

Boron Clusters

Activation of CS₂ and CO₂ by Silylium Cations

Carsten Jenne,* Marc C. Nierstenhöfer, and Valentin van Lessen^[a]

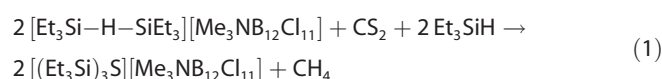
Abstract: The hydride-bridged silylium cation [Et₃Si–H–SiEt₃]⁺, stabilized by the weakly coordinating [Me₃NB₁₂Cl₁₁][−] anion, undergoes, in the presence of excess silane, a series of unexpected consecutive reactions with the valence-isoelectronic molecules CS₂ and CO₂. The final products of the reaction with CS₂ are methane and the previously unknown [(Et₃Si)₃S]⁺ cation. To gain insight into the entire reaction cascade, numerous experiments with varying conditions were performed, intermediate products were intercepted, and their structures were determined by X-ray crystallography. Besides the [(Et₃Si)₃S]⁺ cation as the final product, crystal structures of [(Et₃Si)₂SMe]⁺, [Et₃SiS(H)Me]⁺, and [Et₃SiOC(H)OSiEt₃]⁺ were obtained. Experimental results combined with supporting quantum-chemical calculations in the gas phase and solution allow a detailed understanding of the reaction cascade.

The chemical activation of carbon dioxide is the key step for its utilization as a cheap carbon source.^[1] Typically, such reactions are catalyzed by transition-metal compounds. Much less is known about activation by main group compounds. Potentially promising candidates for the activation of small molecules are, besides others,^[2] Lewis acidic silylium cations, which already found application in catalytic processes.^[3] In condensed phase, with few exceptions,^[4] silylium cations are not free but coordinated to neutral molecules such as solvent molecules or to the counter anion, which significantly reduces their reactivity.^[5] A good compromise between stability and reactivity are hydride-bridged silylium cations [R₃Si–H–SiR₃]⁺,^[6,7] for which stabilization of the empty silicon π-orbital by the hydride is preferred over a Wheland solvent complex [R₃Si–solvent]⁺ for electron-deficient arenes.^[6] In 2012 Müller et al. reported the

insertion of CO₂ into the hydride-bridged silylium cation [R₃Si–H–SiR₃]⁺.^[8] Hydrolysis of the postulated intermediates [R₃SiOC(H)OSiR₃]⁺ and [(Et₃Si)₂OMe]⁺ (R = Et, *i*Pr) yielded formic acid and methanol, respectively, as the final products.^[8] The electrophilic aromatic substitution of arenes with CO₂ mediated by silylium ions is known.^[9] Only limited data are available for reactions of silylium ions with other small main group molecules. In 2010 we published the insertion reaction of sulfur dioxide into a hydride-bridged silylium cation to give [Pr₃SiOS(H)OSiPr₃]⁺.^[10] Recently, the silylium ion mediated activation of carbon monoxide has been reported by Oestreich et al.^[11] Silylium-catalyzed C–F bond activation followed by trapping of carbon disulfide resulted in the formation of an *S*-heterocyclic carbene.^[12]

Since C–F activation of fluoralkyls and -aryls by silylium cations is well known,^[13] fluorine-free weakly coordinating anions like halogenated *closo*-carborates and *closo*-borates are preferred counter anions to study such systems.^[14] Herein, we report on the reaction of the valence-isoelectronic three-atomic molecules CS₂ and CO₂ with hydride-bridged [R₃Si–H–SiR₃]⁺ silylium cations utilizing the chlorinated weakly coordinating [Me₃NB₁₂Cl₁₁][−] counter anion.^[15]

In a typical experiment, [Et₃Si–H–SiEt₃][Me₃NB₁₂Cl₁₁] was dissolved in dry 1,2-difluorobenzene and CS₂ or CO₂ was added at low temperatures. Numerous experiments were performed, in which stoichiometry, temperature and reaction time was varied (see section S2 of the Supporting Information for full experimental details). Even at low temperatures the reactions typically yielded mixtures of products as judged by ²⁹Si NMR spectroscopy. However, the reaction of [Et₃Si–H–SiEt₃][Me₃NB₁₂Cl₁₁] with 10 equivalents of CS₂ and 4 equivalents of Et₃SiH in 1,2-difluorobenzene for 3 h at room temperature (Eq. (1)) yielded colorless crystals of [(Et₃Si)₃S][Me₃NB₁₂Cl₁₁] (Figure 3) in a reproducible manner as the main product. The compound contains the unknown tris(triethylsilyl)sulfonium cation [(Et₃Si)₃S]⁺. Trisilylated sulfonium ions were detected for the first time by Olah and Prakash in 2000 in a low temperature NMR study, in which [Me₃Si]⁺ was reacted with the thiosilylether Me₃Si–S–SiMe₃ in dichloromethane.^[16] Based on this approach very recently Schulz and co-workers have succeeded in the synthesis of the chalconium salts [(Me₃Si)₃Ch][B(C₆F₅)₄] (Ch = S, O).^[17]



Silylium salts [R₃Si–H–SiR₃][Me₃NB₁₂Cl₁₁] with a variety of different substituents (R₃Si = *i*Pr₃Si, *t*Bu₃Si, Me₂EtSi) or performing the reaction at varying reaction conditions did not lead to the formation of trisilylated sulfonium salts (see section S2 in the

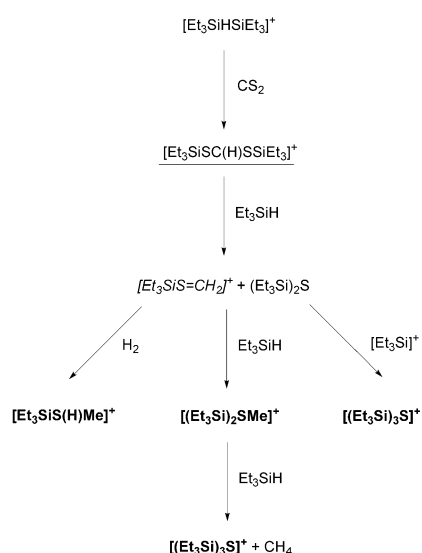
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<https://doi.org/10.1002/chem.202005003>. It contains full synthetic and quantum-chemical details.

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Supporting Information for full experimental details). However, during these experiments several crystal structures of intermediates could be obtained, which give detailed insight into the reaction cascade started by the activation of CS₂ by the silylium cations. Besides crystal structure determinations on the isolated products, low temperature NMR experiments in solution and quantum-chemical calculations were performed to aid the understanding. The following discussion is mainly restricted to R = Et, although some of the intermediates were isolated with other substituents as well.

The reaction cascade (Scheme 1 and Table 1) starts with insertion of CS₂ into the hydride-bridged [Et₃Si–H–SiEt₃]⁺ cation ($\Delta G_r = -97$ kJ mol⁻¹, step 1). Note that this first step likely is more complicated (see Table S15). The CS₂ inserted cation [Et₃SiSC(H)SSiEt₃]⁺ could not be isolated in the solid state even at low temperature, but NMR experiments gave some evidence for its presence (Figures S9 and S12). In the ²⁹Si NMR spectrum this cation was assigned to a resonance at 53.5 ppm. The chemical shift is typical of silylium cations with small molecules



Scheme 1. Proposed reaction cascade for the reaction of CS₂ with [Et₃Si–H–SiEt₃]⁺. Cations written in bold were observed experimentally in crystal structure determinations. The underlined cation was crystallized as its oxygen analogue from the identical reaction with CO₂. The cation written in italics is a proposed intermediate but could not be detected experimentally.

inserted in the Si–H–Si moiety. For the CO₂ analogue [Et₃SiOC(H)OSiEt₃]⁺ a chemical shift of 55.7 ppm was found.^[8] A related SO₂ insertion product was reported before and has been identified by its crystal structure.^[10] From an experiment with CO₂ without excess of silane single crystals of the CO₂ inserted cation in the salt [(Et₃SiOC(H)OSiEt₃)] [Me₃NB₁₂Cl₁₁](Et₃Si)₂O (Figure 1) could be obtained, which presents further evidence of the insertion of CS₂ and CO₂, respectively, into the hydride-bridged [Et₃Si–H–SiEt₃]⁺ cation. The thermodynamics for the identical reaction sequence with CO₂ instead of CS₂ were calculated for comparison and are compiled in Table S16 in the Supporting Information. In general, the reactions with CO₂ are less exergonic than those with CS₂ and the formation of the [(Et₃Si)₃O]⁺ cation according to equation 3 in Table 1 is even endergonic. The calculated Si–O distances in the oxygen analogue are much shorter. It is suggested that transition states due to sterical hindrance become less favorable in the CO₂ case. The structural parameters of the [Et₃SiOC(H)OSiEt₃]⁺ cation are in accordance with those obtained by quantum-chemical calculations. Selected values are given in the caption of Figure 1.

In the second step a hydride from another molecule of Et₃SiH is transferred onto the CS₂ inserted [Et₃SiSC(H)SSiEt₃]⁺ cation, which leads to the elimination of hexaethyldisilathiane (Et₃Si)₂S and the formation of the [Et₃SiS=CH₂]⁺ cation is assumed. This reaction is calculated to be only slightly exergonic by -12 kJ mol⁻¹. Hexaethyldisilathiane (Et₃Si)₂S, was identified

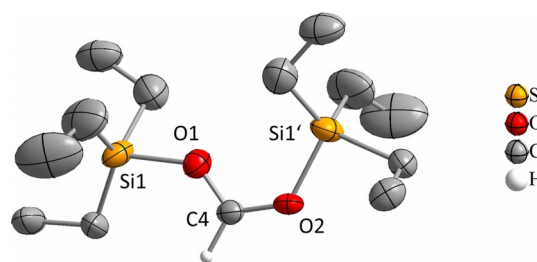


Figure 1. The cation in the crystal structure of [Et₃SiOC(H)OSiEt₃][B₁₂Cl₁₁NMe₃](Et₃Si)₂O (a). Thermal ellipsoids are drawn with 50% probability. Anions, solvent molecules and alkyl-bonded hydrogen atoms, and disordered parts were omitted for clarity. Important structural parameters (PBE0/def2-TZVPP values are given in *italics*): O1–Si1: 180.1(7), 179.5 pm; O1–C4: 122.7(10), 125.8 pm; O2–C4: 132.9(7), 125.0 pm, O2–Si1': 176.0, 180.2 pm; O1–C4–O2: 117.8(7), 123.5 °.

Step	Reaction	$\Delta G_r^{[b]}$ [kJ mol ⁻¹]
1	CS ₂ + [Et ₃ Si–H–SiEt ₃] ⁺ → [Et ₃ SiSC(H)SSiEt ₃] ⁺	–97.2
2	[Et ₃ SiSC(H)SSiEt ₃] ⁺ + Et ₃ SiH → [Et ₃ SiSCH ₂] ⁺ + S(Et ₃ Si) ₂ ^[c]	–11.7
3	S(Et ₃ Si) ₂ + [SiEt ₃] ⁺ → [(Et ₃ Si) ₃ S] ^{+[d]}	–68.5
4.1	[Et ₃ SiSCH ₂] ⁺ + Et ₃ SiH → [(Et ₃ Si) ₂ SMe] ^{+[d]}	–164.3
5	[(Et ₃ Si) ₂ SMe] ⁺ + Et ₃ SiH → [(Et ₃ Si) ₃ S] ^{+[d]} + CH ₄ ^[c]	–83.3
Σ	CS ₂ + 2 [Et ₃ Si–H–SiEt ₃] ⁺ + 2 Et ₃ SiH → 2 [(Et ₃ Si) ₃ S] ⁺ + CH ₄	–425.0
4.2 ^[e]	[Et ₃ SiSCH ₂] ⁺ + H ₂ → [Et ₃ SiS(H)Me] ^{+[d]}	–131.9

[a] A related table for the reaction with CO₂ is given in Table S16 in the Supporting Information. [b] The PBE0/def2-TZVPP free reaction energies in 1,2-dichlorobenzene as solvent are calculated at $T = 298.15$ K and $p = 1$ atm. [c] This compound was identified by NMR spectroscopy; [d] This cation was identified by its crystal structure. [e] Alternative reaction of the [Et₃SiSCH₂]⁺ cation resulting in the formation of the [Et₃SiS(H)Me]⁺ cation as shown in Figure 3 a.

by ^1H , ^{29}Si -HMBC NMR experiments (Figures S9 and S12, ^{29}Si 7.9 ppm, cf. 12.9 ppm for $(\text{Me}_3\text{Si})_2\text{S}^{[16]}$). This reaction step, which includes the oxygen analogue $[\text{Et}_3\text{SiO}=\text{CH}_2]^+$ as product, was also postulated by Müller et al. for the analogous reaction with CO_2 .^[8] Hexaethyldisilathiane reacts as base and forms with another $[\text{Et}_3\text{Si}]^+$ cation the tris(triethylsilyl)sulfonium cation $[(\text{Et}_3\text{Si})_3\text{S}]^+$ (step 3), which was identified by multinuclear NMR spectroscopy and crystal structure determination. This reaction is energetically favored by -130 kJ mol^{-1} and has already been reported by Olah and Prakash and Schulz for $\text{R}=\text{Me}$.^[16,17]

The postulated $[\text{Et}_3\text{SiS}=\text{CH}_2]^+$ cation in step 2 could not be detected even at low temperatures. This cation is very reactive and undergoes fast follow-up reactions, from which two different products could be identified. In the experiments Et_3SiH was present in excess and added to the $\text{S}=\text{C}$ double bond in a hydrosilylation reaction to give the disilylated sulfonium cation $[(\text{Et}_3\text{Si})_2\text{SMe}]^+$ ($\Delta G_r = -164 \text{ kJ mol}^{-1}$, step 4.1), which was characterized by multinuclear NMR spectroscopy and single crystal structure determination. The cation shows a ^{29}Si chemical shift of 46.3 ppm (40.8 ppm for $[(\text{Me}_3\text{Si})_2\text{SMe}]^+$).^[16] For the methyl group attached to the sulfur atom, a ^1H chemical shift of 2.33 ppm (2.37 ppm for $[(\text{Me}_3\text{Si})_2\text{SMe}]^+$)^[16] and a ^{13}C chemical shift of 11.2 ppm (10.8 ppm for $[(\text{Me}_3\text{Si})_2\text{SMe}]^+$)^[16] could be measured. Related cations of the type $[(\text{R}_3\text{Si})_2\text{SMe}]^+$ were also found, when silylium cations with other alkyl substituents were used. In total, three different crystal structures containing a cation of the type $[(\text{R}_3\text{Si})_2\text{SMe}][\text{A}]$ ($\text{R}=\text{Me}$, Et , $t\text{Bu}$) were obtained (Figure 2). The structures are all very similar, but the $\text{S}-\text{Si}$ and $\text{Si}-\text{C}$ distances slightly increase with the sterical demand of the substituents (for actual numbers see caption of Figure 2).

From some reactions we could also crystallize mono silylated cations of the type $[\text{R}_3\text{SiS}(\text{H})\text{Me}][\text{A}]$ ($\text{R}=\text{Et}$, $i\text{Pr}$) (step 4.2, Figure 3 and Figure S28 in the Supporting Information). We

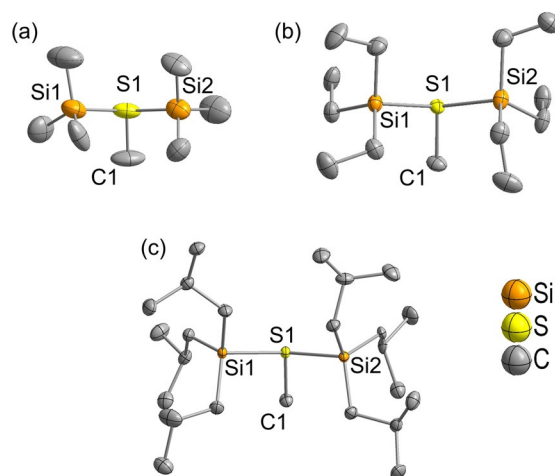


Figure 2. The cations in the crystal structures of $[(\text{Me}_3\text{Si})_2\text{SMe}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]^{1/2}$ ($\text{C}_6\text{H}_4\text{F}_2$) (a), $[(\text{Et}_3\text{Si})_2\text{SMe}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]$ (b) and $[(i\text{Bu}_3\text{Si})_2\text{SMe}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]$ (c). Thermal ellipsoids are drawn with 50% probability. Anions, solvent molecules and several hydrogen atoms are omitted for clarity. Selected bond lengths in pm for (a) $\text{S1}-\text{Si1}$: 225.3(3), $\text{S1}-\text{Si2}$: 223.3(3), $\text{S1}-\text{C1}$: 180.9(6); for (b) $\text{S1}-\text{Si1}$: 224.01(10), $\text{S1}-\text{Si2}$: 224.96(10), $\text{S1}-\text{C1}$: 182.2(3); for (c) $\text{S1}-\text{Si1}$: 226.15(19), $\text{S1}-\text{Si2}$: 227.56(19), $\text{S1}-\text{C1}$: 182.8(4). Further important bond parameters are compiled in Table S19 in the Supporting Information.

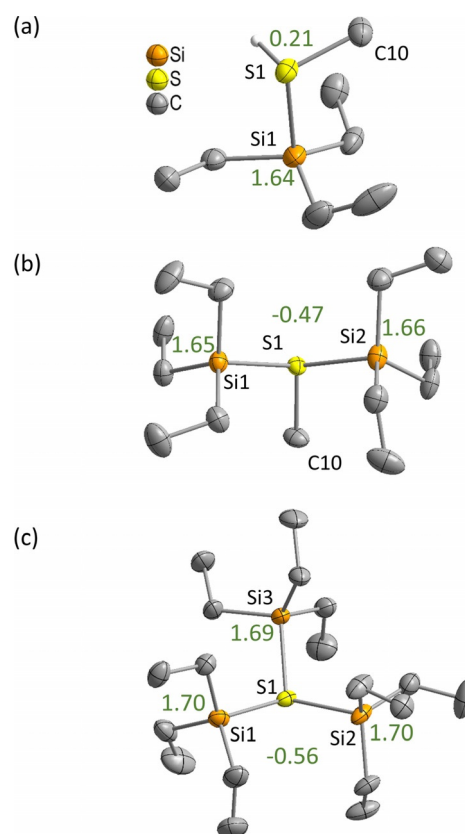


Figure 3. The cations in the crystal structures of $[\text{Et}_3\text{SiS}(\text{H})\text{Me}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]^{1/2}$ ($\text{C}_6\text{H}_4\text{F}_2$) (a), $[(\text{Et}_3\text{Si})\text{SMe}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]$ (b) and $[(\text{Et}_3\text{Si})\text{S}][\text{B}_{12}\text{Cl}_{11}\text{NMe}_3]$ (c). Thermal ellipsoids are drawn with 50% probability. Anions, solvent molecules and C-bonded hydrogen atoms are omitted for clarity. Calculated (PBE0/def2-TZVPP) NBO charges are highlighted in green. Selected structural parameters (calculated values are given in *italics*) for (a) $\text{Si1}-\text{S1}$: 229.84(12), 232.8 pm; $\text{Si1}-\text{C10}$: 181.1(3), 180.8 pm; $\text{Si1}-\text{S1}-\text{C10}$: 106.56(12), 107.9°; for (b) $\text{S1}-\text{Si1}$: 224.01(10), 228.2 pm; $\text{S1}-\text{Si2}$: 224.96(10), 227.6 pm; $\text{S1}-\text{C10}$: 182.2(3), 181.4 pm; $\text{Si1}-\text{S1}-\text{C10}$: 103.46(10), 104.2°; $\text{Si2}-\text{S1}-\text{C10}$: 106.33(10), 102.9°; $\text{Si1}-\text{S1}-\text{Si2}$: 114.16(4), 114.1°; for (c) $\text{S1}-\text{Si1}$: 225.87(7), 226.7 pm; $\text{S1}-\text{Si2}$: 226.07(7), 226.9 pm; $\text{S1}-\text{Si3}$: 225.31(7), 227.1 pm; $\text{Si1}-\text{S1}-\text{Si2}$: 111.49(3), 112.6°; $\text{Si1}-\text{S1}-\text{Si3}$: 108.96(3), 111.2°; $\text{Si2}-\text{S1}-\text{Si3}$: 110.88(3), 112.0°.

suggest that these compounds are side products, which were formed by H_2 addition to the double bond of the proposed $[\text{Et}_3\text{SiS}=\text{CH}_2]^+$ cation ($\Delta G_r = -132 \text{ kJ mol}^{-1}$). The origin of dihydrogen remains unclear. The acidified methyl group in the $[(\text{R}_3\text{Si})_2\text{SMe}]^+$ cation might act as a proton source. In the last reaction step 5 the disilylated cation $[(\text{Et}_3\text{Si})_2\text{SMe}]^+$ reacts with another equivalent of triethylsilane to the trisilylated sulfonium cation $[(\text{Et}_3\text{Si})_3\text{S}]^+$ as the final product. Thus, in the complete reaction cascade two equivalents of $[(\text{Et}_3\text{Si})_3\text{S}]^+$ are generated in steps 3 and 5. The second product of step 5 has to be methane, whose formation could be confirmed by NMR experiments ($\delta(^1\text{H})=0.21$ and $\delta(^{13}\text{C})=-4.2$ (Lit.: $\delta(^1\text{H})=0.21$; $\delta(^1\text{H})=-4.3$),^[18] see Figures S25 and S26). Therefore, the carbon atom in CS_2 is completely reduced to methane (see section 2.9 in the Supporting Information).

When silylium ions carrying two different alkyl groups are used, the entire reaction system becomes even more complicated. From a reaction starting with ethyldimethylsilane the methylated cation $[(\text{Me}_3\text{Si})_2\text{SMe}]^+$ was isolated due to alkyl-

alkyl exchange. Related alkyl-alkyl exchange reactions are known and were reported before by Müller^[8] and Schulz.^[17]

The structures of the mono-, di- and tri-silylated sulfonium cations with R=Et are shown in Figure 3. The structure of the $[(Et_3Si)_3S]^+$ cation can be compared to the recently published structure of the $[(Me_3Si)_3S]^+$ cation.^[17] While the averaged S–Si distances are very similar (225.8 pm vs. 225.1 pm), the $[(Et_3Si)_3S]^+$ is less pyramidal (the sum of Si–S–Si bond angles is 331.3° vs. 326.6°) due to the higher sterical demand of the longer alkyl chains. In general, the sums of the bond angles around the sulfur atoms in all cases are significantly smaller than 360° as expected for pyramidal sulfonium ions. In the monosilylated and disilylated cations the S–CH₃ bonds with 181.2(3) and 182.2(3) pm, respectively, are in perfect agreement with the sum of the covalent radii (181 pm)^[19] and thus correspond to a single bond. In contrast, the S–Si distances in all three cations are much longer than expected (cf. the sum of the covalent radii (216 pm)^[19] and the S–Si distance in Me₃Si–Si–SiMe₃ (215.2(2) pm)^[20], which might be due to the absence of negative hyperconjugation in the sulfonium cations. Interestingly, the S–Si distances decrease the more triethylsilyl groups are attached to the sulfur atom. This contradicts the trend, which would be expected based on sterically hindrance. To shed some light on it, NBO charges were calculated. While the charge on the silicon atoms does not change much between the three cations, the charge on the sulfur atom becomes significantly more negative by going from the monosilylated cation (0.21) to the disilylated cation (–0.47) and to the trisilylated cation (–0.56). Thus, there is an increasing Coulomb attraction between S and Si, which will shorten the sulfur-silicon bond length (Figure 3). In addition, attractive London dispersion interactions between the alkyl substituents, which become more important for larger alkyl groups, also contribute to the Si–S bond shortening.^[21]

In conclusion, the reaction of CS₂ and CO₂ with silylium ions proceeds via several steps and numerous side reactions and most intermediates could be identified and structurally characterized. Together with accompanying quantum-chemical calculations detailed insight into the reaction cascade could be obtained.

Experimental Section

For full synthetic and quantum-chemical details, see the Supporting Information.

CCDC no. 2034324, 2034325, 2034326, 2034327, 2034328, 2034329, 2034330, and 2034331 contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boron clusters · carbon dioxide · carbon disulfide · density functional calculations · silylium cations · weakly coordinating anions

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