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Synthesis of Wiberg's Tetrasilatetrahedrane (tBu$_3$Si)$_4$Si$_4$ by a One-Pot Procedure

Frank Meyer-Wegner, Stefan Scholz, Inge Sänger, Frauke Schödel, Michael Bolte, Matthias Wagner, and Hans-Wolfram Lerner*

Institut für Anorganische Chemie, Goethe-Universität Frankfurt am Main, Max-von-Laue-Strasse 7, 60438 Frankfurt am Main, Germany

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Summary: A one-pot synthesis of the tetrasilatetrahedrane (tBu$_3$Si)$_4$Si$_4$ *was achieved by the reaction of* HSiCl$_3$ *and* Na[SitBu$_3$]. *In this reaction the silane* tBu$_3$SiH *was obtained along with* (tBu$_3$Si)$_4$Si$_4$ *and* tBu$_3$SiSitBu$_3$. *The tetrasilatetrahedrane* (tBu$_3$Si)$_4$Si$_4$ *was also obtained via a one-pot approach by treatment of* Cl$_3$SiSiCl$_3$ *or* Cl$_3$SiSiCl$_2$SiCl$_3$ *with* Na[SitBu$_3$]. *In the reaction of* HSiCl$_3$ *with* Na[SitBu$_3$], *two molecules of the tetrasilatetrahedrane* (tBu$_3$Si)$_4$Si$_4$ *crystallize together with one molecule of* tBu$_3$SiSitBu$_3$ *and one molecule of benzene. Single crystals suitable for X-ray diffraction composed of one molecule of* (tBu$_3$Si)$_4$Si$_4$ *and two molecules of benzene were obtained by recrystallization from benzene.*

Introduction

In 1978, Maier and co-workers reported the first synthesis and determination of the molecular structure of tetra(*tert*-butyl)tetrahedrane, which is a very strained cage compound with a highly symmetrical structure and unusual bonding nature.[1] Since 1988, the chemistry of stable, small-cage compounds consisting of the heavier group 14 elements (Si, Ge, and Sn) has been extensively studied. It has been shown that compounds R_nE_n with tetrahedral (**A**), trigonal-prismatic (**B**), or cubic polyhedra E_n (**C**) of carbon homologues E are accessible only by using sterically demanding groups R (Chart 1).[2,3] Evidently, less sterically demanding substituents do not prevent transformation of the core into less strained compounds.[4,5] Substances with polyhedral structure of type **A**, **B**, and **C** have been synthesized for E = Si and Ge,[2,3] whereas for E = Sn only those of type **B**[6] and **C**[7] but not of type **A** are known.

The only known examples with tetrasilatetrahedrane structures, (tBu$_3$Si)$_4$Si$_4$ (**1**)[8] and (Dis$_2$MeSi)$_4$Si$_4$ (Dis = CH(SiMe$_3$)$_2$) (**2**),[9] were reported in 1993 by Wiberg et al. and 10 years later in 2003 by Sekiguchi and co-workers.

While tetrasilatetrahedrane **1** is stable toward water, air, light, and temperature (decomposition > 300 °C), it seems to be sensitive toward oxidizing agents. It was found that, when using equimolar equivalents of reactants, treatment of **1** with iodine yields quantitatively the cyclotetrasilene **3** (Scheme 1).[10] No reaction could be observed between **1** and M[SitBu$_3$] (M = Li, Na, K).[11] However, **2** can be reduced with KC$_8$ in Et$_2$O, which results in the selective cleavage of the exocyclic Si−Si bond without degradation of the tetrahedrane core, as shown in Scheme 1.[9]

The tetrasilatetrahedrane **1** was prepared by Wiberg and co-workers in a six-step sequence, and its structure was determined by X-ray diffraction.[8,12] We present here a one-pot synthesis of the tetrasilatetrahedrane **1** by the reaction of HSiCl$_3$ with Na[SitBu$_3$]. In addition, Na[SitBu$_3$] also reacts with Cl$_3$SiSiCl$_3$ and Cl$_3$SiSiCl$_2$SiCl$_3$, respectively, which give **1** in a one-pot procedure.

Results and Discussion

Surprisingly, the reaction of 1 molar equiv of Na[SitBu$_3$] with one of HSiCl$_3$, as shown in Scheme 2, is quite different from the reactions of tri-*tert*-butylsilanides M[SitBu$_3$] (M = Li, Na, K) with organyl-substituted chlorosilanes R$_n$SiCl$_{4-n}$.[11,13] Treatment of HSiCl$_3$ with Na[SitBu$_3$] in 1:1 molar ratio in benzene resulted in an immediate reaction, and the mixture quickly became heterogeneous.[14] The ^{29}Si NMR spectrum showed that the silanide had been completely consumed, and new signals appeared that could be assigned to the tetrasilatetrahedrane **1**, the disilane tBu$_3$SiSitBu$_3$, and the silane tBu$_3$SiH. The formation of these products suggested to us the mechanism, as shown in Scheme 2: (i) First Na[SitBu$_3$] deprotonates HSiCl$_3$. (ii) Then, in a second step, transient

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*Corresponding author. Fax: +49-69798-29260. E-mail: lerner@chemie.uni-frankfurt.de.

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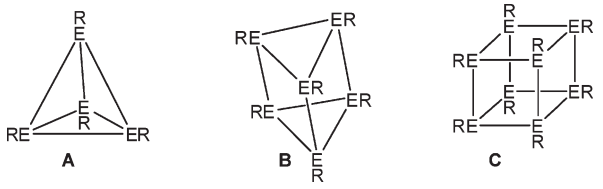
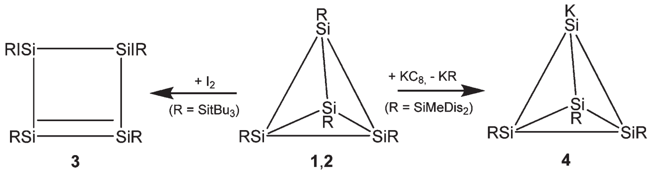
(14) Reaction of HSiCl$_3$ with K[Si(SiMe$_3$)$_3$] gives the cyclotrisilane [(Me$_3$Si)$_2$Si]$_3$: Klinkhammer, K. W. Thesis, University of Stuttgart, Germany, 1998.

Chart 1. Polyhedral Structures of Carbon Homologues



Scheme 1. Chemical Properties of Tetrasilatetrahedranes 1 and 2

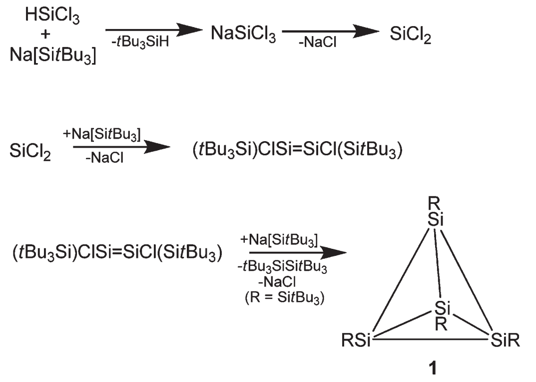


NaSiCl_3 undergoes NaCl elimination to form dichlorosilylene SiCl_2. (iii) Reaction of SiCl_2 with $\text{Na[Si}t\text{Bu}_3]$ and dimerization of the $(t\text{Bu}_3\text{Si})\text{SiCl}$ thus formed gives the disilene $(t\text{Bu}_3\text{Si})\text{ClSi}{=}\text{SiCl}(\text{Si}t\text{Bu}_3)$. (iv) Dehalogenation[15] of the disilene by reaction with $\text{Na[Si}t\text{Bu}_3]$ finally gives the tetrasilatetrahedrane **1**, the disilane $t\text{Bu}_3\text{SiSi}t\text{Bu}_3$, and NaCl. It is interesting to note that the cluster buildup takes place in the presence of unreacted HSiCl_3. Therefore deprotonation of HSiCl_3 must be much slower than cluster formation with $\text{Na[Si}t\text{Bu}_3]$. Filtration and slow concentration of the filtrate resulted in deposition of X-ray quality crystals that contained two molecules of **1**, one molecule of $t\text{Bu}_3\text{SiSi}t\text{Bu}_3$, and one molecule of benzene.[16] The tetrasilatetrahedrane **1** could be separated from $t\text{Bu}_3\text{SiSi}t\text{Bu}_3$ by HPLC or by its precipitation when acetonitrile was added to a tBuOMe solution of **1** and $t\text{Bu}_3\text{SiSi}t\text{Bu}_3$.

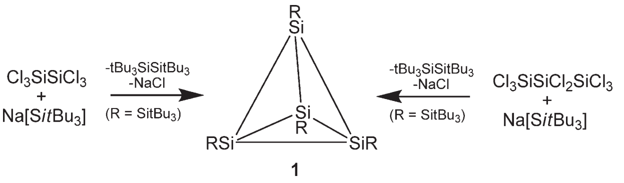
Reaction of nucleophilic reagents with chlorine-substituted polysilanes has received renewed interest in recent years. We have investigated the reaction of $\text{Cl}_3\text{SiSiCl}_3$ with $\text{Na[Si}t\text{Bu}_3]$. When $\text{Cl}_3\text{SiSiCl}_3$ in benzene was treated with 2 molar equiv of $\text{Na[Si}t\text{Bu}_3]$, the reaction mixture underwent a color change to orange-yellow. Three products were formed: the tetrasilatetrahedrane **1**, the disilane $t\text{Bu}_3\text{SiSi}t\text{Bu}_3$, and the chlorosilane $t\text{Bu}_3\text{SiCl}$, as shown in Scheme 3. Due to hydrolysis[11] and oxidation[17] of $\text{Na[Si}t\text{Bu}_3]$, small amounts of $t\text{Bu}_3\text{SiH}$ and $\text{Na[OSi}t\text{Bu}_3]$ also were formed. Tetrasilatetrahedrane **1** could be separated from $t\text{Bu}_3\text{SiSi}t\text{Bu}_3$ by multiple recrystallization. Single crystals composed of one molecule of **1** and two molecules of benzene were isolated by recrystallization from benzene.[18]

The trisilane $\text{Cl}_3\text{SiSiCl}_2\text{SiCl}_3$ reacts with 4 molar equiv of $\text{Na[Si}t\text{Bu}_3]$, surprisingly forming the same products that had been formed in the 1:1 $\text{HSiCl}_3/\text{Na[Si}t\text{Bu}_3]$ reaction. After 1 h, the trisilane had been completely consumed, as determined by ^{29}Si NMR spectroscopy. In the ^{29}Si NMR spectrum of the reaction mixture resonances due to the tetrasilatetrahedrane **1**, the disilane $t\text{Bu}_3\text{SiSi}t\text{Bu}_3$, the chlorosilane $t\text{Bu}_3\text{SiCl}$, and hexachlordisilane $\text{Cl}_3\text{SiSiCl}_3$ as well as polychlorosilanes such as the neopentasilane $\text{Si(SiCl}_3)_4$ were observed. Obviously, a degradation reaction of $\text{Cl}_3\text{SiSiCl}_2\text{SiCl}_3$ with liberation of SiCl_2 had taken place. The dichlorosilylene SiCl_2 that had been formed apparently underwent an insertion reaction into $\text{Cl}_3\text{SiSiCl}_2\text{SiCl}_3$ to give perchlorinated neopentasilane $\text{Si(SiCl}_3)_4$. We had verified that the degradation of $\text{Cl}_3\text{SiSiCl}_2\text{SiCl}_3$ in the presence of catalytic amounts of donors, such as amines, in the first step gives dichlorosilylene SiCl_2 and hexachlordisilane $\text{Cl}_3\text{SiSiCl}_3$ and ultimately produces $\text{Si(SiCl}_3)_4$.[19]

Scheme 2. Synthesis of Tetrasilatetrahedrane 1 from HSiCl_3 and $\text{Na[Si}t\text{Bu}_3]$



Scheme 3. Synthesis of Tetrasilatetrahedrane 1 from Reactions of $\text{Na[Si}t\text{Bu}_3]$ with $\text{Cl}_3\text{SiSiCl}_3$ and $\text{Cl}_3\text{SiSiCl}_2\text{SiCl}_3$



Experimental Section

General Procedures. All experiments were carried out under dry nitrogen or argon with strict exclusion of air and moisture using standard Schlenk techniques or a glovebox. $\text{Na[Si}t\text{Bu}_3]$[11] was prepared according to a literature procedure. Benzene was distilled from sodium/benzophenone prior to use.

The NMR spectra were recorded on a Bruker AM 250, a Bruker DPX 250, a Bruker Avance 300, and a Bruker Avance 400 spectrometer.

Synthesis of 1 from HSiCl_3 and $\text{Na[Si}t\text{Bu}_3]$. To a solution of HSiCl_3 (195 mg, 1.44 mmol) in 5 mL of benzene was added a solution of $\text{Na[Si}t\text{Bu}_3]$ (320 mg, 1.40 mmol) in 5 mL of benzene. The resulting orange-yellow solution quickly became cloudy. After 1 h, the ^{29}Si NMR spectrum showed that the silanide $\text{Na[Si}t\text{Bu}_3]$ had been completely consumed, and new signals appeared that could be assigned to the tetrasilatetrahedrane **1** (δ 52.7, δ 243.7; 6.2%[20]), the disilane $t\text{Bu}_3\text{SiSi}t\text{Bu}_3$ (δ 35.0; 13.8%[20]), the silane $t\text{Bu}_3\text{SiH}$ (δ 17.2, 10.8%[20]), and the remaining HSiCl_3 (δ −6.2, 69.4%[20]). Due to interference of the signals of the tetrasilatetrahedrane **1** and the disilane $t\text{Bu}_3\text{SiSi}t\text{Bu}_3$ in the ^{1}H NMR spectrum (δ 1.36), the progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After the reaction mixture had been filtered and the filtrate had been left to stand at ambient temperature for one day, X-ray quality crystals that consist of two molecules of **1**, one molecule of $t\text{Bu}_3\text{SiSi}t\text{Bu}_3$, and

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[15] Dehalogenation of $(t\text{Bu}_3\text{Si})\text{BrSi}{=}\text{SiBr}(\text{Si}t\text{Bu}_3)$ with $\text{Na[Si}t\text{Bu}_3]$ results in the formation of the tetrasilatetrahedrane **1**; see ref 12.

[16] Structural details: CCDC 744853.

[17] Lerner, H.-W.; Scholz, S.; Bolte, M. *Organometallics* **2002**, *21*, 3827.

[18] Structural details: CCDC 744852.

[19] Donor-induced degradation of $\text{Cl}_3\text{SiSiCl}_2\text{SiCl}_3$ leads to formation of $\text{Si(SiCl}_3)_4$, and in the presence of the silylene trapping agents 2,3-dimethyl-1,3-butadiene gives the [4+1] cycloadduct (δ(^{29}Si) 36.1): Meyer-Wegner, F.; Nadj, A.; Tüllmann, S.; Bolte, M.; Holthausen, M. C.; Wagner, M.; Lerner, H.-W. Unpublished results.

[20] Integral ratio of the signals in the ^{29}Si NMR spectrum.

one molecule of benzene could be obtained from the filtrate.[16] These crystals were dissolved with $t\mathrm{BuOMe}$ (10 mL). After treatment of the solution with acetonitile (6 mL) pure **1** was precipitated from this solution. Pure **1** could also be obtained by HPLC carried out on normal stationary phase (Nucleosil, 5 μm, 250 × 20 mm; eluent heptane). Yield: 44 mg (48%). $^{1}\mathrm{H}$ NMR (250.1 MHz, $\mathrm{C_6D_6}$): δ 1.36 (s, 54H, $t\mathrm{Bu}$). $^{13}\mathrm{C}$ NMR (62.9 MHz, $\mathrm{C_6D_6}$): δ 25.3 ($C\mathrm{CH_3}$), 31.7 ($\mathrm{C}C\mathrm{H_3}$). $^{29}\mathrm{Si}$ NMR (79.5 MHz, $\mathrm{C_6D_6}$): δ 52.7 ($Si t\mathrm{Bu_3}$), −243.7 (Si-$\mathrm{Si}t\mathrm{Bu_3}$). The spectroscopic data are in agreement with those reported in ref 12.

Synthesis of 1 from $\mathbf{Cl_3SiSiCl_3}$ and $\mathbf{Na[Si}t\mathbf{Bu_3]}$. A mixture of $\mathrm{Cl_3SiSiCl_3}$ (315 mg, 1.14 mmol), $\mathrm{Na[Si}t\mathrm{Bu_3]}$ (596 mg, 2.68 mmol), and 10 mL of benzene was stirred for 2 h at ambient temperature. After 2 h, we observed in the $^{29}\mathrm{Si}$ NMR spectrum of the reaction solution the resonances that could be assigned to the tetrasilatetrahedrane **1** (δ 52.7, δ −243.7; 5.6%[20]), the disilane $t\mathrm{Bu_3SiSi}t\mathrm{Bu_3}$ (δ 35.0; 20.6%[20]), the chlorosilane $t\mathrm{Bu_3SiCl}$ (δ 33.5; 6.8%[20]), $\mathrm{Cl_3SiSiCl_3}$ (δ −6.5; 62.5%[20]), and other Si-containing compounds ($t\mathrm{Bu_3SiH}$, $\mathrm{Na[OSi}t\mathrm{Bu_3]}$, etc. (4.5%[20])). After filtration, cocrystals composed of two molecules of **1**, one molecule of $t\mathrm{Bu_3SiSi}t\mathrm{Bu_3}$, and one molecule of benzene were grown from the filtrate at ambient temperature. Purification of the tetrasilatetrahedrane **1** and separation from $t\mathrm{Bu_3SiSi}t\mathrm{Bu_3}$ was achieved by multiple recrystallizations. Single crystals of the composition of one molecule of **1** and two molecules of benzene were isolated by recrystallization from benzene.[18] Yield: 31 mg (26%). For selected data for **1** see above.

Synthesis of 1 from $\mathbf{Cl_3SiSiCl_2SiCl_3}$ and $\mathbf{Na[Si}t\mathbf{Bu_3]}$. A solution of $\mathrm{Cl_3SiSiCl_2SiCl_3}$ (124 mg, 0.34 mmol) and $\mathrm{Na[Si}t\mathrm{Bu_3]}$ (284 mg, 1.28 mmol) in 10 mL of benzene in 1:4 molar stoichiometry was stirred for one day at ambient temperature. The $^{29}\mathrm{Si}$ NMR spectrum of the reaction solution showed resonances due to the tetrasilatetrahedrane **1** (δ 52.7, δ −243.7; 8.2%[20]), the disilane $t\mathrm{Bu_3SiSi}t\mathrm{Bu_3}$ (δ 35.0; 38.9%[20]), the chlorosilane $t\mathrm{Bu_3SiCl}$ (δ 33.5; 13.2%[20]), the hexachlorodisilane $\mathrm{Cl_3SiSiCl_3}$ (δ −6.5; 38.1%[20]), the perchloroneopentasilane $\mathrm{Si(SiCl_3)_4}$ (δ 3.5, δ −82.0; 7.3%[20]), and other chlorine-substituted polysilanes (2.3%[20]) ($\mathrm{(Cl_3Si)_3SiSiCl_2SiCl_3}$ (δ 5.9, 3.7, −4.1, −80.5) and $\mathrm{(Cl_3Si)_3SiCl}$ (δ −0.3, −32.2)). After filtering, single crystals composed of two molecules of **1**, one molecule of $t\mathrm{Bu_3SiSi}t\mathrm{Bu_3}$, and one molecule of benzene were isolated. Yield: 37 mg (31%). For selected data for **1** see above.

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