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1-Triflato-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane and 1,3-bis-triflato-5,7-dimethyl-1,3,5,7-tetrasilaadamantane; synthesis, complexation study and X-ray structure of 1-hydroxy-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane

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Abstract

The symmetrical 1,3,5,7-tetramethyl-1,3,5,7-tetrasilaadamantane (**1**) reacts with 1.5 molar equivalents of ICl–AgOTf at room temperature to furnish the hitherto unknown 1-triflato-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (**9**) chemoselectively, in near quantitative yields. The treatment of **9** with 2 mol equivalents of ICl–AgOTf affords the bis-triflate **10** in high yields. Control experiments showed that reaction of **1** with ICl (1 mol equivalents)–CCl_4 is sluggish, giving 18% conversion to 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (**2**) after 23 h at room temperature. Addition of $AlBr_3$ catalyzes the process, allowing 73% conversion after 21 h at room temperature. The ICl–AgOTf reagent eliminates the need to prepare and isolate **2** as an intermediate for the synthesis of **9**. In silicon NMR spectra, the ^{29}Si Si–OTf resonance of **10** is slightly upfield compared with that of **9**. Treatment of **9** with a saturated solution of $B(C_6F_5)_3$ in CH_2Cl_2 at room temperature shows only minor deshielding at silicon as determined by ^{29}Si-NMR spectroscopy. Attempts to generate donor–acceptor complexes by treatment of **9** with $Al(OTf)_3$–CD_3CN and with liquid BCl_3 gave no notable changes in the Si–OTf NMR chemical shift. In attempts to grow crystals from **9** and **10**, white crystals suitable for X-ray analysis were obtained from a sample of **9**, the molecular structure of which was shown to be 1-hydroxy-3,5,7-trimethyl-1,3,5,7-tetra-silaadamantane (**11**), generated by hydrolysis of the Si–OTf bond. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 1-Triflato-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane; 1,3-Bistriflato-5,7-dimethyl-1,3,5,7-tetrasilaadamantane; ICl–AgOTf; Synthesis and complexation with super Lewis acids; S_N2-Si and S_Ni-Si; Hydrolysis of Si–OTf

1. Introduction

Synthesis of 1,3,5,7-tetramethyl-1,3,5,7-tetrasilaadamantane (**1**) via gas phase pyrolysis of TMS and TMSCl (Fig. 1) was reported by Fritz and coworkers 30 years ago [1]. The chloride **2** and bromide **3** were later synthesized by a ligand redistribution approach involving the treatment of 1,3,5-hexamethyl-1,3,5-trisilacyclohexane $(Me_2Si–CH_2)_3$ with $AlCl_3$ or $AlBr_3$ [2].

Compound **3** was also prepared from **4** via treatment with Br_2–CCl_4 [3]. The tetrasila-adamantane skeleton is exceptionally stable, and **2** is unreactive in typical solvolytic reactions due to a combination of bridgehead structure, which precludes backside nucleophilic attack, and increased ground state stability of the rigid but strain free cage skeleton. Whereas chlorosilane **2** does not react with MeOH or H_2O, it does react with NaOMe–MeOH to give methoxysilane **5** which is solvolytically more reactive than **2**. Compounds **2** and **3** react with various quaternary ammonium fluorides to give fluorosilane **6** in good yields. Based on a series of reactivity studies, Homer and Sommer [4] proposed an S_N2-Si process for these transformations (proceeding with retention of configuration).

In 1988, Fritz and Honold [3] reported on the cleavage of Si–C bonds in a series of Si-methylated carbosilanes with ICl or ICl–$AlBr_3$. As part of that study it was reported that **1** reacts with ICl in CCl_4 solvent to give a

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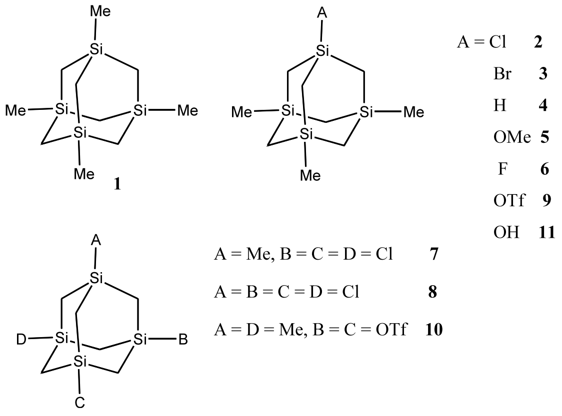

Fig. 1. List of compounds.

mixture of tri- and tetrachlorosilanes **7** and **8** (in about 1:1 ratio).

We became interested in the possibility that Si–Cl derivatives from **1** (e.g. **2**, **7**, and **8**) might serve as a starting point for the synthesis of the hitherto unknown silaadamantyl triflates such as **9** (Fig. 1), and to track down the limits of this process. A second goal was to examine their complexation with super Lewis acids. In relation to previous studies by Olah, Laali and Farooq on $R_3SiOTf–BX_3$ systems, in which polarized Lewis acid–base adducts are formed [5], boron Lewis acids were targeted. We were interested in using commercially available and easily handled $B(C_6F_5)_3$, which has not been previously employed for complexations with R_3SiOTf. As part of a study on the effect of Lewis acids on silicon chemical shifts of trialkylsilyl halides, Olah and Field [6] reported on complexation of bromosilane **3** with $AlBr_3–CH_2Br_2$ giving significant deshielding at silicon.

We now report on the development of facile one-pot preparations of silaadamantyl triflates **9** and **10** directly from **1** at room temperature, and model complexation studies on **9**. In the course of attempts to grow suitable crystals from **9**, the crystal structure of compound **11**, formed via hydrolysis of **9**, was solved.

2. Results and discussion

2.1. Initial studies

Attention was initially focused on the synthesis of Si–Cl derivatives from **1**. To this end, a solution of **1** and ICl (one equivalent) in CCl_4 was allowed to stir at room temperature. ^{1}H-NMR analysis of the reaction mixture after 23 h indicated 18% conversion of **1**–**2**. Addition of a small quantity of $AlBr_3$ to the reaction mixture increased the conversion to 33% after a total reaction time of 48 h. NMR analysis of the brown solid obtained after work-up showed a silane to chlorosilane ratio of 1.8:1.0. By repeating this experiment with a starting ICl: **1**: $AlBr_3$ molar ratio of 1:1:0.2, 73% conversion of **1**–**2** was achieved (74% by NMR after work-up). In this process, MeI is formed as a byproduct and competes with **1** for ICl to give MeCl and I_2. However, use of an excess of ICl might lead to over chlorination (mixture of mono- and di-). The slow conversion of **1**–**2** and the need for product separation, led us to consider an alternate route to silaadamantyl triflate **9**.

*2.2. Synthesis of the monotriflate **9***

The treatment of **1** with ICl–AgOTf in dichloromethane provides direct access to 1-triflato-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (**9**) (Fig. 2).

If **1** and ICl–AgOTf are employed in nearly equimolar amounts, some unreacted **1** remains and traces of **2** are also produced. The use of 1.5 equivalents of ICl–AgOTf relative to **1** gives the highest yields and chemoselectivity (almost quantitative for formation of **9**).[2] In reactions in which ICl was used in excess relative to AgOTf (in this case AgOTf was added to a solution of **1** and ICl in CH_2Cl_2), the reaction mixture consisted of about 70% **2**, 20% **9** and the remainder was unreacted **1** (NMR assay).

Given the bond polarizations of Si^+Me^- and I^+Cl^-, conversion of **1**–**9** could be explained via a mechanism which closely resembles 'S_Ni-Si' [7] (Fig. 3), in which the I^+ end of the ICl dipole assists methyl departure in a cyclic transition state (in the actual S_Ni-Si formalism the leaving group is an *n*-donor halogen) (see Fig. 3).

The catalytic effect of $AlBr_3$ probably stems from ICl coordination with $AlBr_3$. Combination of larger bond polarity and high affinity of silicon for triflate makes the in-situ formed 'I-OTf' an excellent reagent for displacement at silicon.

*2.3. Synthesis of the bis-triflate **10***

Treatment of the mono-triflate **9** with ca. two equivalents of ICl–AgOTf in CH_2Cl_2 at room temperature, affords the bis-triflate **10** (Fig. 4), which is stable to aqueous work-up and was isolated in near quantitative yield (NMR).

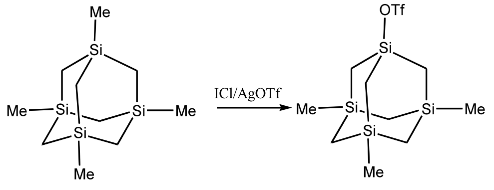

Fig. 2. Synthesis of monotriflate **9**.

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[2] In one prep of the mono-triflate **9** from **1** (using 1.5 equivalents ICl–AgOTf) a mixture of mono-OTf and di-OTf (88:12) was obtained.

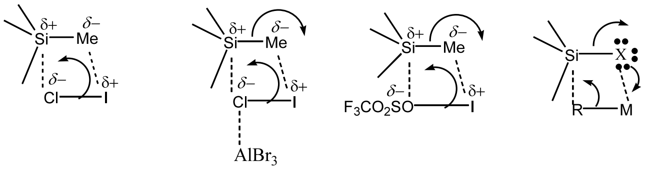

Fig. 3. Mechanistic considerations.

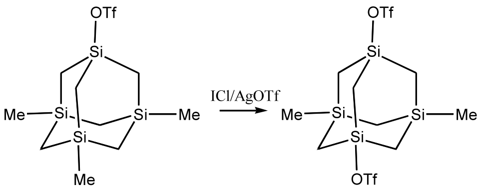

Fig. 4. Synthesis of bis-triflate.

An attempt to prepare higher triflates directly from **1** with a large excess of ICl–AgOTf led to a complex mixture of products. In another experiment, bis-triflate **10** was allowed to react with ICl–AgOTf in CH_2Cl_2. In this case, unreacted **10** was recovered and there was no NMR evidence for the formation of a higher triflate. It is noteworthy that introduction of a second triflate group has a noticeable *shielding* effect on the Si–OTf resonance which changes from δ 35.8 in **9** to δ 31.7 in **10**, in the ^{29}Si-NMR spectrum.

2.4. Structural analysis

Numerous attempts were made to grow suitable crystals of **9** and **10** for X-ray analysis. However, the low melting-waxy nature of these compounds was problematic. Slow evaporation of a chloroform solution of **9** at room temperature in an open system gave white crystals, identified by X-ray analysis as the Si–OH derivative **11** formed by slow hydrolysis of the Si–OTf bond during crystallization attempts (see below for crystallographic details; for NMR data see Section 4).

2.5. Crystal structure of 11

X-ray diffraction quality single crystals were grown from chloroform by slow evaporation of solvent. A single crystal with dimensions of 0.21 × 0.08 × 0.08 mm was selected and mounted on a thin glass fiber using epoxy glue. The data were collected at 22 °C using a narrow frame method with scan widths of 0.3° in ω and exposure times of 10 s. A hemisphere of intensity data were collected in 1081 frames with the crystal-to-detector distance of 50.4 mm, which corresponds to a maximum 2θ value of 54.1°. Frames were integrated with the BRUKER SAINT program. A semi-empirical absorption correction based upon simulated ψ-scans was applied to the data set. The structure was solved by a combination of direct methods and difference Fourier methods, and refined with full-matrix least-squares techniques. All the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were either directly located from the difference Fourier maps or calculated based on the idealized geometry. Details of the data collection, structure solution and refinement are given in Table 1.

The unit cell contains two crystallographically independent, but chemically equivalent molecules. Fig. 5 shows the ORTEP representation of one of the two molecules in the unit cell with selected bond distances and bond angles given in the caption. The only previously determined X-ray structures for the tetrasilaadamantane cage compounds are the tetramethyl- **1** [9] and the trimethyl-monobromo derivative **3** [10]. The structure of compound **11** closely resembles that of **3**. If the H atoms are omitted from the structure, the molecule has idealized C_{4h} symmetry. All the bond distances and bond angles are in the normal range.

2.6. Complexation studies

In light of previous studies on the complexation of R_3SiOTf with liquid BCl_3 [5] and the reported complexation of **3** with $AlBr_3$–CH_2Br_2 at room temperature [6], silyl triflates **9** and **10** appeared ideal models for the generation of donor–acceptor complexes. We examined the complexation of **9** with $B(C_6F_5)_3$ and $Al(OTf)_3$ (both commercially available) at room temperature, and with liquid BCl_3 at low temperature. Addition of one

Table 1
Data for crystal structure analysis of **11**

Compound	1-Hydroxy-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane
Temperature (°C)	22
Formula	$C_9H_{22}O_1Si_4$
Space group	$P\bar{1}$ (#2)
a (Å)	9.2049(7)
b (Å)	12.177(1)
c (Å)	14.986(1)
α (°)	67.329(1)
β (°)	80.682(2)
γ (°)	80.308(2)
V (Å^3)	1519.1(2)
Z	4
D_{calc} (g cm^{-3})	1.131
μ (Mo–K$_\alpha$) (mm^{-1})	0.365
Crystal size (mm)	0.21 × 0.08 × 0.08
Number of unique data	7259
Number of data used/σ cutoff	3038/$I > 3.00\sigma(I)$
$T_{min/max}$; abs cor	0.911/1.00
Number of atoms per asym uint (including H)	253
Max/min peaks in final difference Map (e Å^{-3})	0.48/−0.26
Final R/R_w (%)	5.67/7.19
Goodness-of-fit on F^2	1.258

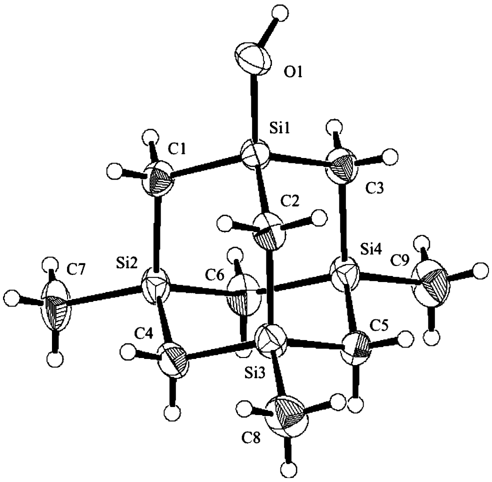

Fig. 5. The ORTEP representation of compound **11**. Selected bond distances (Å) and bond angles (°): Si(1)–O(1) = 1.656(3), Si(1)–C(1) = 1.859(5), Si(2)–C(1) = 1.863(5), Si(2)–C(4) = 0.857(6), Si(3)–C(2) = 1.873(5), Si(3)–C(8) = 1.879(6), Si(4)–C(3) = 1.878(5), Si(4)–C(9) = 1.869(5), O(1)–Si(1)–C(1) = 110.1(2), C(1)–Si(2)–C(4) = 107.4(2), C(2)–Si(3)–C(4) = 107.7(2), C(3)–Si(4)–C(5) = 107.0(2).

equivalent of $B(C_6F_5)_3$ to **9** in CH_2Cl_2–CD_2Cl_2 caused the Si–OTf resonance to move from δ 35.8 to δ 39.0 in the ^{29}Si-NMR spectrum. Addition of excess $B(C_6F_5)_3$ (ca. four equivalents is maximum because of solubility limitations) caused further deshielding to δ 41.9. The Si–Me resonance (^{1}H-NMR) changed from δ 2.3 in **9** to δ 2.5 in the complex, suggesting a small long-range influence which might stem from hyperconjugation through the cage (see later conclusions). Further deshielding of the Si–OTf resonance was observed by cooling the sample to −60 °C (δ 43.7). Thus a maximal $\Delta\delta^{29}$Si of ca. 8 ppm was achieved. As shown previously by Olah and associates [8], $Al(OTf)_3$ is almost insoluble in regular non-coordinating organic solvents; only in strongly coordinating solvents such as MeCN and acetone is it reasonably soluble. In one NMR experiment, $Al(OTf)_3$ was mixed with **9** in CD_3CN. In this case, no noticeable changes in the silicon resonance were observed. If there is equilibrium complexation, the Lewis acid greatly favors the solvent. Solubility issues prevent low temperature studies.

In another experiment, **9** was treated with excess liquid BCl_3 at low temperature in a manner similar to the previously reported studies with R_3SiOTf [5]. However, based on the silicon NMR spectrum, a persistent donor–acceptor complex between **9** and BCl_3 was not detected.

2.7. Mass spectral analyses

Conventional EI-mass spectra of **1** and some of its derivatives have been reported [3]. With parent tetrasilaadamantane and its monochloro-derivative, skeletal rearrangement in the gas phase involving simultaneous rupture of 3-bonds and concomitant H transfer has been reported [11]. In the present study, we recorded CI-mass spectra for **1**, **9**, **10**, and **11** using an ion-trap GC-MS and detected interesting features worth mentioning. For **1**, whereas the most abundant cation is m/z 241 (the silicenium ion; loss of Me) there is another prominent ion at m/z 259 (formally corresponding to a silyloxonium ion formed by addition of H_2O (present in the ion source) to the silicenium ion. For **9**, apart from the ion at 391 [O-protonated triflate; $(M+H)^+$], ions at m/z 393 and 375 were observed. The former corresponds to its silyloxonium ion and the latter to the silicenium ion (loss of Me). Cations observed from the bis-triflate **10** were m/z 527 (silyloxonium ion; loss of Me and H_2O attachment), 525 (M^+), 544 ($M \cdot H_3O^+$) and 393 (possibly originates from **9** present as impurity; see above). Prominent cations formed via silanol **11** were m/z 261 (loss of Me and H_2O attachment to the silicenium ion) and 243 (loss of Me).

3. Conclusions

An efficient method for the sequential conversion of **1** to its mono- and bis-triflate derivatives with ICl–AgOTf has been developed. In line with previous studies [7], this transformation may be viewed as an S_Ni-Si process via a quasi-cyclic transition state involving Si–Me and the in-situ formed ‘I-OTf’. Attempts to prepare a tris (or tetrakis) tetrasila-triflate were unsuccessful.

The finding that introduction of a second triflate has a shielding effect on the ^{29}Si Si–OTf chemical shift, that only two Si–Me bonds can be transformed into Si–OTf linkages, and that Si–Me resonance in **9** moves downfield on Si–OTf complexation with $B(C_6F_5)_3$ may manifest the onset of *hyperconjugation* in the tetrasilaadamantane cage.[3] This aspect is being examined in a separate study by DFT calculations on model Si–X compounds derived from various silaadamantanes (mono through tetra), including their silicenium ions.

In order to generate positive charge at silicon, complexation of **9** with several Lewis superacids was examined. Despite an established tendency for R_3SiOTf to coordinate boron Lewis acids, in the case of **9**, only $B(C_6F_5)_3$ caused noticeable deshielding at silicon (maximum $\Delta\delta^{29}$Si around 8 ppm).

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[3] Hyperconjugation could be visualized by the following mechanisms: As X becomes more electron-withdrawing and as partial positive charge starts to develop at silicon; (i) electron rich C–Si sigma bond(s) could donate into the back-lobe of the developing p-orbital at silicon; (ii) silicon may undergo rehybridization–pyramidalization with C–Si bond donating into an appropriate empty orbital at silicon; (iii) C–Si could donate into the Si–X *anti*-bonding orbital.

The molecular structure of compound **11** formed by hydrolysis of **9** has been determined. The facile conversion of **11**–**12** might provide new opportunities for functionalization of the tetrasilaadamantane cage.

4. Experimental

ICl, AgOTf, $B(C_6F_5)_3$ and $Al(OTf)_3$ were all high purity commercial samples (from Aldrich) which were used as received. CH_2Cl_2 was distilled from P_2O_5. BCl_3 (99.9%; lecture bottle from Aldrich) was used as received. Compound **1** [1] was a gift sample from Professor Fritz (Karlsruhe). ^{1}H-NMR: δ 0.10 (s), -0.27 (s); ^{13}C-NMR: δ 5.10, 0.25; ^{29}Si-NMR: δ 2.32; white crystalline solid, m.p. ~121–122 °C.

NMR spectra were recorded on a Varian INOVA 500 MHz instrument using a 5 mm broad-band probe. ^{1}H-NMR (500 MHz; $CDCl_3$ with TMS; $C\mathit{H}Cl_3$ @ 7.22); ^{13}C-NMR (125.7 MHz; $CDCl_3$ with TMS; $\mathit{C}HCl_3$ @ 77.23); ^{29}Si-NMR (99.3 MHz; $CDCl_3$ with TMS); ^{19}F-NMR (470.3 MHz; $CFCl_3$ and $CDCl_3$).

Mass spectra were recorded in the CI mode (methane) on a Thermoquest Polaris ion-trap instrument coupled to Trace-GC (helium carrier gas). Highly dilute (methylene chloride) samples were introduced into the capillary column (Supelco MDN-5; 30 m; GC conditions: 60 °C for 1 min, 15° min^{-1} to 250 °C; inj: 250 °C).

4.1. Synthesis of **9**

AgOTf (193 mg. 0.75 mmol) was added to a solution of ICl (120 mg, 0.74 mmol) in dry CH_2Cl_2 (ca. 16.5 ml). The two-phase mixture was stirred at room temperature (r.t.) for ca. 30 min. and diluted with additional CH_2Cl_2 (8.5 ml). A solution of **1** (127 mg, 0.49 mmol) in dry CH_2Cl_2 (~2 ml) was then introduced and enough CH_2Cl_2 was added to bring the total solvent volume to 50 ml. After ca. 4.75 h, more AgOTf (22 mg, 0.085 mmol) was added and stirring was continued for 17.75 h, after which time the magenta color of the reaction mixture was largely discharged. The mixture was decanted through filter paper to remove insoluble silver salts, and the purple-pink filtrate was concentrated to a reddish oil containing some particulate matter. This material was treated with CH_2Cl_2, passed through a disposable pipet packed with a cotton plug, and concentrated to an oil of characteristic odor and still containing some insoluble matter (total mass, 0.20 g). Repetition of this procedure (dissolution in CH_2Cl_2, filtration through a cotton plug and removal of solvent) gave almost pure **9** as an oil (197 mg, 0.50 mmol; close to quantitative conversion based on **1**). ^{29}Si-NMR: δ 35.8, 2.34; ^{13}C-NMR: δ 118.57 (CF_3), 7.81 (CH_2), 4.56 (CH_2), 3.97 (Me); ^{1}H-NMR: δ 0.39 (CH_2), 0.21 (Me), -0.16 (CH_2); ^{19}F-NMR: δ -77.83. For MS data, see Section 2.7.

When silyl triflate **9** was stored under refrigeration, slow deposition of small quantities of solid material was observed.

In a preliminary experiment in which ICl was employed in only13% excess [**1** (0.11 mmol), ICl (0.13 mmol), AgOTf (0.14 mmol)], a 3.4:1 molar mixture of **9** and **1** (77% conversion) containing a trace of chlorosilane **2** was obtained (^{29}Si and ^{1}H-NMR assay).

4.2. Synthesis of **10**

A previously prepared sample of **9** stored in a freezer (oil containing some solid) was treated with dry CH_2Cl_2, filtered and concentrated to a straw-colored mobile liquid (122 mg) which was used in part for the synthesis of **10** in the following manner. AgOTf (72 mg, 0.28 mmol) was added at r.t. to a magnetically stirred solution of ICl (38 mg, 0.23 mmol) in dry CH_2Cl_2 (ca. 5 ml; 25 ml RB-flask). After 20 min., a solution of **9** (42 mg, 0.10 mmol) in CH_2Cl_2 (ca. 2 ml) was introduced. Within 2 min, the color of the CH_2Cl_2 phase changed from brown to purple, and the solid phase changed in appearance. After the air above the solution was displaced with dry nitrogen and the reaction vessel was stoppered and covered with aluminum foil, the reaction mixture was stirred for ca. 23 h at r.t. The insoluble silver salts were then removed by filtration and the purple filtrate was swirled with (aq.) $Na_2S_2O_3$ (131 mg in 20 ml of water) until the purple color was discharged. The mixture was transferred to a separatory funnel with additional CH_2Cl_2 (10 ml) and the cloudy organic phase was isolated, washed with water (whereupon it clarified), dried ($MgSO_4$) and concentrated to a straw-colored liquid (43 mg), identified by NMR analysis as the bis-triflate **10** containing minor impurities. ^{29}Si-NMR: δ 31.92, -1.21; ^{1}H-NMR: δ 1.00 (CH_2, 2H), 0.53 (CH_2, 8H), 0.33 (Me, 6H), -0.05 (CH_2, 2H); ^{13}C-NMR: δ 118.46 (CF_3), 10.50, 7.63, 4.18, 2.70; ^{19}F-NMR: δ -77.44. For MS data, see Section 2.7.

4.3. Synthesis of **2** using ICl–$AlBr_3$

A solution of ICl (67.6 mg, 0.41 mmol) and **1** (107 mg, 0.41 mmol) in CCl_4 (5 ml) was treated with $AlBr_3$ (20 mg, 0.07 mmol), and the mixture was stirred at r.t. for almost 2 days. The progress of reaction was monitored by ^{1}H-NMR until optimal conversion to **2** was achieved (73% before work-up; MeI was also present). The purple reaction mixture was then washed with H_2O, extracted with CH_2Cl_2, dried ($MgSO_4$) and concentrated. During solvent removal (Bucchi rotary evaporator; T ~ 55 °C), I_2 (or ICl) was sublimed to give **2** as white solid. ^{1}H-NMR: δ 0.27, 0.17, -0.22 (all singlets). The ^{1}H-NMR spectroscopic data were in good agreement with the literature [4].

4.4. Complexation studies

(a) A solution of **9** (30 mg, clear oil containing 23 mol% of **1**) and $B(C_6F_5)_3$ (61 mg) in dry, freshly distilled CH_2Cl_2 was prepared for NMR analysis. Several drops each of CD_2Cl_2 and TMS were added. Silicon NMR spectra were recorded at r.t. and exhibited resonances at δ 39.03 and 2.45. Addition of more $B(C_6F_5)_3$ (178 mg, saturated solution) shifted the silicon resonances to δ 41.95 and 2.57. When the sample was cooled to -60 °C, ^{29}Si resonances at δ 43.75 and 2.23 were observed; (b) a sample of **9** (50 mg) was added to a 5 mm NMR tube and cooled at dry-ice–acetone temperature. BCl_3 was condensed into the NMR tube under an argon atmosphere and CD_2Cl_2 (several drops) was added. Silicon NMR analysis at -60 °C showed no noticeable deshielding in the Si–OTf resonance; (c) to a solution of **9** (38 mg, 0.09 mmol) in CD_3CN (0.63 ml) was added $Al(OTf)_3$ (131 mg, 0.27 mmol, saturated). The mixture was then filtered through a cotton plug into a 5 mm NMR tube (cloudy solution). NMR analysis (r.t.) showed no measurable changes relative to a sample of **9** alone in CD_3CN.

4.5. NMR data for compound **11** (formed by slow hydrolysis of **9** in $CHCl_3$; see Section 2.4)

^{29}Si-NMR: δ 14.48 (Si–OH), 2.51 (Si–Me); ^{1}H-NMR: δ: 1.89 (OH), 0.12 (Me; 9H), -0.008 (CH_2, 6H), -0.29 (CH_2, 6H). For MS data see Section 2.7.

5. Supplementary material

Crystallographic data for compound **11** have been deposited with the Cambridge Crystallographic Data Center, CCDC no 179304. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) G. Fritz, F. Diem, H. Kohler, D. Kummer, H. Scheer, Angew. Chem. Int. Ed. Engl. 9 (1970) 464;
(b) Review: G. Fritz, Angew. Chem. Int. Ed. Engl. 26 (1987) 1111.
[2] C.L. Frye, J.M. Klosowski, D.R. Weyenberg, J. Am. Chem. Soc. 92 (1970) 6379.
[3] G. Fritz, J. Honold, Z. Anorg. Allg. Chem. 556 (1988) 23.
[4] G.D. Homer, L.H. Sommer, J. Am. Chem. Soc. 95 (1973) 7700.
[5] G.A. Olah, K. Laali, O. Farooq, Organometallics 3 (1984) 1337.
[6] G.A. Olah, L.D. Field, Organometallics 1 (1982) 1485.
[7] (a) L.H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill, New York, 1965;
(b) G.A. Olah, K.K. Laali, Q. Wang, G.K.S. Prakash, Onium Ions (chapter 9), Wiley, New York, 1998.
[8] G.A. Olah, O. Farooq, S.M.F. Farnia, J.A. Olah, J. Am. Chem. Soc. 110 (1988) 2560.
[9] E.W. Krahe, R. Mattes, K.F. Tebbe, H.G. von Schnering, G. Fritz, Z. Anorg. Allg. Chem. 393 (1972) 74.
[10] S.N. Gurkova, A.I. Gusev, V.A. Sharapov, T.K. Gar, V.N. Alekseev, Zh. Strukt. Khim. 20 (1979) 356.
[11] R.S. Gohlke, R.J. Robinson, Org. Mass Spectrom. 3 (1970) 967.