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Structure and Reactivity of Triflimide-Bridged Bis(Trimethylsilyl) Cation

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Preparation of a triflimide-bridged bis-silylium monocation $[(Me_3Si)_2NTf_2]^+$ has been accomplished as a $[HCB_{11}Cl_{11}]^-$ salt. Its structure has been analyzed and potency in halide abstraction illustrated.

Silylium cations (R₃Si⁺) are uniquely reactive Lewis acids with particular affinity for harder Lewis bases.^{1,2} They have been used in catalysis, ³ especially in the context of C-F bond activation, 4-6 but are also of special interest as powerful but gentle abstractors of halides and pseudohalides in the syntheses of otherwise difficult to access cations.^{2,3,7} Realization of the full potential of silylium cations in condensed phases requires the use of especially robust and weakly coordinating anions,⁸ in order to approach the reactivity of the "naked" silylium cation. Carborane anions have proven especially advantageous. 9 - 11 A crystallographically characterized example of a true three-coordinate silylium cation has been reported. 12 However, where the silylium reagent is intended to be used as a (pseudo)halide abstractor,¹ 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 X^- leads to the formation of R₃Si-X, which can then form an adduct with the remaining R_3Si^* . If the formation of such a [R₃Si-X-SiR₃]⁺ adduct deactivates silylium and prevents the abstraction from happening, the reaction will not surmount 50% conversion even if base-free R₃Si⁺ is initially used. The reports of isolation of $[(Me_3Si)_2X][B(C_6F_5)_4)]$ (X = F, Cl, Br, I, OTf) by Schulz et al. served as guiding examples for our group.^{13,14} We have subsequently used the carborane version [(Me₃Si)₂OTf][HCB₁₁Cl₁₁] (and its analog [(Et₃Si)₂OTf][HCB₁₁Cl₁₁]) to abstract a (pseudo)halide from C-X bonds in organic and organometallic compounds, with the generation of reactive

cations.^{15,16,17} Me₃SiOTf binds Me₃Si⁺ more strongly than does Me₃SiH and so [(Me₃Si)₂OTf]⁺ is readily isolated in the reaction of Me₃SiH with Ph₃C⁺ in the presence of Me₃SiOTf. [(Me₃Si)₂OTf][HCB₁₁Cl₁₁] is a solid, not an oil, and thus can be more effectively purified. The presence of the convenient ¹⁹F NMR reporter is also a plus, as it allows to monitor the release of free Me₃SiOTf 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 Me₃SiX and Me₃SiOTf – a ready ¹H NMR spectroscopic verification of the stoichiometry of the desired reaction.

The properties of triflate are sometimes compared with those of the triflimide anion $NTf_2^- = [(F_3CSO_2)_2N]^-$. Both HOTf and HNTf₂ are considered superacids, and their relative strength depends on the medium.¹⁸ HNTf₂ often outperforms HOTf in organic catalysis.¹⁹ Metal bis(triflimides) appear to be more Lewis acidic than the analogous metal triflates.²⁰ Although the nitrogen in NTf2- is of course less electronegative than the oxygen in 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 [(Me₃Si)₂OTf][HCB₁₁Cl₁₁] and evaluate its properties. The reaction of [Ph₃C][HCB₁₁Cl₁₁] with Me₃SiH in the presence of either Me₃SiNTf₂ (prepared in situ from HNTf₂ and allyltrimethylsilane)²¹ or HNTf₂ proceeded smoothly and led to the isolation of [(Me₃Si)₂NTf₂][HCB₁₁Cl₁₁] 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 ¹H, ¹³C, ²⁹Si, and ¹⁹F NMR spectra, in addition to the expected ¹H and ¹³C NMR resonances for the [HCB₁₁Cl₁₁]⁻ anion. The ¹⁹F NMR resonance for [(Me₃Si)₂NTf₂][HCB₁₁Cl₁₁] (-75.8 ppm) is shifted downfield from the neutral Me₃SiNTf₂ (-78.2 ppm), similarly to the downfield shift of [(Me₃Si)₂OTf][HCB₁₁Cl₁₁] (-74.1 ppm) vs Me₃SiOTf (-78.2 ppm). The downfield shift upon coordination of a Me_3Si^+ is likely a consequence of the diminution of electron density on the fluorine atoms. The magnitude of this shift is smaller for NTf₂

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because of the presence of two CF₃ groups instead of one in OTf, thus а lesser expected effect per fluorine. [(Me₃Si)₂NTf₂][HCB₁₁Cl₁₁] is dramatically more soluble in nonpolar solvents. Whereas [(Me₃Si)₂OTf][HCB₁₁Cl₁₁] displayed only sub-millimolar solubility in C_6D_6 and none in pentane, [(Me₃Si)₂NTf₂][HCB₁₁Cl₁₁] appears to be freely soluble in benzene and even gives rise to ca. 3 mM concentration in pentane (NMR evidence, see ESI).

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Scheme 1. Synthesis of [(Me₃Si)₂NTf₂][HCB₁₁Cl₁₁] (top), its reaction with Me₃SiOTf with ²⁹Si and ¹⁹F NMR chemical shifts given (middle), and its use in the synthesis of a perfluorotrityl cation (bottom).

In order to evaluate the thermodynamic preference of the trimethylsilyl cation to bind to Me₃SiOTf vs Me₃SiNTf₂, [(Me₃Si)₂NTf₂][HCB₁₁Cl₁₁] was treated with 0.95 equiv. Me₃SiOTf in o-C₆H₄Cl₂. The resultant homogenous mixture displayed only a single ²⁹Si NMR resonance and two ¹⁹F NMR resonances (one for the NTf₂ groups and the other for the OTf groups) at ambient temperature, indicating a fast equilibrium among [(Me₃Si)₂NTf₂]⁺, [(Me₃Si)₂OTf]⁺, Me₃SiNTf₂, and Me₃SiOTf. The equilibrium constant of ca. 20 favored $[(Me_3Si)_2OTf]^+$. We also performed a van't Hoff study in the 20-100 °C range in 1:9 mixture of $C_6D_5CD_3/o$ - $C_6H_4Cl_2$. The K_{eq} values were in the 1.5-2.5 range, corresponding to $\Delta H = 1.1 \pm 0.4$ kcal/mol and $\Delta S = 4.5$ \pm 1.1 cal/(mol×K). These data show that [(Me₃Si)₂NTf₂]⁺ is slightly less stabilized thermodynamically than [(Me₃Si)₂OTf]⁺. In other words, Me₃Si⁺ displays a slight preference to bind to Me₃SiOTf over Me₃SiNTf₂. Therefore, [(Me₃Si)₂NTf₂]⁺ should function as a slightly more powerful (pseudo)halide abstractor.

Testing this notion, we used [(Me₃Si)₂NTf₂][HCB₁₁Cl₁₁]_{on}to

abstract a trifluoroacetate group from PATHOMPADING SIGE

solution. This reaction resulted in a 60% isolated yield of [F₁₅Tr][HCB₁₁Cl₁₁], comparable to that previously reported in a

reaction using [(Me₃Si)₂OTf][HCB₁₁Cl₁₁].¹⁶ The data for the

F15Tr⁺ are also consistent with the recent reports by Riedel et al

Figure 1. POV-Ray rendition of the ORTEP²⁴ drawing (50% thermal ellipsoids) showing one of the two independent [(Me₃Si)₂NTf₂][HCB₁₁Cl₁₁] 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); Σ4Si1-CH₃, 345.2; Σ4Si2-CH₃, 344.3

The structure of [(Me₃Si)₂NTf₂][HCB₁₁Cl₁₁] was determined by single-crystal X-ray crystallography (Figure 1). The asymmetric unit was found to contain two independent units of [(Me₃Si)₂NTf₂][HCB₁₁Cl₁₁]. 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 Me₃Si 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.^{25,26} It appears to prefer to bind via the oxygen(s) to harder, more oxophilic Lewis acids.²⁷ The Si-O(=S) bond lengths of ca. 1.80-1.81 Å are comparable to those found in $[(Me_3Si)_2OTf][B(C_6F_5)_4]$ (1.81-1.82 Å),13 and $Et_3Si[CHB_{11}Cl_{10}OTf]$ (ca. 1.79 Å),²⁸ and are slightly longer than those in [(Me₃Si)₃SO₄][B(C₆F₅)₄)] (1.76-1.78 Å).²⁹ The sums of C-Si-C angles in the four independent SiMe₃ groups were found to be in the narrow 344°-346° range, similar to these known R₃Si⁺-O(=S) adducts. The two Me₃Si groups are connected to the oxygens of the NTf₂ 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 HNTf₂³⁰ and an "isolated" NTf₂- anion such as in [C₃(NPr₂)₃]NTf₂,³¹ the N-S bond lengths of our silylated triflimide (ca. 1.56 Å) are more similar to the anionic NTf₂ (*ca.* 1.56 Å) than neutral HNTf₂ (*ca.* 1.64 Å). However, when comparing the S-N-S bond angle the opposite trend is seen with (Me₃Si)₂NTf₂⁺ (123.8°) being more similar to HNTf₂ (128.4°) than NTf₂- (101.8°).



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In summary, we have been able to prepare an adduct of trimethylsilylium cation with trimethylsilyl triflimide in the form of the $[(Me_3Si)_2NTf_2][HCB_{11}Cl_{11}]$ salt. It appears that Me_3Si^+ binds Me_3SiNTf_2 slightly less strongly than Me_3SiOTf . 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 Statement

The data supporting this article have been included as part of the Supplementary Information. Crystallographic data for $[(Me_3Si)_2NTf_2][HCB_{11}Cl_{11}]$ has been deposited at the Cambridge Structural Database under CCDC 2428563 and can be obtained

from via www.ccdc.cam.ac.uk/data_request/cif, or by emailing da-ta request@ccdc.cam.ac.uk. DOI: 10.1039/D5CC01223F

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