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Silicon Tetrakis(trifluoromethanesulfonate): A Simple Neutral Silane Acting as a Soft and Hard Lewis Superacid

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Dedicated to Professor Gottfried Huttner

Abstract: A facile synthesis and isolation of pristine silicon tetrakis(trifluoromethanesulfonate), $\text{Si}(\text{OTf})_4$, is reported, acting as the first neutral silicon-based Lewis superacid suitable towards soft and hard Lewis bases. Its OTf groups have a dual function: they are excellent leaving groups and modulate the degree of reactivity towards soft and hard Lewis bases. Exposed to soft Lewis donors, $\text{Si}(\text{OTf})_4$ leads to $[\text{L}_2\text{Si}(\text{OTf})_4]$ complexes (L = isocyanide, thioether and carbonyl compounds) with retention of all Si–OTf bonds. In contrast, it can cleave C–X bonds ($\text{X} = \text{F}, \text{Cl}$) of hard organic Lewis bases with a high tendency to form SiX_4 ($\text{X} = \text{F}, \text{Cl}$) after halide/triflate exchange. Most notable, $\text{Si}(\text{OTf})_4$ allows a gentle oxydefluorination of mono- and bis(trifluoromethyl)benzenes, resulting in the formation of the corresponding benzoylium species, which are stabilized by the weakly coordinating $[\text{Si}(\text{OTf})_6]^-$ dianion.

Main group Lewis acids (LA) are valuable functional species and mediators in many branches of chemistry, including homogeneous catalysis, synthesis of frustrated Lewis pairs (FLP) and weakly coordinating anions (WCA).^[1] LAs that are stronger than monomeric SbF_5 in the gas phase are classified as Lewis superacids (LSA), a feature that is generally assessed by calculation of the fluoride ion affinities (FIA).^[2] While the FIA scales the Lewis acidity towards the hard Lewis base F^- , the related hydride ion affinity (HIA) defines the scale of soft Lewis acidity. In this regard, it has been proposed that a LA that exceeds the HIA of $\text{B}(\text{C}_6\text{F}_5)_3$ as a reference compound is considered as a soft LSA.^[3] Silicon-based LAs are particularly attractive because of the high abundance and low toxicity of this element. Accordingly, Lewis superacidic silylium ions, R_3Si^+ , have become valuable catalysts in organic synthesis but require the use of potent WCAs.^[4] Large progress has been

achieved during the last years with reports on the first neutral silicon LSAs in form of the perhalogenated bis(catecholato)silanes $\text{Si}(\text{cat}^X)_2$ ($\text{X} = \text{Cl}, \text{Br}$, Figure 1).^[5,6] Other silicon(IV)-based LAs are routinely used in organic synthesis, with the commercially available TMSOTf ($\text{TMS} = \text{Me}_3\text{Si}$) arguably being prevalent,^[7] but far from being a LSA.^[3] Bis- and tris(triflate) silanes potentially represent stronger LAs, but have mainly served as building blocks for polysilane syntheses^[8,9] or as precursors for silicon-based polycations^[10,11] with cleavage of the Si–OTf bonds. Donor-free $\text{Si}(\text{OTf})_4$ has not been isolated to date,^[9] but recently, a high FIA was calculated for $\text{Si}(\text{OTf})_4$ suggesting its Lewis superacidity.^[12]

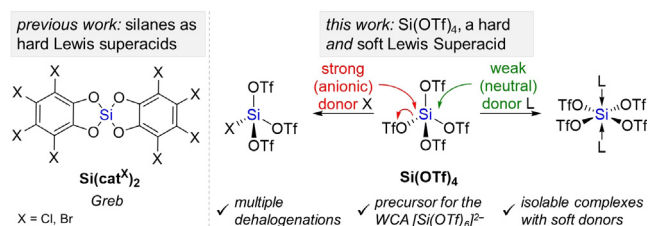


Figure 1. Previously studied silane Lewis superacids (LSA) and the hard and soft LSA $\text{Si}(\text{OTf})_4$ presented herein (OTf = CF_3SO_3^- , WCA = weakly coordinating anion).

Herein, we describe a facile access to pristine $\text{Si}(\text{OTf})_4$ and demonstrate that the OTf substituents are not only excellent leaving groups but also enable an unprecedented Lewis superacidic reactivity of a silane towards both hard and soft donors.

The easy access to $\text{Si}(\text{OTf})_4$ in multi-gram scale succeeds in 81% yields through the reaction of SiI_4 with four molar equivalents of AgOTf in CH_2Cl_2 . The colorless liquid solidifies below 0°C and can be stored indefinitely at -30°C under an inert atmosphere. The observed singlet ^{29}Si NMR resonance at $\delta = -121.7$ ppm (CD_2Cl_2) is in good agreement with the reported value of -118.2 ppm for in situ generated $\text{Si}(\text{OTf})_4$ in CH_2Cl_2 .^[9]

In order to assess the Lewis acidity also in the “soft dimension”, the isodesmic HIA of $\text{Si}(\text{OTf})_4$ in addition to the FIA was calculated using the TMS-reference system^[12,13] (Table 1, for computational details see Supporting Information). The obtained FIA is in good agreement with the value that was determined by Greb (519 kJ mol^{-1}).^[12] Both the FIA and HIA are well above the respective thresholds of SbF_5 and $\text{B}(\text{C}_6\text{F}_5)_3$, qualifying $\text{Si}(\text{OTf})_4$ as a hard and soft LSA. Notably, also the second ion affinities are particularly high (approx.

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Table 1: DFT-derived first and second ion affinities (fluoride: FIA, hydride: HIA) for selected Lewis acids (LA) in kJ mol^{-1} .

Lewis acid (LA)	FIA ^[a]		HIA ^[a]	
	LA/LA-F ⁻	LA-F ⁻ /LA-F ₂ ²⁻	LA/LA-H ⁻	LA-H ⁻ /LA-H ₂ ²⁻
SiF ₄	324	-180	315	-258
Si(cat ^C) ₂	495	69	491	21
Si(cat ^B) ₂	497	79	492	32
Si(OTf)₄	521	216	547	212
SbF ₅	500	-	-	-
B(C ₆ F ₅) ₃	443	-	514	-

[a] PW6B95-D3B]/def2-QZVPP//B3LYP-D3B]/def2-SVP.

400 kJ mol^{-1} above $[\text{XSiF}_4]^-/[\text{X}_2\text{SiF}_4]^{2-}$ and indicate a high tendency for the formation of hexacoordinate species.

The Lewis superacidity was confirmed experimentally by reaction with $[\text{PPh}_4][\text{SbF}_6]$, which led to fluoride abstraction with subsequent formation of $(\text{TfO})\text{SiF}_3$ and SiF_4 (¹⁹F and ²⁹Si NMR) among other, unidentified products. In agreement with the high HIA, addition of $\text{Si}(\text{OTf})_4$ to the hydridoborate salt $[\text{Mes}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ in CD_2Cl_2 led to hydride abstraction. Consequently, the SiH species $[\text{HSi}(\text{OTf})_4]^-$ and $[\text{H}_2\text{Si}(\text{OTf})_3]^-$ were detected by ¹H and HSi HMQC NMR spectroscopy (see Supporting Information for details). To the best of our knowledge, $\text{Si}(\text{OTf})_4$ represents the first isolable neutral silicon compound that is a soft LSA.

These results were corroborated by Lewis acidity scaling using different Lewis base NMR probes. Employing one molar equivalent of the hard phosphine oxide OPEt_3 (Gutmann-Beckett method),^[14] a strong low-field shift was observed for $\delta^{31}\text{P}$ ($\Delta\delta^{31}\text{P} = 51.2$ ppm), which is well above the $\Delta\delta^{31}\text{P}$ reported for the OPEt_3 adducts of $\text{Si}(\text{cat}^{\text{Br}})_2$ (33.2 ppm)^[5] and silylium ions (43.9 ± 2.7 ppm).^[15,16] Higher $\Delta\delta^{31}\text{P}$ values were only obtained with cationic LSAs such as $[(m\text{-}(\text{CH}_3)_2\text{C}_6\text{H}_4)\text{Si}(\text{terpy})]^{3+}$ and $[\text{catB}]^+$ (61.1 and 60.7 ppm).^[11,16] Upon cooling, crystals of the ion pair $[(\text{OPEt}_3)_2\text{Si}(\text{OTf})_2][\text{Si}(\text{OTf})_6]$ are formed illustrating the expected lability of the Si-OTf bonds. With two molar equivalents of OPEt_3 , the bis-adduct $[(\text{OPEt}_3)_2\text{Si}(\text{OTf})_4]$ ($\Delta\delta^{31}\text{P} = 33.5$ ppm) was isolated in 48% yield (VT-NMR and molecular structures in Supporting Information).

After addition of the soft Lewis base crotonaldehyde (CA, Childs method)^[17] to $\text{Si}(\text{OTf})_4$, the formation of *cis*- and *trans*- $[(\text{CA})_2\text{Si}(\text{OTf})_4]$ could be clearly detected by multinuclear NMR spectroscopy. The high induced shift for the H₃ protons ($\Delta\delta^1\text{H} = 1.52$ ppm) complies with the soft Lewis superacidity of $\text{Si}(\text{OTf})_4$ and exceeds the

$\Delta\delta^1\text{H}$ of the adduct $[(\text{CA})\text{B}(\text{C}_6\text{F}_5)_3]$ (1.05 ppm).^[18] In contrast, it was shown by Ghosez that addition of TMSOTf to CA does not lead to a measurable $\Delta\delta^1\text{H}$ and a 1:1 mixture of HOTf and CA gave a $\Delta\delta^1\text{H}$ of only 1.28 ppm.^[19]

Furthermore, we applied a scaling method developed recently by Müller, based on the weak *p*-fluorobenzonitrile donor (FBN).^[20] From an equimolar mixture of $\text{Si}(\text{OTf})_4$ and FBN only the bis-adducts *cis*- and *trans*- $[(\text{FBN})_2\text{Si}(\text{OTf})_4]$ are formed (molecular structure of the latter in Figure S124). The induced shifts ($\delta^{19}\text{F} = -89.7, -90.1$ ppm; $^1J_{\text{CF}} = 267, 267$ Hz) are similar to those for the FBN adduct of a weakly iodo-stabilized silylium ion.^[20] This emphasizes that $\text{Si}(\text{OTf})_4$ acts as a strong LA with retention of the Si-OTf bonds.

In this context, the reaction of $\text{Si}(\text{OTf})_4$ with soft neutral donors afforded unprecedented $[\text{L}_2\text{Si}(\text{OTf})_4]$ complexes (L = isocyanide, thioether or carbonyl compounds, Figure 2) in 56–91% yield, which were fully characterized. The only crystallographic evidence for a Si^{IV} complex with an aldehyde compound exists for the silylium adduct $[(\text{PhCHO})\text{SiEt}_3]^+$,^[21] while, to the best of our knowledge, Si^{IV} complexes with external thioether and isocyanide ligands were unknown. In accordance with the downfield-shifted $\delta^{13}\text{C}_{\text{CO}} = 208.4$ ppm for the benzophenone complex $[(\text{Ph}_2\text{CO})_2\text{Si}(\text{OTf})_4]$ in CD_2Cl_2 (cf. $\delta^{13}\text{C}_{\text{CO}} = 196.8$ ppm for Ph_2CO),^[22] the C=O distance of 1.275(4) Å is strongly elongated in the solid-state structure compared to Ph_2CO (1.2229(17) Å).^[23] A shortening of the N≡C distance is observed for $[(\text{XylINC})_2\text{Si}(\text{OTf})_4]$ (1.145(3) Å) in comparison to the “free” isocyanide (1.160(3) Å),^[24] whereas, in Si^{II} isocyanide complexes, back-bonding causes an elongation of the N–C bond.^[25]

Investigation of the thermochemistry of $[\text{L}_2\text{SiX}_4]$ complex formation (X = OTf, F) by DFT calculations elucidates that the extraordinary Lewis acidity of $\text{Si}(\text{OTf})_4$ in comparison to SiF_4 is not due to inherently different reorganization energies

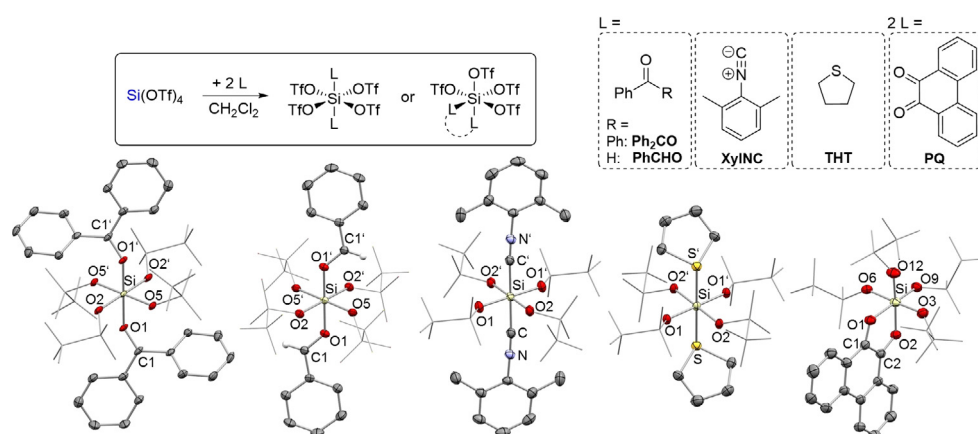


Figure 2. Top: Synthesis of the $[\text{L}_2\text{Si}(\text{OTf})_4]$ complexes; bottom: their molecular structures (ellipsoids at 50% probability; H atoms are omitted and OTf reduced to wireframe).^[34] Selected distances (Å) for L = Ph_2CO : C–O 1.275(4), Si–O1 1.796(2), PhCHO : C–O 1.263(2), Si–O1 1.7816(12), XylINC (two independent molecules): N–C 1.145(2)/1.146(2), Si–C 1.9631(17)/1.9602(18), THT : S–Si 2.3593(4), PQ : Si–O1 1.828(2), Si–O2 1.845(2).

E_{reorg} (for details see SI, Table S5). In the gas phase, the association of $[\text{L}_2\text{Si}(\text{OTf})_4]$ (ΔE_{ass}) is exothermic and exergonic, which is in stark contrast to the corresponding $[\text{L}_2\text{SiF}_4]$ complexes where $\Delta G_{\text{ass}} > 0$. This is in keeping with our results and experimental reports for SiF_4 .^[26] The E_{reorg} necessary to deform tetrahedral SiX_4 to the square-planar geometry adapted in *trans*- $[\text{L}_2\text{SiX}_4]$ decrease in the order $\text{SiF}_4 > \text{SiCl}_4 > \text{SiBr}_4$ and are considered crucial for complex formation [Eq. (1)].^[27]

$$-\Delta E_{\text{ass}} = E_{\text{int}} - (E_{\text{reorg}}^{\text{SiX}_4} + 2E_{\text{reorg}}^{\text{L}}) \quad (1)$$

However, the here calculated $E_{\text{reorg}}[\text{Si}(\text{OTf})_4]$ (288–329 kJ mol^{-1}) are in a similar range as $E_{\text{reorg}}[\text{SiF}_4]$ (298–304 kJ mol^{-1}). Consequently, the high affinity of $\text{Si}(\text{OTf})_4$ towards the L donors is due to much higher interaction energies E_{int} between the prepared monomers for $[\text{L}_2\text{Si}(\text{OTf})_4]$ (466–569 kJ mol^{-1}) against $E_{\text{int}}[\text{L}_2\text{SiF}_4]$ (128–329 kJ mol^{-1}).

We further investigated the applicability of $\text{Si}(\text{OTf})_4$ as a halide and hydride acceptor. Due to the lability of the Si–OTf bond, hydride/triflate exchange was observed when exposing $\text{Si}(\text{OTf})_4$ to Et_3SiH with formation of $\text{HSi}(\text{OTf})_3$ and Et_3SiOTf (^1H and ^{29}Si NMR). Remarkably, H^-/OTf^- exchange even occurs with the weaker hydride donor PhSiH_3 ,^[28] affording a mixture of $\text{HSi}(\text{OTf})_3$ and $\text{PhSiH}_2(\text{OTf})$ ($\delta^{29}\text{Si} = -8.5$ ppm).^[9] The formation of tritylium with two equivalents of trityl chloride was monitored by ^1H and ^{13}C NMR spectroscopy ($\delta^{13}\text{C} = 211.1$ ppm) after mixing in CD_2Cl_2 (Figure 3). The ^{29}Si NMR spectra show the formation of SiCl_4 and $[\text{Si}(\text{OTf})_6]^{2-}$ ($\delta^{29}\text{Si} = -18.8$ and -215.6 ppm). Layering of the solution with *n*-hexane afforded yellow crystals suitable for a single-crystal X-ray diffraction (SC-XRD) analysis; the latter confirmed the formation of $[\text{Ph}_3\text{C}]_2[\text{Si}(\text{OTf})_6]$ (Figure 3). Likewise, $[\text{Si}(\text{OTf})_6]^{2-}$ and SiX_4 are formed from the reaction of $\text{Si}(\text{OTf})_4$ with two molar equivalents of $[\text{NBu}_4]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) as evidenced by ^{29}Si NMR. Accordingly, $\text{Si}(\text{OTf})_4$ can act both as a strong halide and triflate acceptor.

This feature allows for the oxydefluorination (ODF) of trifluoromethyl benzenes with concurrent stabilization of resulting benzoylium species through the $[\text{Si}(\text{OTf})_6]^{2-}$ WCA (Figure 4). When exposing PhCF_3 to $\text{Si}(\text{OTf})_4$, F^-/OTf^- exchange to $\text{PhCF}_2(\text{OTf})$ and $\text{FSi}(\text{OTf})_3$ took place within 1 h at 20 °C. However, ^{19}F NMR spectra indicated the formation of increasing amounts of Tf_2O and $\text{F}_n\text{Si}(\text{OTf})_{4-n}$ ($n = 2-4$). Accordingly, the $[\text{PhCO}]_2[\text{Si}(\text{OTf})_6]$ ODF product

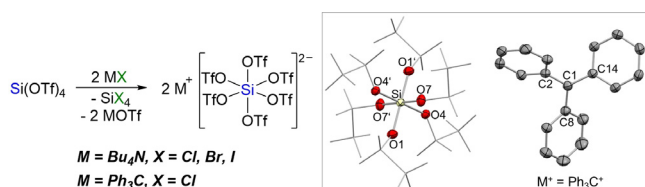


Figure 3. Halide abstraction from Ph_3CCl and Bu_4NX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) together with the molecular structure of $[\text{Ph}_3\text{C}]_2[\text{Si}(\text{OTf})_6]$ (ellipsoids at 50% probability; H atoms are omitted and OTf reduced to wireframe; only one of the cations is depicted).^[34]

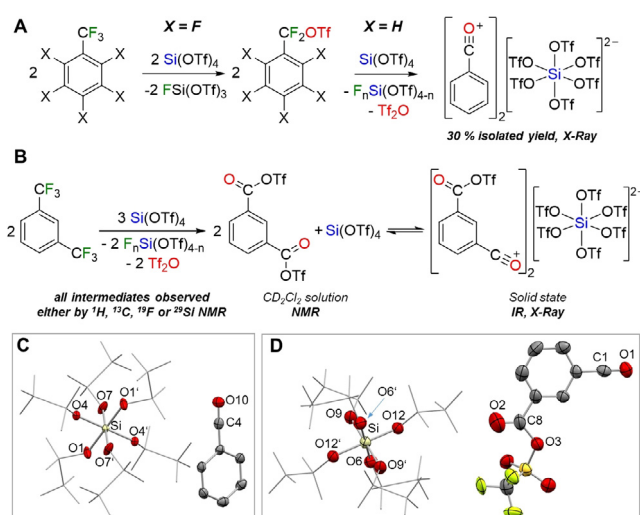


Figure 4. Oxydefluorination of trifluoromethyl benzenes (A/B), together with X-ray structures of $[\text{PhCO}]_2[\text{Si}(\text{OTf})_6]$ (C) and $[m\text{-(CO)(COOTf)}_2\text{C}_6\text{H}_4]_2[\text{Si}(\text{OTf})_6]$ (D) (ellipsoids at 50% probability; H atoms are omitted and Si-bound OTf reduced to wireframe; only one of the respective cations is depicted).^[34]

could be isolated in 30% yield from the reaction mixture and fully characterized ($\tilde{\nu}_{\text{CO}} = 2224$ cm^{-1} , $d(\text{C}\equiv\text{O}) = 1.124(5)$ Å, consistent with literature values,^[29] Figure 4a,c). $[\text{PhCO}]_2[\text{Si}(\text{OTf})_6]$ was independently synthesized from $\text{Si}(\text{OTf})_4$ and benzoyl triflate, PhCOOTf , in 92% yield. The latter is a high boiling liquid and not dissociated in contrast to $[\text{PhCO}]_2[\text{Si}(\text{OTf})_6]$, which illustrates the weakly coordinating nature of the $[\text{Si}(\text{OTf})_6]^{2-}$ anion.^[30]

In the literature, the ODF of ArylCF_3 species with the Brønsted superacid HOTf and subsequent Friedel–Crafts-type arylations afforded aromatic ketones, but the electrophilic intermediates could not be detected.^[31] Perfluorotoluene is at the threshold of deactivation for the reaction with $\text{Si}(\text{OTf})_4$ as there was no evidence for ODF and only partial conversion to $\text{C}_6\text{F}_5\text{CF}_2(\text{OTf})$ and $\text{FSi}(\text{OTf})_3$ took place after 14 days (66% by ^{19}F NMR, Figure 4a). A related F^-/OTf^- exchange reaction between $\text{C}_6\text{F}_5\text{CF}_3$ and the LSA $\text{B}(\text{OTf})_3$ was reported by Petrov.^[32]

In contrast, *m*-bis(trifluoromethyl)benzene, *m*-(CF_3)₂ C_6H_4 , was gradually oxydefluorinated with $\text{Si}(\text{OTf})_4$ in CD_2Cl_2 as monitored by NMR (Figure 4b, for more details about observed intermediates see Supporting Information). After three weeks at 40 °C, the formation of *m*-(COOTf)₂ C_6H_4 was observed (with approx. 10% of residual *m*-(COOTf)(CF_2OTf) C_6H_4 , based on ^1H NMR integrals).^[33] Cooling to 4 °C led to formation of crystals of $[(\text{CO})\text{-(COOTf)}_2\text{C}_6\text{H}_4]_2[\text{Si}(\text{OTf})_6]$ suitable for a SC-XRD analysis, which confirmed the complete ODF (Figure 4d). In the solid state structure, the OTf adjacent to the carbonyl group features a C8–O2 distance of 1.20(2) Å, while the linear CCO unit comprises a much shorter C1–O1 distance of 1.119(6) Å. Independently, we obtained the same compound in 62% yield with two characteristic IR vibrational modes at 1807 ($\text{C}=\text{O}$) and 2250 cm^{-1} ($\text{C}\equiv\text{O}$) by reacting *m*-(COOTf)₂ C_6H_4 with $\text{Si}(\text{OTf})_4$.^[30]

According to the DFT-derived triflate ion affinities of the involved species in CH_2Cl_2 (TIA_{solv} , for details see Supporting Information, Table S8), the abstraction of both triflates from $m\text{-(COOTf)}_2\text{C}_6\text{H}_4$ by $\text{Si}(\text{OTf})_4$ is unfavorable. In agreement with the experimental observations, the TIA_{solv} of $\text{Si}(\text{OTf})_4$ ($1^{\text{st}}/2^{\text{nd}}$ 106/92 kJ mol^{-1}) are in the range of PhCO^+ and $[m\text{-(CO)}(\text{COOTf})\text{C}_6\text{H}_4]^+$ (106 and 142 kJ mol^{-1}), whereas the TIA_{solv} of $[m\text{-(CO)}_2\text{C}_6\text{H}_4]^{2+}$ is considerably higher (200 kJ mol^{-1}).

In summary, we have demonstrated by theoretical and experimental investigations that $\text{Si}(\text{OTf})_4$ represents the first neutral silane derivative with both hard and soft Lewis superacidity. The OTf substituents at silicon in $\text{Si}(\text{OTf})_4$ are not only excellent leaving groups but can also modulate the degree of Lewis acidity which imparts its high reactivity towards halide sources and soft neutral donors. This is showcased by the generation of benzylium cations from mono- and bis(trifluoromethyl)benzenes and their stabilization through the weakly coordinating $[\text{Si}(\text{OTf})_6]^{2-}$ counterion. Investigations on the suitability of our method towards selective transformations of CF_3 -functionalized aryl compounds for organic synthesis by using $\text{Si}(\text{OTf})_4$ are currently underway.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: benzylium cations · C–X bond activation · main group complexes · silanes · weakly coordinating anions

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