chloride ion on one of the silicon atoms with

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**Figure 1.** X-ray crystallographically determined molecular structures of the anions  $[Si_3Cl_9]^-$  (top left),  $[Si_6Cl_{15}]^-$  (top right),  $[Si_6Cl_{12}\cdot 2Cl]^{2-}$  (bottom left), and  $[Si_{32}Cl_{45}]^-$  (bottom right).

subsequent heterolytic cleavage of the Si–Si bond and formation of SiCl<sub>4</sub> and an [SiCl<sub>3</sub>]<sup>-</sup> anion.<sup>22</sup> [SiCl<sub>3</sub>]<sup>-</sup> ions have previously been proposed as key intermediates of the so-called "Benkeser reactions", which employ a HSiCl<sub>3</sub>/R<sub>3</sub>N combination to introduce SiCl<sub>3</sub> groups into various different substrates via a nucleophilic pathway.<sup>25–33</sup> In view of these mechanistic models, [SiCl<sub>3</sub>]<sup>-</sup> represents an important link between the chemistries of Si<sub>2</sub>Cl<sub>6</sub>, on the one hand, and HSiCl<sub>3</sub>, on the other hand. A second link relates [SiCl<sub>3</sub>]<sup>-</sup> to SiCl<sub>2</sub> chemistry because the ion can be viewed as a chloride-stabilized dichlorosilylene. However, only a small amount of experimental data have been gathered on [SiCl<sub>3</sub>]<sup>-</sup> to date, despite its importance for preparative (organo)silicon chemistry and its formal analogy to the well-known [CX<sub>3</sub>]<sup>-</sup> ions (X = Cl, Br, I; compare the Appel,<sup>34</sup> Corey–Fuchs,<sup>35</sup> and haloform<sup>36</sup> reactions).

Collision-induced dissociation experiments carried out in a mass spectrometer on mixtures of Si(SiCl<sub>3</sub>)<sub>4</sub> and [Et<sub>4</sub>N]Cl in  $CH_2Cl_2$  produced a peak at m/z 134.9, which is assignable to [SiCl<sub>3</sub>]<sup>-</sup> and thus indicates that this ion can indeed be generated in the gas phase.<sup>37</sup> Moreover, the above-mentioned species [Si<sub>3</sub>Cl<sub>9</sub>]<sup>-</sup> can be viewed not only as a chloride adduct of the trisilane Si<sub>3</sub>Cl<sub>8</sub> but also as the trapping product of [SiCl<sub>3</sub>]<sup>-</sup> by 1 equiv of the starting material Si2Cl6. This latter result encouraged us to try to trap [SiCl<sub>3</sub>]<sup>-</sup> also with other Lewis acids and thereby to prove its intermediate appearance. In order to be able to unequivocally distinguish between the trapping reagent and a coordinating  $[SiCl_3]^-$  ion, the Lewis acid needs to be silicon-free, which led to our choice of boron trihalides. Herein, we report on the reactions of  $Si_2X_6$  with  $[R_4N]X$  in the presence of  $BX_3$  (X = Cl, I) and on the characterization of the unique Si-B adduct [I<sub>3</sub>SiBI<sub>3</sub>]<sup>-</sup> by means of X-ray crystallography. The electronic structure of the anion was elucidated by quantum-chemical calculations.

#### RESULTS AND DISCUSSION

**Reactions between Si<sub>2</sub>X<sub>6</sub>, [R<sub>4</sub>N]X, and BX<sub>3</sub> (X = Cl, l).** In order to avoid halogen scrambling, we first selected BCl<sub>3</sub> to trap the putative  $[SiCl_3]^-$  ion. A fundamental problem in designing the experiment lies in the fact that the Lewis acid has to already be present when the highly reactive  $[SiCl_3]^-$  is generated. Thus, Si<sub>2</sub>Cl<sub>6</sub> and BCl<sub>3</sub> will necessarily compete for the added chloride ions, and one has to make sure that Cl<sup>-</sup> will not just neutralize the boron Lewis acid without getting a chance to dispropor-

tionate Si<sub>2</sub>Cl<sub>6</sub>. We have previously shown that the Lewis acidity of BCl<sub>3</sub> is comparable to that of *cyclo*-Si<sub>6</sub>Cl<sub>12</sub>.<sup>23</sup> which made us confident that the chloride affinity of Si<sub>2</sub>Cl<sub>6</sub> is also sufficiently high to abstract chloride ions from preformed [BCl<sub>4</sub>]<sup>-</sup> complexes in a dynamic equilibrium. A formal metathesis reaction could therefore lead from [BCl<sub>4</sub>]<sup>-</sup> and Si<sub>2</sub>Cl<sub>6</sub> to [Cl<sub>3</sub>SiBCl<sub>3</sub>]<sup>-</sup> and SiCl<sub>4</sub>.

Given these considerations, we first prepared a suspension of  $[Et_4N][BCl_4]$  in an NMR tube by mixing equimolar solutions of BCl<sub>3</sub> and  $[Et_4N]Cl$  in  $CH_2Cl_2.^{38}$  After 1 equiv of neat Si\_2Cl\_6 had been added at room temperature, an exothermic reaction occurred, but the visual appearance of the mixture remained essentially the same. The sample was vacuum-sealed and investigated by <sup>11</sup>B and <sup>29</sup>Si NMR spectroscopy. The <sup>11</sup>B NMR spectrum showed only one resonance, which was assignable to the  $[BCl_4]^-$  ion ( $\delta = 6.6$ ).<sup>39</sup> The <sup>29</sup>Si NMR spectrum contained no signal for residual Si<sub>2</sub>Cl<sub>6</sub> ( $\delta = -6.6$ ),<sup>24</sup> but numerous other resonances with chemical shift values characteristic of SiCl<sub>4</sub> ( $\delta$ = -18.9),<sup>22</sup> [Si(SiCl<sub>3</sub>)<sub>3</sub>]<sup>-</sup> ( $\delta$  = -137.9 and +29.9),<sup>37</sup> and chloride diadducts of (SiCl<sub>3</sub>-substituted) cyclohexasilanes (such as  $[Si_6Cl_{12} \cdot 2Cl]^{2-}$  in Figure 1).<sup>22</sup> These observations lead to the conclusion that disproportionation of Si<sub>2</sub>Cl<sub>6</sub> can indeed be induced by [BCl4]- ions. However, under the conditions applied, the vast majority of the generated [SiCl<sub>3</sub>]<sup>-</sup> intermediates further react with yet unconsumed Si<sub>2</sub>Cl<sub>6</sub> rather than with BCl<sub>3</sub>. As a consequence, the usually observed products of the chloride-induced assembly of PCSs are formed (Scheme 1a).<sup>22</sup>

Scheme 1. Reactions between  $Si_2X_{6}$ ,  $[R_4N]X$ , and  $BX_3$  (X = Cl, I)

(a) 1 Cl <sub>3</sub> Si–SiCl <sub>3</sub>	+ 1 BCl <sub>3</sub>	+ 1 CI⁻	CH <sub>2</sub> Cl <sub>2</sub>	$\begin{split} &SiCl_4 + [Si(SiCl_3)_3]^- + [Si_6Cl_{12}\bullet2Cl]^{2-} \\ &+ [1,1-(SiCl_3)_2Si_6Cl_{10}\bullet2Cl]^{2-} + [BCl_4]^- \end{split}$
(b) 1 Cl <sub>3</sub> Si–SiCl <sub>3</sub>	+ 2 Bl <sub>3</sub>	+ 1 Cl⁻	rt CH₂Cl₂	$[I_3Si-BI_3]^- + [BCI_nI_{4-n}]^- + SiCI_4 + SiCI_3I$
(c) 1 I <sub>3</sub> Si–SiI <sub>3</sub>	+ 1 Bl <sub>3</sub>	+ 1 I <sup>_</sup>	rt CH₂Cl₂	[I <sub>3</sub> Si–BI <sub>3</sub> ] <sup>−</sup> + [BCII <sub>3</sub> ] <sup>−</sup> + [BI <sub>4</sub> ] <sup>−</sup>

We next repeated the previous experiment but switched from  $BCl_3$  to  $BI_3$  for the following reasons: (i)  $BI_3$  is a much stronger Lewis acid than BCl<sub>2</sub>, (ii) iodinated products should crystallize more readily than their chlorinated congeners, (iii) the higher electron count of iodo substituents should facilitate product analysis by X-ray crystallography and energy-dispersive X-ray (EDX) spectroscopy. As a downside of this approach, two types of halogen atoms are now present in the sample such that various mixed-halogen species are likely to be formed. Indeed, an <sup>11</sup>B NMR spectroscopic investigation of the sample revealed the presence of all five possible tetrahalogenoborate anions  $[BCl_nI_{4-n}]^-$  (n = 0-4), and the corresponding <sup>29</sup>Si NMR spectrum contained the signals of SiCl<sub>4</sub> and SiCl<sub>3</sub>I (see the Supporting Information for more details). The NMR tube was stored at room temperature in the dark in order to avoid photolysis of iodoborane species. After 24 h, single crystals had grown on top of an amorphous precipitate, which were identified as [Et<sub>4</sub>N][I<sub>3</sub>SiBI<sub>3</sub>] by means of X-ray crystallography (Figure 2). Compound [Et<sub>4</sub>N][I<sub>3</sub>SiBI<sub>3</sub>] represents the desired borane adduct of an [SiX<sub>3</sub>]<sup>-</sup> ion; however, all originally siliconbonded chloro substituents have been replaced by iodine atoms. Improved yields of the adduct should thus be achievable by employing Si<sub>2</sub>Cl<sub>6</sub> and BI<sub>3</sub> in a 1:2 ratio rather than a 1:1 ratio. A corresponding synthesis was subsequently carried out



Figure 2. Solid-state structure of  $[Et_4N][I_3SiBI_3]$  (cation omitted for clarity; Si, blue; B, green): side view of the anion (left) and projection along the B–Si axis (right). Selected bond lengths [Å] and bond angles [deg]: Si–B = 1.977(6), Si–I = 2.457(2)/2.454(2)/2.451(2), B–I = 2.261(6)/2.249(6)/2.246(6); Si–B–I = 108.5(3)/110.8(3)/109.4(3), B–Si–I = 112.9(2)/112.2(2)/112.3(2), I–B–I = 108.9(2)/108.9(3)/110.2(3), I–Si–I = 106.8(1)/106.3(1)/105.9(1).

on a preparative scale and furnished crystals of  $[Et_4N][I_3SiBI_3]$  in 44% yield (Scheme 1b).

With the aim of minimizing the number of byproducts from which  $[Et_4N][I_3SiBI_3]$  has to be separated, we finally conducted the synthesis starting from  $Si_2I_6^{40}$   $[Et_4N]I$ , and  $BI_3$  in a stoichiometric ratio of 1:1:1 (Scheme 1c). Single crystals of [Et<sub>4</sub>N][I<sub>3</sub>SiBI<sub>3</sub>] grew upon storage of the mixture in the dark at room temperature for 10 days. The comparatively long reaction time is likely due to the poor solubilities of  $Si_2I_6$  and  $[Et_4N]I$  in CH<sub>2</sub>Cl<sub>2</sub>. An <sup>11</sup>B NMR spectrum recorded on the mother liquor revealed almost exclusively the resonance of the [BI4]<sup>-</sup> ion (cf. the Supporting Information for a plot of the spectrum).<sup>41</sup> Consequently, this sample of the Si-B adduct was used for elemental analysis and EDX spectroscopy. In contrast to  $[Et_4N][BI_4]$ , the target compound  $[Et_4N][I_3SiBI_3]$  is only sparingly soluble in CH<sub>2</sub>Cl<sub>2</sub> as well as all other common inert solvents. We, nevertheless, noticed a loss of crystalline material during extensive washing. In parallel, a resonance at  $\delta = -32.4$ , which we assign to an unknown decomposition product, became increasingly apparent in the <sup>11</sup>B NMR spectrum of the washing solution. The yield of the single-crystalline [Et<sub>4</sub>N]-[I<sub>3</sub>SiBI<sub>3</sub>] left over after repeated rinsing with CH<sub>2</sub>Cl<sub>2</sub> amounted to 31%.

**Characterization of** [Et<sub>4</sub>N][I<sub>3</sub>SiBI<sub>3</sub>]. The generally poor solubility of the adduct  $[Et_4N][I_3SiBI_3]$  precluded its characterization by solution-phase NMR spectroscopy. Solid-state magic-angle-spinning NMR spectroscopy also did not provide interpretable data, likely because the <sup>29</sup>Si NMR resonance is severely broadened due to coupling with the <sup>10</sup>B and <sup>11</sup>B nuclei (S = 3 and  $3/_2$ , respectively). The quadrupolar nature of the boron nuclei leads to a further broadening of the <sup>29</sup>Si NMR resonance. The experimental characterization of  $[Et_4N][I_3SiBI_3]$  will therefore be based on elemental analysis, EDX spectroscopy, and X-ray crystallography.

Elemental analysis of  $[Et_4N][I_3SiBI_3]$  gave satisfactory values for hydrogen [2.32% (requires: 2.17%)], carbon [11.05%]

(10.33%)], nitrogen [1.60% (1.51%)], iodine [79.7% (81.8%)], and silicon [3.51% (3.02%)]. According to EDX analysis, the crystals contained silicon and iodine in a ratio of Si:I = 1:5.7  $(\pm 0.04)$ . We note that the experimentally determined carbon/ hydrogen/nitrogen content is slightly too high, while the iodine content is somewhat too low. A contamination of the sample with a small amount of  $[Et_4N][BI_4]$  could well account for these deviations, however, the corresponding <sup>11</sup>B resonance should be detectable by NMR spectroscopy, which is not the case. Moreover, our EDX measurements do not support the presence of excess iodine (with respect to silicon). As an alternative explanation, we propose that the sample contains a few chloro substituents in place of the iodo substituents: In addition to the signals assignable to silicon and iodine atoms, the EDX measurements indeed showed a small signal indicating the presence of chlorine atoms (cf. the Supporting Information for a plot of the spectrum). As a conceivable chlorine source, we identified the solvent CH2Cl2, which undergoes some halogen exchange with BI3 to furnish small amounts of CH2ICl and BClI<sub>2</sub> (cf. the Supporting Information).

The ultimate proof of the composition of [Et<sub>4</sub>N][I<sub>3</sub>SiBI<sub>3</sub>] was provided by X-ray crystallography (Figure 2 and Table 1). The crystal lattice of the compound contains [Et<sub>4</sub>N]<sup>+</sup> cations and  $[I_3SiBI_3]^-$  anions in a 1:1 ratio. The anion can be interpreted as the adduct between  $[SiI_3]^-$  and  $BI_3$  with an Si-B bond length of 1.977(6) Å [cf. Si–B = 2.018(2) Å in the adduct between  $[SiEt_3]^-$  and 9H-9-borafluorene<sup>42</sup>]. As a prominent structural feature, [I<sub>3</sub>SiBI<sub>3</sub>]<sup>-</sup> adopts an almost perfectly staggered conformation with the absolute values of the smaller I-Si-B-I torsion angles ranging from  $56.8(3)^{\circ}$  to  $63.0(3)^{\circ}$ . The average Si-I bond length amounts to 2.454 Å and thus lies close to that of  $Si_2I_6$  [2.425(1) Å; Table 1]. The average B-I bond length also possesses almost the same value as that in the comparable P-B adduct Cy<sub>3</sub>PBI<sub>3</sub> (2.252 vs 2.241 Å; Cy = cyclohexyl). Both the silicon and boron centers are fully pyramidalized, which points toward a strong covalent Si-B bond

**Quantum-Chemical Calculations.** In order to obtain more information about the electronic structure of the  $[I_3SiBI_3]^-$  anion, quantum-chemical calculations were performed to answer the following questions: (i) Is the molecule mainly bound by a covalent Si–B bond or do intramolecular dispersion interactions between the six iodo substituents also play an important role? (ii) What is the driving force behind the observed Cl/I exchange reaction on the silicon center?

The computational studies were carried out using density functional theory. Geometry optimizations were conducted using the D3(BJ) dispersion-corrected<sup>45–49</sup> PBE0<sup>50</sup> hybrid functional in conjunction with the def2-QZVP<sup>51</sup> basis set. Final gas-phase single-point energies were obtained at the B2PLYP-

Table 1. Comparison of Experimentally Determined Bond Lengths and Bond Angles of  $[Et_4N][I_3SiBI_3]$  with the Corresponding Calculated Values<sup>*a*</sup>

entry	$[Et_4N]^+[I_3SiBI_3]^-$	calcd [I <sub>3</sub> SiBI <sub>3</sub> ] <sup>-</sup>	$[Et_3Si(H)BFlu]^-$	Cy <sub>3</sub> PBI <sub>3</sub>	I <sub>3</sub> SiSiI <sub>3</sub>
Si-B [Å]	1.977(6)	2.011	2.018(2)		
Si–I (avg) [Å]	2.454	2.474			2.425(1)
B–I (avg) [Å]	2.252	2.228		2.241	
$\Sigma(I-Si-I)$ [deg]	319.0	316.8			333.3
$\Sigma(I-B-I)$ [deg]	328.0	335.2		326.7	

<sup>*a*</sup>Key geometric parameters of three selected literature-known compounds are included for comparison.  $[Et_3Si(H)BFlu]^-$  = adduct between  $[SiEt_3]^-$  and 9*H*-9-borafluorene;  $Cy_3P$  = tricyclohexylphosphane.<sup>42-44</sup> Calculated bond lengths obtained at the PBE0-D3/def2-QZVP level of theory.

D3(BJ)<sup>52</sup>/def2-QZVP//PBE0-D3(BJ)/def2-QZVP level of theory. Gibbs free energies were obtained by summing the dispersion-corrected electronic energies, ro-vibrational corrections from a modified harmonic oscillator statistical treatment based on harmonic frequencies, and solvation corrections computed by means of the COSMO-RS<sup>53</sup> model (2014 parametrization for dichloromethane). All calculations were conducted with the *TURBOMOLE 7.0.2* program package<sup>54,55</sup> and *COSMOtherm*, version C3.0, release 16.01.<sup>56</sup> For further computational details, see the Supporting Information.

The solid-state structure of the  $[I_3SiBI_3]^-$  anion in a staggered conformation was reproduced in good accordance in the gas phase at the PBE0-D3(BJ)/def2-QZVP level of theory (Table 1). The strongly pyramidalized boron atom indicates a covalent B-Si bond. This assumption is supported by analysis of the localized molecular orbitals (LMOs) obtained at the PBE0/def2-QZVP(-g) level of theory. The LMO representing the B-Si bond is predominantly of the  $\sigma$  type with a major localization at the silicon center (populations: Si, 0.748; B, 0.335). The atomic orbitals involved in the B-Si bond are mainly of s character at the silicon center (s, 75.0%; p, 23.8%) and mainly of p character for the boron atom (s, 40.2%; p, 61.3%), which matches the expectation of an s-type lone pair at the  $[SiI_3]^-$  fragment, forming a strong bond with the vacant  $p_z$  orbital of the Lewis acid BI<sub>3</sub>. The calculated dissociation free energy of  $\Delta G_{\text{Diss}} = 24.3 \text{ kcal/mol}$  for  $[I_3 \text{SiBI}_3]^-$  further indicates a relatively strong B-Si bond [B2PLYP-D3(BJ)/def2-QZVP+COSMO-RS(CH<sub>2</sub>Cl<sub>2</sub>)//PBE0-D3(BJ)/def2-QZVP values].

Analysis of the relative energy contributions to the dissociation free energy (Table 2) indicates that dispersion

## Table 2. Dissociation Free Energies and Its Components [kcal/mol] at the B2PLYP-D3(BJ)/def2-QZVP+COSMO-RS(CH,Cl<sub>2</sub>)//PBE0-D3(BJ)/def2-QZVP Level of Theory<sup>a</sup>

structure	$\Delta G_{ m Diss}$	$\Delta E_{\rm E}$	$\Delta G_{ m RRHO}$	$\Delta G_{ m solv}$	$\Delta E_{\mathrm{D3}}$
[I <sub>3</sub> SiBI <sub>3</sub> ] <sup>-</sup>	24.3	35.9	-16.5	-4.2	9.1
$^{t}\Delta G_{\rm Diss} = {\rm dissc}$	ciation free	energy; $\Delta$	$E_{\rm E} = {\rm electron}$	nic gas-phas	se energy

difference;  $\Delta G_{\text{RRHO}}$  = ro-vibrational energy correction difference;  $\Delta G_{\text{solv}}$  = relative solvation energy correction difference;  $\Delta E_{\text{D3}}$  = D3 dispersion energy difference.

interactions ( $\Delta E_{D3} = 9.1 \text{ kcal/mol}$ ) contribute significantly to stabilization of the  $[\text{SiI}_3]^-$  and  $\text{BI}_3$  fragments upon bond formation (for more detailed information on the atom pairwise dispersion treatment and the corresponding energy components in all considered compounds, see the Supporting Information).

Because the full mechanism of the formation of  $[I_3SiBI_3]^$ has yet to be elucidated, we investigated the reaction free energies for a stepwise halide exchange between the  $[SiX_3]^$ and  $BX_3$  fragments (Scheme 2). This consideration indicates that the Cl<sup>-</sup>/l<sup>-</sup> exchange starting from  $[SiCl_3]^-$  with BI<sub>3</sub> is overall strongly exergonic ( $\Delta G_R = -18.2 \text{ kcal/mol}$ ). Each exchange step is exergonic itself until a complete halide exchange between the silicon and boron fragments has taken place. We conclude that the strongly exergonic exchange reactions represent the driving force of the  $[I_3SiBI_3]^$ formation. The reaction free energy is dominated by the enthalpic component.

#### CONCLUSION

It has been postulated that the deprotonation of HSiCl<sub>3</sub> with amine bases as well as the chloride-induced disproportionation of Si<sub>2</sub>Cl<sub>6</sub> result in the formation of  $[SiCl_3]^-$  ions as the primary intermediates. However, to date, only a small amount of experimental evidence exists to support this suggestion. We have now shown that the treatment of Si<sub>2</sub>Cl<sub>6</sub> with  $[Et_4N]Cl$  in the presence of BI<sub>3</sub> leads to the single-crystalline adduct  $[Et_4N][I_3SiBI_3]$ . The isolation of  $[Et_4N][I_3SiBI_3]$  not only represents the first successful trapping of a trihalogenosilanide with a boron Lewis acid but also reveals a quantitative Cl/I exchange reaction at the silicon center under the conditions applied. The same product was obtained from a mixture of Si<sub>2</sub>I<sub>6</sub>/  $[Et_4N]I$ , and BI<sub>3</sub>.

The Si–B bond length amounts to 1.977(6) Å (calculated value: 2.011 Å); the SiI<sub>3</sub> and BI<sub>3</sub> fragments are pronouncedly pyramidalized. These experimental observations, together with quantum-chemical calculations, point toward a strong, yet highly polarized covalent bond. The atomic orbitals involved in bonding possess mainly s character at the silicon center and p character at the boron center. In addition to the direct Si–B dative bond, intramolecular dispersion interactions between the six iodo substituents contribute significantly to the stability of the [I<sub>3</sub>SiBI<sub>3</sub>]<sup>-</sup> anion ( $\Delta G_{\text{Diss}} = 24.3$  kcal/mol; D3 dispersion contribution of 9.1 kcal/mol).

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00216.

Experimental details, characterization data including plots of <sup>1</sup>H, <sup>11</sup>B, and <sup>29</sup>Si NMR spectra, EDX data for [Et<sub>4</sub>N][I<sub>3</sub>Si–BI<sub>3</sub>], and computational details (PDF) X-ray crystal structure analysis (CIF) XYZ plot (XYZ)

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Scheme 2. Calculated Relative Gibbs Free Energies of the Species Involved in Progressive Halide Exchange between  $[SiCl_3]^-$  and BI<sub>3</sub> at the B2PLYP-D3(BJ)/def2-QZVP+COSMO-RS(CH<sub>2</sub>Cl<sub>2</sub>)//PBE0-D3(BJ)/def2-QZVP Level of Theory<sup>*a*</sup>



"All energies [kcal/mol] are given relative to the corresponding starting compound  $[SiCl_3]^-$  in the context of the given model reaction.

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#### **Author Contributions**

J.T. designed and conducted all syntheses (assisted by B.K.) and collected the X-ray data; M.Bu. carried out all quantumchemical calculations; M.Bo. processed the X-ray data and solved and refined the structure; H.-W.L. was involved in the study design; M.W. supervised the experimental studies; M.W., J.T., M.Bu., and S.G. wrote the paper, and all of the authors discussed the results and commented on the manuscript.

#### Notes

The authors declare no competing financial interest.

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