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Reactions of a Cyclotrisilane with Chalcogen Transfer Reagents [1]

Manfred Weidenbruch[1,*], **Andreas Grybat**[1], **Wolfgang Saak**[1], **Eva-Maria Peters**[2], and **Karl Peters**[2]

[1] Fachbereich Chemie, Universität Oldenburg, D-26111 Oldenburg, Germany
[2] Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany

Summary. Treatment of hexa-*tert*-butylcyclotrisilane (**1**) with Et_3PTe afforded the telluratrisiletane **5** in high yield. Irradiation of **1** in the presence of phenyl isothiocyanate furnished the 1,4-dithia-2,5-disilacyclohexane-3,6-diimine ring compound **6**. The structures of **5** and **6** were determined by X-ray crystallography.

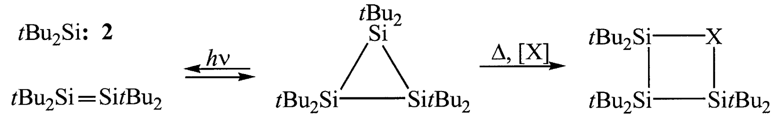
Keywords. Silicon; Chalcogens; Silaheterocycles.

Reaktionen eines Cyclotrisilans mit Chalkogen-Transfer-Reagentien [1]

Zusammenfassung. Einwirkung von Et_3PTe auf Hexa-*tert*-butylcyclotrisilan lieferte das Telluratrisiletan **5** in hoher Ausbeute. Belichten von **1** in Gegenwart von Phenylisothiocyanat ergab das 1,4-Dithia-2,5-disilacyclohexan-3,6-diimin-Ringsystem **6**. Der Aufbau von **5** und **6** wurde durch Röntgenstrukturanalysen gesichert.

Introduction

Cyclotrisilanes are the smallest and at the same time the most recently discovered representatives of the cyclooligosilanes [2]. The strain within the three-membered ring system is reflected by two typical reaction modes [3]. Under protection from light or in the absence of a catalyst, cleavage of one Si–Si bond occurs to give, depending on the type of the reaction partner, either open-chain trisilanes or ring expansion products. On the other hand, exposure to light results in the synchronous cleavage of two Si–Si bonds to furnish a silylene and a disilene, species which have been characterized by numerous trapping reactions.



3 **1** **4**, X = S, Se

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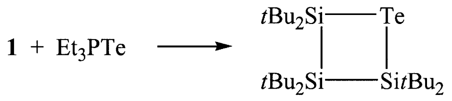
[*] Corresponding author

The behaviour of hexa-*tert*-butylcyclotrisilane (**1**) has been investigated widely; for example, it reacts with sulfur or selenium to furnish the ring expanded thia- or selenatrisiletanes **4**. In contrast, so far no reaction has been observed with tellurium [4]. Di-*tert*-butylsilylene (**2**) and tetra-*tert*-butyldisilene (**3**) are formed under photolytic conditions and undergo secondary addition reactions with various multiple bond systems to yield a wide variety of three- or higher membered ring systems [3]. We now report on the formation of a previously unknown telluratrisiletane as well as the photochemical reaction of **1** in the presence of phenylisothiocyanate.

Results and Discussion

Although **1** does not react with tellurium alone, addition of a small amount of triethylphosphane to a mixture of the components gives rise to a reaction, recognizable on account of the change in colour from yellow to colourless, which is complete within 90 minutes.



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The NMR spectroscopic characterization of the colourless, crystalline telluratrisiletane **5** turned out not to be easy since the ^{1}H NMR spectrum surprisingly contained only one signal for the methyl protons. However, the ^{13}C NMR spectrum revealed two sets of signals for the primary and the quaternary carbon atoms. The ^{29}Si-NMR spectrum furnished more information in the form of two strongly deshielded signals at 31.19 and 68.84 ppm with the expected $^{1}J_{\mathrm{Si,Te}}$, $^{2}J_{\mathrm{Si,Te}}$, and $^{1}J_{\mathrm{Si,Si}}$ coupling constants. Final verification of the structure of **5** as well as some noteworthy details were provided by an X-ray crystallographic analysis (Fig. 1).

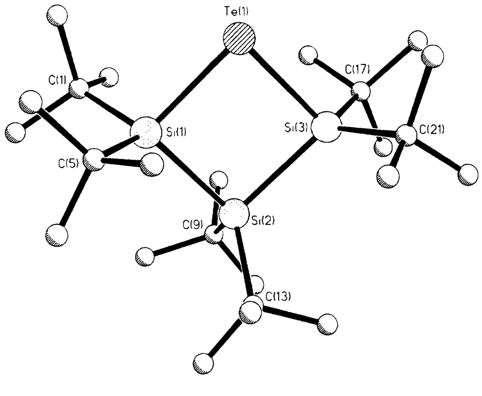
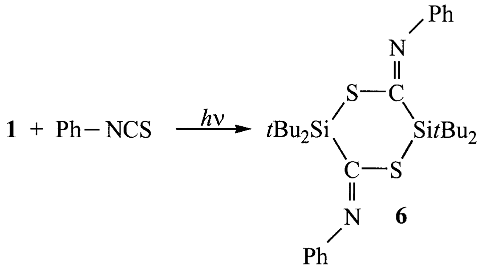


Fig. 1. Molecule of **5** in the crystal (H atoms omitted); selected bond lengths (pm) and angles (deg): Te–Si(1) 252.4(1), Te–Si(3) 252.76(9), Si(1)–Si(2) 251.25(12), Si(2)–Si(3) 251.35(12), Si(1)–Te–Si(3) 88.21(3), Si(2)–Si(1)–Te 91.54(3), Si(1)–Si(2)–Si(3) 88.79(4), Si(2)–Si(3)–Te 91.45(3)

As demonstrated by the 360° sum of the endocyclic angles, the four-membered ring of **5** is completely planar. The Si–Si bond lengths are considerably stretched and correspond to those in the cyclotrisilane **1**. This is not self-evident, since the ring strain should be reduced upon transformation of the three-membered ring in **1** to the four-membered ring in **5**. However, the concomitantly increasing interactions between the sterically demanding exocyclic substituents will effect increases in the Si–Si bond lengths as has been observed, for example, in hepta-*tert*-butylcyclotetrasilane [6].

Structurally characterized heterocyclic compounds containing silicon and tellurium atoms in the ring are still rather rare. The first cyclic compound of this type was obtained by *Jutzi et al.* from the reaction of decamethylsilococene with a phosphane telluride which surprisingly furnished a five-membered ring product containing two silicon and three tellurium atoms in the ring [7]. The corresponding telluradisilirane was obtained from the reaction of tetramesityldisilene with tellurium [8]. Finally, photolysis of **1** in the presence of a tellurophene afforded a four-membered ring, the 1,3-ditellura-2,4-disiletane system [9]. Thus, compound **5** supplements the series of structurally characterized smaller rings based on silicon and tellurium atoms.

In previous investigations we found that CS_2 and CO_2 could function as chalcogen transfer reagents similar to the phosphane chalcogenides. Thus, irradiation of **1** in the presence of CO_2 furnished hexa-*tert*-butylcyclotrisiloxane $(^tBu_2SiO)_3$ as the final product. Analogous reactions with CS_2 led to various heterocyclic products containing silicon and sulfur in the rings [3, 10]. Isothiocyanates should be even better sulfur transfer reagents since they would afford the relatively stable isocyanides after abstraction of sulfur.



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In fact, however, irradiation of **1** in the presence of phenyl isothiocyanate did not result in abstraction of sulfur. Instead, a compound was obtained for which analytical and spectroscopic data are indicative of a 1:1 adduct of silylene **2** with the isothiocyanate. Clarification of the structure of the product again required X-ray crystallography (Fig. 2) which identified the compound as the novel ring system 1,4-dithia-2,5-disilacyclohexane-3,6-diimine **6**. The heterocyclic six-membered ring of **6** adopts the chair conformation. The hardly stretched endo- and exocyclic bond lengths show that the compound is practically free of strain.

We can as yet only speculate on the mechanism of formation of **6**. One plausible pathway appears to consist of the addition of silylene **2** to the C=S double bond of the isothiocyanate with formation of a three-membered ring and subsequent σ-dimerization to furnish the isolated six-membered ring product. A comparable reaction sequence has been observed for the photolysis of **1** in the presence of alkyl

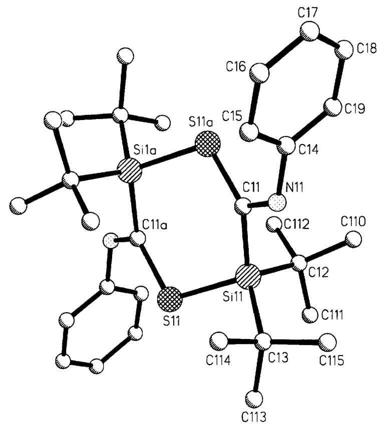

Fig. 2. Molecule of **6** in the crystal (H atoms omitted); selected bond lengths (pm) and angles (deg): S(1)–Si(1) 215.4(1), Si(1)–C(1) 189.8(3), S(1)–C(1A) 179.6(4), C(1)–N(1) 126.8(4), S(1)–Si(1)–C(1) 112.0(1), Si(1)–C(1)–S(1A) 124.7(2), Si(1)–S(1)–C(1A) 108.5(1), Si(1)–C(1)–N(1) 114.3(3), N(1)–C(1)–S(1A) 120.0(3)

or aryl cyanides. These reactions also proceed *via* a [2+1] cycloaddition of **2** to the C≡N bond with subsequent σ-dimerization to furnish 1,4-diaza-2,5-disilacyclohexa-3,6-dienes as final products [11].

Experimental

General procedures

All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. Photolyses were carried out using a high-pressure mercury immersion lamp (Heraeus TQ 150). The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM 300 spectrometer using C_6D_6 as solvent. The ^{29}Si NMR spectrum was recorded on a Bruker AMX 300 spectrometer. Mass spectra were recorded on a Vatrian-MAT 212 instrument. Elemental analyses were performed by *Analytische Laboratorien*, D-51779 Lindlar, Germany.

2,2,3,3,4,4-Hexa-tert-butyl-1-telluratrisiletane (**5**)

At room temperature, tellurium (0.21 g, 1.70 mmol) and a catalytic amount of triethylphosphane (3 drops) were added to a solution of **1** (0.71 g, 1.70 mmol) in 50 ml of petroleum ether (40–60°C). After 90 min the yellow colour of **1** had disappeared. To complete the reaction, the resulting mixture was stirred for 12 h at room temperature. Excess tellurium was filtered off, and the solvent was removed. Crystallization of the residue at −50°C from a minimum amount of *n*-hexane afforded 0.80 g (87%) of colourless crystals of **5**.

M.p.: 150–151°C; ^{1}H NMR: $\delta = 1.38$ (s) ppm; ^{13}C NMR: $\delta = 23.78$ (C_q), 29.05 (C_q), 32.91 (C_p), 34.13 (C_p) ppm (C_q and C_p refer to quaternary and primary carbon atoms); ^{29}Si NMR: $\delta = 31.19$ (s, Si(1), Si(3), $^{1}J_{Si,Te} = 260.0$ Hz, $^{1}J_{Si,Si} = 44.8$ Hz), 68.84 (s, Si(2), $^{2}J_{Si,Te} = 45.4$ Hz) ppm; MS (CI, isobutane): *m/z* (%) = 557 [MH^+] (100); $C_{24}H_{54}Si_3Te$ (554.54); calcd.: C 51.98, H 9.82%; found: C 51.79, H 10.02.

N,N-Diphenyl-2,2,5,5-tetra-tert-butyl-1,4-dithia-2,5-disilacyclohexane-3,6-diimine (**6**)

A solution of **1** (0.65 g, 1.50 mmol) and phenyl isothiocyanate (0.34 g, 2.5 mmol) in 80 ml of petroleum ether (40–60°C) was irradiated for 5 h at room temperature. The solvent was removed, and the red residue was redissolved in a minimum amount of *DME*. Cooling to −50°C furnished 0.12 g (21%) of colourless crystals of **6**.

M.p.: 109–110°C; ^{1}H NMR: $\delta = 1.21$ (s, 36 H), 6.95–7.21 (m, 10 H) ppm; ^{13}C NMR: $\delta = 23.67$ (C_q), 28.81 (C_p), 119.59, 124.86, 129.21, 151.43, 168.79 (CN) ppm; MS (CI, isobutane): *m*/*z* (%) = 556 [MH$^+$] (20); $C_{30}H_{46}N_2S_2Si_2$ (555.01); calcd.: C 64.92, H 8.30, N 5.05%; found: C 64.03, H 8.43, N 4.85.

X-ray structure analyses of **5** *and* **6**

Crystal and numerical data of the structure determinations are given in Table 1. In each case, the crystal was mounted in a thin-walled glass capillary. Data collection was performed at 296(2) K on a Siemens STOE AED 2 (**5**) or a Siemens P4 diffractometer (**6**) using graphite-monochromated MoK_α radiation.

The structures were solved by direct phase determination using the SHELX program systems and refined by full-matrix least-squares techniques against F^2 (**5**) or F (**6**) with the SHELXL [12] or SHELXTL PLUS program systems. Hydrogen atoms were placed in the calculated positions; all other atoms were refined anisotropically.

Table 1. Crystallographic data for **5** and **6**

	5	**6**
Empirical formula	$C_{24}H_{54}Si_3Te$	$C_{30}H_{46}N_2S_2Si_2$
Molar mass ($g \cdot mol^{-1}$)	555.54	505.01
a (pm)	928.1(1)	1150.2(1)
b (pm)	1984.6(1)	1169.8(1)
c (pm)	1634.8(1)	1246.5(1)
α (deg)	90	88.673(8)
β (deg)	90.06(1)	72.09(1)
γ (deg)	90	83.884(9)
$V \times 10^6$ (pm^3)	3011.1(4)	1623.4(3)
Z	4	2
D_{calcd} ($g \cdot cm^{-3}$)	1.223	1.135
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Crystal dimensions (mm^3)	0.53×0.46×0.27	0.35×0.45×0.25
Data collection mode	ω–2θ	ω
$2\theta_{max}$ (deg)	50	55
No. of reflections	5414	8580
No. of unique reflections	5296	7462
No. of observed reflections	4467	5295
Linear abs. coefficient (mm^{-1})	1.116	0.26
Data to parameter ratio	20.88	16.29
R (R_w) [$I > 2\sigma(I)$]	0.037	0.066 (0.066)
$wR2$ [all data]	0.098	0.069
Residual electron density (eÅ^{-3})	1.00; −0.32	0.50; −0.39

Additional material about the structure determination may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, referring to the deposition numbers CSD-408 635 (**5**) and CSD-408 627 (**6**), the names of the authors, and the citation of the present paper.

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References

[1] Silicon Compounds with Strong Intramolecular Steric Interactions, Part 67. Part 66: Weidenbruch M, Will P, Marsmann H, Peters K, von Schnering HG (1998) Z Anorg Allg Chem **624**: 15
[2] Masamune S, Hanzawa Y, Murakami S, Bally T, Blount JF (1982) J Am Chem Soc **104**: 1150
[3] Review: Weidenbruch M (1995) Chem Rev **95**: 1479
[4] Weidenbruch M, Schäfer A (1984) J Organomet Chem **269**: 231
[5] Schäfer A, Weidenbruch M, Peters K, von Schnering HG (1984) Angew Chem **96**: 311; Angew Chem Int Ed Engl **23**: 302
[6] Weidenbruch M, Kroke E, Pohl S, Saak W, Marsmann H (1995) J Organomet. Chem **499**: 229
[7] Jutzi P, Möhrke A, Müller A, Bögge A (1989) Angew Chem **101**: 1527; Angew Chem Int Ed Engl **28**: 1518
[8] Tan RPK, Gillette GR, Powell DR, West R (1991) Organometallics **10**: 546
[9] Weidenbruch M, Kirmaier L, Kroke E, Saak W (1997) Z Anorg Allg Chem **623**: 1277
[10] Brand-Roth B (1990) Thesis, University of Oldenburg, Germany
[11] Weidenbruch M, Schäfer A, Peters K, von Schnering HG (1986) J Organomet Chem **314**: 25
[12] Sheldrick GM, SHELXL 93 (1993) University of Göttingen, Germany

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