



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

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Cite this: *Chem. Commun.*, 2025, 61, 10816

Received 5th March 2025,  
Accepted 2nd June 2025

DOI: 10.1039/d5cc01223f

rsc.li/chemcomm

**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  $^{19}\text{F}$  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  $^1\text{H}$  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  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^{19}\text{F}$  NMR spectra, in addition to the expected  $^1\text{H}$  and  $^{13}\text{C}$  NMR resonances for the  $[\text{HCB}_{11}\text{Cl}_{11}]^-$  anion. The  $^{19}\text{F}$  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.

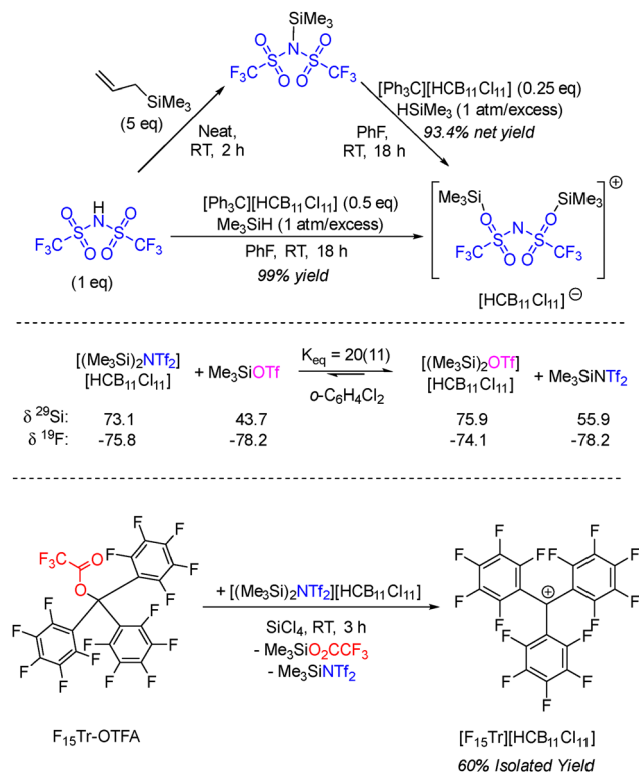
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† Electronic supplementary information (ESI) available: NMR spectra, X-ray crystallographic data. CCDC 2428563. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5cc01223f>

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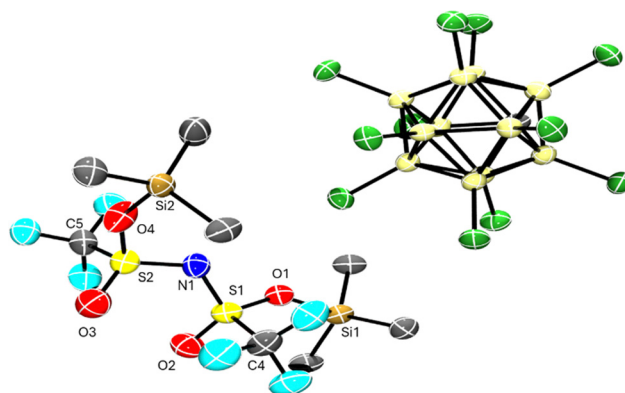


**Scheme 1** Synthesis of  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  (top), its reaction with  $\text{Me}_3\text{SiOTf}$  with  $^{29}\text{Si}$  and  $^{19}\text{F}$  NMR chemical shifts given (middle), and its use in the synthesis of a perfluorotriyl cation (bottom).

$[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  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†).

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  $\text{F}_{15}\text{Tr-OTFA}$  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 (°):  $\text{Si1}-\text{O1}$ , 1.818(4);  $\text{Si2}-\text{O4}$ , 1.802(4);  $\text{S1}-\text{O1}$ , 1.472(4);  $\text{S2}-\text{O4}$ , 1.479(4);  $\text{S1}-\text{O2}$ , 1.423(4);  $\text{S2}-\text{O3}$ , 1.414(5);  $\text{N1}-\text{S1}$ , 1.577(5);  $\text{N1}-\text{S2}$ , 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 trifluoromethanesulfonate anion. In binding to Lewis acids, there are examples of trifluoromethanesulfonate 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  $\text{Si}-\text{O}(\text{=S})$  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  $\text{C}-\text{Si}-\text{C}$  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  $\text{S}-\text{O}$  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  $\text{N}-\text{S}$  bond lengths of our silylated trifluoromethanesulfonate (*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  $\text{S}-\text{N}-\text{S}$  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 trifluoromethanesulfonate 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  $[(\text{Me}_3\text{Si})_2\text{NTf}_2][\text{HCB}_{11}\text{Cl}_{11}]$  has been deposited at the Cambridge Structural Database under CCDC 2428563.

We are thankful for the support of this research by the Office of Science of the US Department of Energy, Basic Energy Sciences (grant DE-SC0023280 to O. V. O.).

## Conflicts of interest

There are no conflicts to declare.

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