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

Authors: André Hermannsdorfer and Matthias Driess*

Abstract: A facile synthesis and isolation of pristine silicon tetrakis(trifluoromethanesulfonate), Si(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, Si(OTf)_4 leads to [L_2Si(OTf)_4] complexes (L = isocyanide, thioether and carbonyl compounds) with retention of all Si–OTf bonds. In contrast, it can cleave C–X bonds (X = F, Cl) of hard organic Lewis bases with a high tendency to form SiX_4 (X = F, Cl) after halide/triflate exchange. Most notable, Si(OTf)_4 allows a gentle (WCA). LAs that are stronger than monomeric SbF_5 in Lewis pairs (FLP) and weakly coordinating anions including homogeneous catalysis, synthesis of frustrated species and mediators in many branches of chemistry, previously studied silane Lewis superacids (LSA) and the tris(trifluoromethyl)benzenes, resulting in the formation of the corresponding benzoylium species, which are stabilized by the weakly coordinating [Si(OTf)_4] dianion.

Main Group Complexes

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). 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). While the FIA scales the Lewis acidity towards the hard Lewis base F^-, the related hydridic 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 B(C_6F_5)_3 as a reference compound is considered as a soft LSA. Silicon-based LAs are particularly attractive because of the high abundance and low toxicity of this element. Accordingly, Lewis superacidic silylum ions, R_Si^+, have become valuable catalysts in organic synthesis but require the use of potent WCA. 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 Si(cat)_2 (X = Cl, Br, Figure 1). Other silicon(IV)-based LAs are routinely used in organic synthesis, with the commercially available TMSOTf (TMS = Me_3Si) arguably being a soft donor. More recently, a high FIA was calculated for Si(OTf)_4 suggesting its Lewis superacidity.

Herein, we describe a facile access to pristine Si(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 Si(OTf)_4 in multi-gram scale succeeds in 81% yields through the reaction of SiH 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 _29Si NMR resonance at δ = -121.7 ppm (CD_2Cl_2) is in good agreement with the reported value of -118.2 ppm for in situ generated Si(OTf)_4 in CH_2Cl_2.

In order to assess the Lewis acidity also in the “soft dimension”, the isoosmotic HIA of Si(OTf)_4, in addition to the FIA was calculated using the TMS-reference system (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). Both the FIA and HIA are well above the respective thresholds of SbF_5 and B(C_6F_5)_3, qualifying Si(OTf)_4 as a hard and soft LSA. Notably, also the second ion affinities are particularly high (approx.
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\(^{(c)}\) | HIA\(^{(c)}\) |
|----------------|-------------|-------------|
| SF\(_3\)        | -180        | 315         | 258         |
| Si(cat\(^{5}\))\(_2\) | 495         | 491         | 21          |
| Si(OTf)\(_4\) | 497         | 492         | 32          |
| Si(OTf)\(_4\) | 521         | 547         | 212         |
| SiF\(_4\)      | 500         | –           | –           |
| B(C\(_6\)F\(_5\))\(_3\) | 443         | –           | –           |

\(^{[a]}\) PW6B95-D3BJ/def2-QZVPP//B3LYP-D3BJ/def2-SVP.

400 kJ mol\(^{-1}\) above \([\text{XSiF}_3]\)^\(-/\text{[X}_2\text{SiF}_3]\)^\(-\) and indicate a high tendency for the formation of hexacoordinate species.

The Lewis superacidity was confirmed experimentally by reaction with \([\text{PPPh}_3]_2[\text{SiF}_4]\), which led to fluoride abstraction with subsequent formation of \((\text{TO})\text{SiF}_3\) and SiF\(_3\) \((19F\) and \(29Si\) NMR) among other, unidentified products. Employing one molar mixture of Si(OTf)\(_4\) and exceeds the soft Lewis superacidity of \(\text{Si(OTf)}_4\) by 180 kJ mol\(^{-1}\). The induced shifts \((\Delta\nu^\text{H}) = -89.7, -90.1\) ppm; \(J_{\text{CF}}\) = 267, 267 Hz) are similar to those for the FBN adduct of a weakly iodo-stabilized silylium ion. This emphasizes that Si(OTf)\(_4\) acts as a strong LA with retention of the Si–OTf bonds.

In contrast, it was shown by Ghosez that addition of TMSOTf to CA does not lead to a measurable \(\Delta\nu^\text{H}\) and a 1:1 mixture of HOTf and CA gave a \(\Delta\nu^\text{H}\) of only 1.28 ppm.

Furthermore, we applied a scaling method recently by Müller, based on the weak \(p\)-fluorobenzonitrile donor (FBN). From an equimolar mixture of Si(OTf)\(_4\) and FBN only the bis-adducts cis- and trans-[(FBN)Si(OTf)\(_4\)] are formed (molecular structure of the latter in Figure S124).

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 \((\Delta\nu^\text{P} = 51.2\) ppm\) in agreement with the high HIA, addition of Si(OTf)\(_4\) to the hydridoborate salt \([\text{Mes}_3\text{PH}][\text{H}B(\text{C}_6\text{F}_5)_3]\) in CDCl\(_3\) led to hydride abstraction. Consequently, the SiH species \([\text{HSi(OTf)}_4]\) and \([\text{H}_2\text{Si(OTf)}_4]\) were detected by \(^1H\) and HSi HMQC NMR spectroscopy (see Supporting Information for details).

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In this context, the reaction of Si(OTf)\(_4\) with soft neutral donors afforded unprecedented \([\text{L}_2\text{Si(OTf)}_4]\) 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 silylum 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 \(\delta^\text{13C}_{\text{CO}} = 208.4\) ppm for the benzophenone complex \([\text{Ph}_2\text{CO}]\text{Si(OTf)}_4\) in CDCl\(_3\) (cf. \(\delta^\text{13C}_{\text{CO}} = 196.8\) ppm for \(\text{Ph}_2\text{CO}\))\(^{[22]}\) the C=O distance of 1.275(4) Å is strongly elongated in the solid-state structure compared to \(\text{Ph}_2\text{CO}\) (1.2229(17) Å)\(^{[23]}\). A shortening of the N=C distance is observed for \([\text{XylNC}]\text{Si(OTf)}_4\) (1.145(3) Å) in comparison to the “free” isocyanide (1.160(3) Å)\(^{[24]}\) whereas in Si\(^{IV}\) isocyanide complexes, backbonding causes an elongation of the N–C bond\(^{[25]}\).

Figure 2. Top: Synthesis of the \([\text{L}_2\text{Si(OTf)}_4]\) complexes; bottom: their molecular structures (ellipsoids at 50% probability; H atoms are omitted and OTf reduced to wireframe).\(^{[34]}\) Selected distances (Å) for \(\text{L} = \text{Ph}_2\text{CO}: \text{C}–\text{O} 1.275(4), \text{Si}–\text{O} 1.796(2), \text{PhCHO}: \text{C}–\text{O} 1.263(2), \text{Si}–\text{O} 1.781(12), \text{XyINC} (\text{two independent molecules}): \text{N}–\text{C} 1.145(2)/1.146(2), \text{Si}–\text{C} 1.9631(7)/1.9602(18), \text{THT}: \text{S}–\text{Si} 2.3539(4), \text{PO}: \text{Si}–\text{O} 1.828(2), \text{Si}–\text{O} 1.845(2).\)

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

\(\Delta\nu^\text{H}\) of the adduct \([\text{(CA)B(C}_2\text{F}_3)]\) (1.05 ppm)\(^{[18]}\)
\( E_{\text{ent}} \) (for details see Table S5). In the gas phase, the association of \([L_2Si(OTf)_4]\) (AEsolv) is exothermic and exergonic, which is in stark contrast to the corresponding \([L_2SiF_4]\) complexes where \( \Delta G_{\text{gas}} > 0 \). This is in keeping with our results and experimental reports for SiF_4. The \( E_{\text{ent}} \) necessary to deform tetrahedral \( SiX_4 \) to the square-planar geometry adapted in trans-[L-SiX_4] decrease in the order \( SiCl > SiBr > SiI \) and are considered crucial for complex formation [Eq. (1)].

\[
-\Delta E_{\text{ent}} = E_{\text{ent}} - \left( E^\text{cis} + E^\text{trans} \right)
\]

However, the here calculated \( E_{\text{ent}}[Si(OTf)_4] \) (288–329 kJ mol\(^{-1}\)) are in a similar range as \( E_{\text{ent}}[SiF_4] \) (298–304 kJ mol\(^{-1}\)). Consequently, the high affinity of Si(OTf)_4 towards the L donors is due to much higher interaction energies \( E_{\text{ent}} \) between the prepared monomers for \([L_2Si(OTf)_4] \) (466–569 kJ mol\(^{-1}\)) against \( E_{\text{ent}}[L_2SiF_4] \) (128–329 kJ mol\(^{-1}\)).

We further investigated the applicability of Si(OTf)_4 as a halide and hydride acceptor. Due to the lability of the Si–OTf bond, hydride/triflate exchange was observed when exposing Si(OTf)_4 to Et_3SiH with formation of HSi(OTf)_3 and Et_3SiOTf (\(^1\)H and \(^{29}\)Si NMR). Remarkably, H/OTf exchange even occurs with the weaker hydride donor PhSiH_3,\(^{28}\) affording a mixture of HSi(OTf)_3 and PhSiH_2(OTf) (\(^3\)J\(^{19}\)F = 8.5 ppm).\(^{29}\) The formation of tritylum with two equivalents of trityl chloride was monitored by \(^1\)H and \(^{13}\)C NMR spectroscopy (\(^3\)J\(^{13}\)C = 211.1 ppm) after mixing in CD_2Cl_2 (Figure 2). The \(^{29}\)Si NMR spectra show the formation of SiCl_4 and [Si(OTf)_4]\(^{2-}\) (\(^3\)J\(^{29}\)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 [PhCO][Si(OTf)_6] (Figure 3). Likewise, [Si(OTf)_4]\(^2-\) and SiX_4 are formed from the reaction of Si(OTf)_4 with two molar equivalents of [NBu_4]X (X = Cl, Br, I) as evidenced by \(^{29}\)Si NMR. Accordingly, Si(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 the LSA B(OTf)_3 and SiX_4, which confirms the complete ODF (Figure 4). After three weeks at 40 °C, the formation of m-(COOTf)_2CH_4 was observed (approx. 10% of residual m-(COOTf)(CF_2OTf)CH_4 based on \(^1\)H NMR integrals).\(^{30}\) Cooling to 4 °C led to formation of crystals of [(CO)(COOTf)]_2CH_4[Si(OTf)_4] 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 1.19(6) Å. Independently, we obtained the same compound in 62% yield with two characteristic IR vibrational modes at 1807 (C=O) and 2250 cm\(^{-1}\) (C=O) by reacting m-(COOTf)_2CH_4 with Si(OTf)_4.\(^{31}\)
According to the DFT-derived triflate ion affinities of the involved species in CH₂Cl₂ (TIA₄, for details see Supporting Information, Table S8), the abstraction of both triflates from m-(COOTf)₂C₆H₄ by Si(OTf)₂ is unfavorable. In agreement with the experimental observations, the TIA₄ of Si(OTf)₂ (114 to 122 kJ mol⁻¹) are in the range of PhCO⁺ and [m-(CO)(COOTf)C₆H₄]⁺ (106 and 142 kJ mol⁻¹), whereas the TIA₄ of [m-(CO)₂C₆H₄]⁺ is considerably higher (200 kJ mol⁻¹).

In summary, we have demonstrated by theoretical and experimental investigations that Si(OTf)₂ represents the first neutral silane derivative with both hard and soft Lewis superacidity. The OTf substituents at silicon in Si(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 benzoylium cations from mono- and bis(trifluoromethyl)benzenes and their stabilization through the weakly coordinating [Si(OTf)]⁻counterion. Investigations on the suitability of our method towards selective transformations of CF₂-functionalized aryl compounds for organic synthesis by using Si(OTf)₂ are currently underway.

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Conflict of interest

The authors declare no conflict of interest.

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

[1] a) O. Sereda, S. Tabassum, R. Wilhelm in Topics in Current Chemistry (Ed.: B. List), Springer, Berlin, Heidelberg, 2009, pp. 349–393; b) I. M. Riddelstone, A. Kraft, J. Schaefer, I. Koshima, T. Asahi, K. Soai, Angew. Chem. Int. Ed. 2018, 57, 13982–14024; c) A. R. Nödling, K. Müller, Angew. Chem. 2013, 130, 8219–8226.

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