



# Structure and reactivity of a triflimide-bridged bis(trimethylsilyl) cation†

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**Preparation of a triflimide-bridged bis-silylium monocation  $[(\text{Me}_3\text{Si})_2\text{NTf}_2]^+$  has been accomplished as a  $[\text{HCB}_{11}\text{Cl}_{11}]^-$  salt. Its structure has been analyzed and its potency in halide abstraction illustrated.**

Silylium cations ( $\text{R}_3\text{Si}^+$ ) are uniquely reactive Lewis acids with particular affinity for harder Lewis bases.<sup>1,2</sup> They have been used in catalysis,<sup>3</sup> especially in the context of C–F bond activation,<sup>4–6</sup> but are also of special interest as powerful but gentle abstractors of halides and pseudohalides in the syntheses of otherwise difficult to access cations.<sup>2,3,7</sup> Realization of the full potential of silylium cations in condensed phases requires the use of especially robust and weakly coordinating anions,<sup>8</sup> in order to approach the reactivity of the “naked” silylium cation. Carborane anions have proven especially advantageous.<sup>9–11</sup> A crystallographically characterized example of a true three-coordinate silylium cation has been reported.<sup>12</sup> However, where the silylium reagent is intended to be used as a (pseudo)halide abstractor,<sup>1</sup> a “naked” silylium cation is not necessary, nor is it necessary to use a reagent whose composition includes nothing besides the silylium cation and a weakly coordinating anion. Abstraction of a (pseudo)halide  $\text{X}^-$  leads to the formation of  $\text{R}_3\text{Si-X}$ , which can then form an adduct with the remaining  $\text{R}_3\text{Si}^+$ . If the formation of such a  $[\text{R}_3\text{Si-X-SiR}_3]^+$  adduct deactivates silylium and prevents the abstraction from happening, the reaction will not surmount 50% conversion even if base-free  $\text{R}_3\text{Si}^+$  is initially used. The reports of isolation of  $[(\text{Me}_3\text{Si})_2\text{X}][\text{B}(\text{C}_6\text{F}_5)_4]$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OTf}$ ) by Schulz *et al.* served as guiding examples for our group.<sup>13,14</sup> We have subsequently used the carborane version  $[(\text{Me}_3\text{Si})_2\text{OTf}][\text{HCB}_{11}\text{Cl}_{11}]$  (and its analog  $[(\text{Et}_3\text{Si})_2\text{OTf}][\text{HCB}_{11}\text{Cl}_{11}]$ ) to abstract a (pseudo)halide from C–X bonds in organic and organometallic compounds, with the generation of reactive cations.<sup>15–17</sup>  $\text{Me}_3\text{SiOTf}$

binds  $\text{Me}_3\text{Si}^+$  more strongly than does  $\text{Me}_3\text{SiH}$  and so  $[(\text{Me}_3\text{Si})_2\text{OTf}]^+$  is readily isolated in the reaction of  $\text{Me}_3\text{SiH}$  with  $\text{Ph}_3\text{C}^+$  in the presence of  $\text{Me}_3\text{SiOTf}$ .  $[(\text{Me}_3\text{Si})_2\text{OTf}][\text{HCB}_{11}\text{Cl}_{11}]$  is a solid, not an oil, and thus can be more effectively purified. The presence of the convenient <sup>19</sup>F NMR reporter is also a plus, as it allows to monitor the release of free  $\text{Me}_3\text{SiOTf}$  upon halide abstraction. Lastly, if the target (pseudo)halide for abstraction is not itself a triflate, the reaction ideally yields a 1 : 1 mixture of  $\text{Me}_3\text{SiX}$  and  $\text{Me}_3\text{SiOTf}$  – a ready <sup>1</sup>H NMR spectroscopic verification of the stoichiometry of the desired reaction.

The properties of triflate are sometimes compared with those of the triflimide anion  $\text{NTf}_2^- = [(\text{F}_3\text{CSO}_2)_2\text{N}]^-$ . Both  $\text{HOTf}$  and  $\text{HNTf}_2$  are considered superacids, and their relative strength depends on the medium.<sup>18</sup>  $\text{HNTf}_2$  often outperforms  $\text{HOTf}$  in organic catalysis.<sup>19</sup> Metal bis(triflimides) appear to be more Lewis acidic than the analogous metal triflates.<sup>20</sup> Although the nitrogen in  $\text{NTf}_2^-$  is of course less electronegative than the oxygen in  $\text{OTf}^-$ , the presence of two triflyl groups increases charge delocalization and steric encumbrance, which makes triflimide less of a nucleophile or a base, in at least some situations. With this in mind, we wished to access a triflimide analog of  $[(\text{Me}_3\text{Si})_2\text{OTf}][\text{HCB}_{11}\text{Cl}_{11}]$  and evaluate its properties.

The reaction of  $[\text{Ph}_3\text{C}][\text{HCB}_{11}\text{Cl}_{11}]$  with  $\text{Me}_3\text{SiH}$  in the presence of either  $\text{Me}_3\text{SiNTf}_2$  (prepared *in situ* from  $\text{HNTf}_2$  and allyltrimethylsilane)<sup>21</sup> or  $\text{HNTf}_2$  proceeded smoothly and led to the isolation of  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  as a fine white crystalline solid in 99% yield (Scheme 1). In solution at ambient temperature, it displayed a single resonance for the cation in each of its <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, and <sup>19</sup>F NMR spectra, in addition to the expected <sup>1</sup>H and <sup>13</sup>C NMR resonances for the  $[\text{HCB}_{11}\text{Cl}_{11}]^-$  anion. The <sup>19</sup>F NMR resonance for  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  (–75.8 ppm) is shifted downfield from the neutral  $\text{Me}_3\text{SiNTf}_2$  (–78.2 ppm), similarly to the downfield shift of  $[(\text{Me}_3\text{Si})_2\text{OTf}][\text{HCB}_{11}\text{Cl}_{11}]$  (–74.1 ppm) *vs.*  $\text{Me}_3\text{SiOTf}$  (–78.2 ppm). The downfield shift upon coordination of a  $\text{Me}_3\text{Si}^+$  is likely a consequence of the diminution of electron density on the fluorine atoms. The magnitude of this shift is smaller for  $\text{NTf}_2^-$  because of the presence of two  $\text{CF}_3$  groups instead of one in  $\text{OTf}^-$ , thus a lesser expected effect per fluorine.

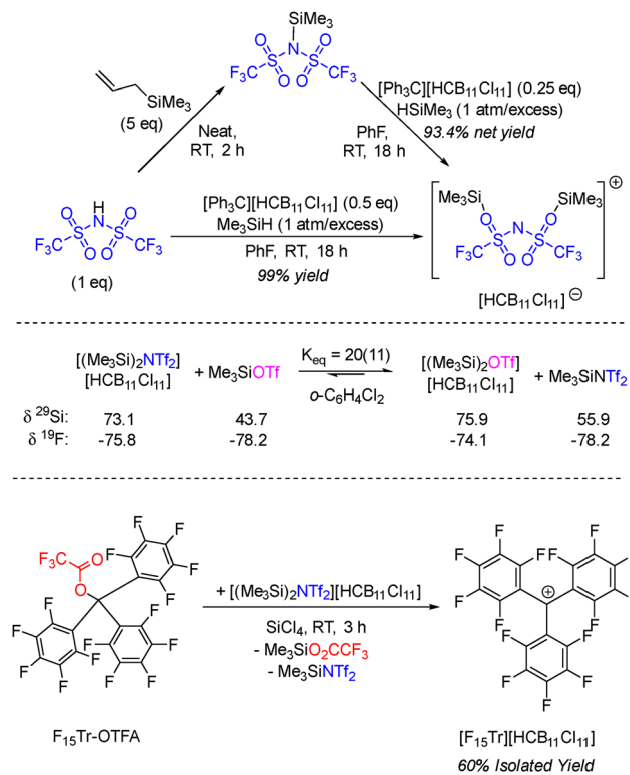
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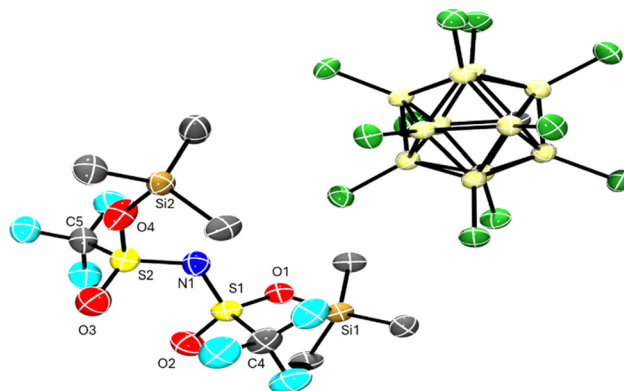


**Scheme 1** Synthesis of  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  (top), its reaction with  $\text{Me}_3\text{SiOTf}$  with  $^{29}\text{Si}$  and  $^{19}\text{F}$  NMR chemical shifts given (middle), and its use in the synthesis of a perfluorotrityl cation (bottom).

$[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  is dramatically more soluble in non-polar solvents. Whereas  $[(\text{Me}_3\text{Si})_2\text{OTf}][\text{HCB}_{11}\text{Cl}_{11}]$  displayed only sub-millimolar solubility in  $\text{C}_6\text{D}_6$  and none in pentane,  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  appears to be freely soluble in benzene and even gives rise to *ca.* 3 mM concentration in pentane (NMR evidence, see ESI<sup>†</sup>).

In order to evaluate the thermodynamic preference of the trimethylsilyl cation to bind to  $\text{Me}_3\text{SiOTf}$  vs.  $\text{Me}_3\text{SiNTf}_2$ ,  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  was treated with 0.95 equiv.  $\text{Me}_3\text{SiOTf}$  in *o*- $\text{C}_6\text{H}_4\text{Cl}_2$ . The resultant homogenous mixture displayed only a single  $^{29}\text{Si}$  NMR resonance and two  $^{19}\text{F}$  NMR resonances (one for the  $\text{NTf}_2$  groups and the other for the  $\text{OTf}$  groups) at ambient temperature, indicating a fast equilibrium among  $[(\text{Me}_3\text{Si})_2\text{NTf}_2]^+$ ,  $[(\text{Me}_3\text{Si})_2\text{OTf}]^+$ ,  $\text{Me}_3\text{SiNTf}_2$ , and  $\text{Me}_3\text{SiOTf}$ . The equilibrium constant of *ca.* 20 favored  $[(\text{Me}_3\text{Si})_2\text{OTf}]^+$ . We also performed a van't Hoff study in the 20–100 °C range in 1:9 mixture of  $\text{C}_6\text{D}_5\text{CD}_3$ /*o*- $\text{C}_6\text{H}_4\text{Cl}_2$ . The  $K_{\text{eq}}$  values were in the 1.5–2.5 range, corresponding to  $\Delta H = 1.1 \pm 0.4 \text{ kcal mol}^{-1}$  and  $\Delta S = 4.5 \pm 1.1 \text{ cal (mol K)}^{-1}$ . These data show that  $[(\text{Me}_3\text{Si})_2\text{NTf}_2]^+$  is slightly less stabilized thermodynamically than  $[(\text{Me}_3\text{Si})_2\text{OTf}]^+$ . In other words,  $\text{Me}_3\text{Si}^+$  displays a slight preference to bind to  $\text{Me}_3\text{SiOTf}$  over  $\text{Me}_3\text{SiNTf}_2$ . Therefore,  $[(\text{Me}_3\text{Si})_2\text{NTf}_2]^+$  should function as a slightly more powerful (pseudo)halide abstractor.

Testing this notion, we used  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  to abstract a trifluoroacetate group from  $\text{F}_{15}\text{Tr}-\text{OTFA}$  in a  $\text{SiCl}_4$  solution. This reaction resulted in a 60% isolated yield of  $[\text{F}_{15}\text{Tr}][\text{HCB}_{11}\text{Cl}_{11}]$ , comparable to that previously reported in



**Fig. 1** POV-Ray rendition of the ORTEP<sup>24</sup> drawing (50% thermal ellipsoids) showing one of the two independent  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  units with select atom labelling. Hydrogen atoms are omitted for clarity. Select bond distances (Å) and angles (°): Si1–O1, 1.818(4); Si2–O4, 1.802(4); S1–O1, 1.472(4); S2–O4, 1.479(4); S1–O2, 1.423(4); S2–O3, 1.414(5); N1–S1, 1.577(5); N1–S2, 1.562(5);  $\Sigma \angle \text{Si1}-\text{CH}_3$ , 345.2;  $\Sigma \angle \text{Si2}-\text{CH}_3$ , 344.3.

a reaction using  $[(\text{Me}_3\text{Si})_2\text{OTf}][\text{HCB}_{11}\text{Cl}_{11}]$ .<sup>16</sup> The data for the  $\text{F}_{15}\text{Tr}^+$  are also consistent with the recent reports by Riedel *et al.* of its salts with other counteranions.<sup>22,23</sup>

The structure of  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  was determined by single-crystal X-ray crystallography (Fig. 1). The asymmetric unit was found to contain two independent units of  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$ . The differences between the geometries of these two cations were not meaningful. There are no close contacts between the Si atoms and the carborane anions. The silicon atoms of the  $\text{Me}_3\text{Si}$  groups are bound to the oxygens of the triflimide anion. In binding to Lewis acids, there are examples of triflimide utilizing its nitrogen, a single oxygen, or two oxygens.<sup>25,26</sup> It appears to prefer to bind *via* the oxygen(s) to harder, more oxophilic Lewis acids.<sup>27</sup> The Si–O(=S) bond lengths of *ca.* 1.80–1.81 Å are comparable to those found in  $[(\text{Me}_3\text{Si})_2\text{OTf}][\text{B}(\text{C}_6\text{F}_5)_4]$  (1.81–1.82 Å),<sup>13</sup> and  $\text{Et}_3\text{Si}[\text{CHB}_{11}\text{Cl}_{10}\text{OTf}]$  (*ca.* 1.79 Å),<sup>28</sup> and are slightly longer than those in  $[(\text{Me}_3\text{Si})_3\text{SO}_4][\text{B}(\text{C}_6\text{F}_5)_4]$  (1.76–1.78 Å).<sup>29</sup> The sums of C–Si–C angles in the four independent  $\text{SiMe}_3$  groups were found to be in the narrow 344°–346° range, similar to these known  $\text{R}_3\text{Si}^+-\text{O}(\text{=S})$  adducts. The two  $\text{Me}_3\text{Si}$  groups are connected to the oxygens of the  $\text{NTf}_2$  fragment. The bonds between sulfur and the Si-bound oxygens are *ca.* 0.05 Å longer than the terminal S–O bonds. When compared to the parent  $\text{HNTf}_2$ <sup>30</sup> and an “isolated”  $\text{NTf}_2^-$  anion such as in  $[\text{C}_3(\text{NPr}_2)_3]\text{NTf}_2$ ,<sup>31</sup> the N–S bond lengths of our silylated triflimide (*ca.* 1.56 Å) are more similar to the anionic  $\text{NTf}_2^-$  (*ca.* 1.56 Å) than neutral  $\text{HNTf}_2$  (*ca.* 1.64 Å). However, when comparing the S–N–S bond angle the opposite trend is seen with  $(\text{Me}_3\text{Si})_2\text{NTf}_2^+$  (123.8°) being more similar to  $\text{HNTf}_2$  (128.4°) than  $\text{NTf}_2^-$  (101.8°).

In summary, we have been able to prepare an adduct of trimethylsilylium cation with trimethylsilyl triflimide in the form of the  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  salt. It appears that  $\text{Me}_3\text{Si}^+$  binds  $\text{Me}_3\text{SiNTf}_2$  slightly less strongly than  $\text{Me}_3\text{SiOTf}$ . The new reagent provides another option for a silylium reagent for (pseudo)halide abstraction that also possesses increased solubility in solvents of low polarity.



## Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for [(Me<sub>3</sub>Si)<sub>2</sub>NTf<sub>2</sub>][HCB<sub>11</sub>Cl<sub>11</sub>] has been deposited at the Cambridge Structural Database under CCDC 2428563.

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## Conflicts of interest

There are no conflicts to declare.

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