Supplementary Information

"Synthesis and Coordination Ability of a Partially Silicon Based Crown Ethers"

Kirsten Reuter,^a Günther Thiele,^b Thomas Hafner,^c Frank Uhlig^c and Carsten von Hänisch^{a*}

 ^a Fachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften (WZMW), Philipps-Universität Marburg, Hans-Meerwein-Straße, 35043 Marburg, Germany, Fax: +49-6421-2825653. E-Mail: haenisch@chemie.uni-marburg.de
^b Department of Chemistry, 210 Lewis Hall, University of California, Berkeley, California 94720, United States
^c Institut für Anorganische Chemie, TU Graz, 6330 Graz, Austria

Content

Alternative Synthesis Path for $O(Si_2Me_4Cl)_2$ (5)	S2
Experimental Section	\$3
Crystal Structure Data	S5
XYZ Data of the Optimized Structures	S7
Citations	S11

Alternative Synthesis Path for O(Si₂Me₄Cl)



Another suitable reaction path for compound **3** seemed to be the asymmetric chlorination of 1,1,2,2-tetramethyl-1,2diphenyldisilane by the use of trifluoromethanesulfonic acid (TfOH)^[1] and subsequent chlorination with HNEt₃Cl leading to compound **4**. The asymmetric chlorodisilane **4** reacts in aqueous solution to the condensed species **5**, which can be purified



Scheme 1: Synthesis path for the Si based fragment of a hybrid crown ether based on the substitution of phenyl groups at the silicon atoms with trifluoromethanesulfonic acid (TfOH). Abstraction of the phenyl groups as the final step is not possible with strong acids.

via column chromatography. However, the O atom in **5** inhibits the following abstraction of the terminal phenyl groups by strong acids as can be seen from the reaction with $HCl_{(solv)}$, which leads to the chlorinated compound **4** (Scheme 3). Since the O atom is preferably being attacked by acids rather than the Ph-groups, this synthesis path turned out to be an impasse.

Experimental Section

General: Except the synthesis of compound **5**, all working procedures were conducted under rigorous exclusion of oxygen and moisture using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before use. NMR spectra were recorded with BRUKERACANCEHD 300, BRUKERDRX400 or with BRUKERAVANCE 500 and visualized with MESTRENOVA.^[2] IR vibrational spectra were gathered with the BRUKER ALPHA ATR-FT-IR. The starting materials 1,2-dihydrido-1,1,2,2-tetramethyldisilane^[3] and 1,2-diphenyl-1,1,2,2-tetramethyldisilane^[4] were prepared by reported methods.

Me₄Si₂HCl (1): To 26.0 g (0.22 mol, 3eq.) of 1,1,2,2-tetramethyldisilane diluted in 600 mL of THF, 17.0 g (0.73 mol, 1eq.) of TCCA at -20 °C was slowly added. The reaction was allowed to warm to room temperature and stirred for 4 h. The solvent and the raw product were separated *in vacuo* from the cyanuric acid, followed by distillative removal of THF and purification of compound **1** (bp. 125-128 °C) at ambient pressure. 21,5 g (64%) of **1** was obtained as a colourless oil.

¹H NMR (C₆D₆, 300 MHz): $\delta = 0.09$ (d, ³*J*_{HH} = 4.5 Hz, C*H*₃, 6H), 0.34 (s, C*H*₃, 6H), 3.89 (h, ³*J*_{HH} = 4.5 Hz, S*iH*, 1H) ppm; ¹³C NMR (C₆D₆, 75 MHz): $\delta = -7.3$ (s, *CH*₃), 2.4 (s, *CH*₃) ppm; ²⁹Si{H} NMR (C₆D₆, 60 MHz): $\delta = -39.1$ (s, *Si*H), 22.8 (s, *Si*Cl) ppm; ²⁹Si NMR (C₆D₆, 60 MHz): $\delta = -39.1$ (d *br*, ¹*J*_{SiH} = 181.3 Hz, *Si*H), 22.8 (br, *Si*Cl) ppm. IR: $\tilde{v} = 2963$ (m), 1261(s), 1091(s), 1019(s), 799(vs), 701(w).

 $O(Si_2Me_4H)_2$ (2): At ambient temperature, 5.0 mL of H₂O was added to 10.0 mL (9.30 g, 0.61 mol) of 1 diluted in 50 mL of *n*-pentane and stirred for 1 h. The aqueous phase was removed and washed two times with 30 mL of *n*-pentane. The combined organic phases were dried over MgSO₄ for 4 h and subsequently filtered. The solvent was removed *in vacuo* and 7,55 g (99%) of product 2 was obtained as a colourless oil.

¹H NMR (C_6D_6 , 300 MHz): δ = 0.16 (d, ${}^{3}J_{HH}$ = 4.6 Hz, CH₃, 12H), 0.27 (s, CH₃, 12H), 3.92 (h, ${}^{3}J_{HH}$ = 4.6 Hz, SiH, 2H) ppm; ¹³C NMR (C_6D_6 , 75 MHz): δ = -6.7 (s, CH₃), 2.7 (s, CH₃) ppm; ²⁹Si{H} NMR (C_6D_6 , 60 MHz): δ = -43.1 (s, SiH), 6.0 (s, SiO) ppm; ²⁹Si NMR (C_6D_6 , 60 MHz): δ = -43.1 (d br, ${}^{1}J_{SiH}$ = 172.8 Hz, SiH), 6.0 (br, SiO) ppm. IR: \tilde{v} = 2957(m), 2093(m), 1411(w), 1257(s), 1024(vs), 910(m), 882(s), 767(vs), 699(m), 655(s), 417(w).

 $O(Si_2Me_4Cl)_2$ (3): At -20 °C, 1.27 g (5.5 mmol, 2eq.) of TCCA was slowly added to 2.05 g (8.2 mmol, 3eq.) of 2 diluted in 50 mL of THF. The reaction was allowed to warm to room temperature and stirred for 4 h. The solvent was removed under at reduced pressure and the product dissolved in *n*-pentane. Insoluble cyanuric acid was removed *via* filtration and the product washed two times with *n*-pentane. The solvent was removed *in vacuo* and 2.31 g (88%) of compound 3 was obtained as a colourless oil.

¹H NMR (C₆D₆, 300 MHz): δ = 0.25 (s, CH₃, 12H), 0.38 (s, CH₃, 12H) ppm; ¹³C NMR (C₆D₆, 75 MHz): δ = 1.4 (s, CH₃), 1.9 (s, CH₃) ppm; ²⁹Si{H} NMR (C₆D₆, 60 MHz): δ = 2.4 (s, SiO), 16.7 (s, SiCl) ppm. IR \tilde{v} = 2955(w), 1400(w), 1249(s), 1038(s), 823(s), 765(vs), 721(m), 686(m), 666(s), 651(s), 554(w), 482(s), 407(s).

PhMe₄Si₂Cl (4): At 0 °C, 1.28 g (8.6 mmol, 1eq.) of freshly distilled trifluoromethanesulfonic acid was slowly added to 2.32 g (8.6 mmol, 1eq.) of 1,2-diphenyl-1,1,2,2-tetramethyldisilane diluted in 60 mL of toluene. The solution was allowed to warm to ambient temperature and stirred for additional 3 h. Subsequently, 2.37 g (17.2 mmol, 2eq.) of triethylammoniumchloride was added and the suspension was stirred for 9 d. Insoluble salts were filtered and the solvent was removed at reduced pressure. After distillative purification (32 °C, $1 \cdot 10^{-3}$ mbar) 0.94 g (48%) of **4** was obtained as a colourless oil.

¹H NMR (C₆D₆, 300 MHz): δ = 0.17 (s, CH₃, 6H), 0.20 (s, CH₃, 6H), 7.02-7.04 (m, H_{arom.}, 3H), 7.26-7.29 (m, H_{arom.}, 2H) ppm; ¹³C NMR (C₆D₆, 75 MHz): δ = -4.6 (s, CH₃), 2.1 (s, CH₃), 128.4 (s, C_{arom.}), 129.4 (s, C_{arom.}), 134.2 (s, C_{arom.}), 136.9 (s, C_{arom.}) ppm; ²⁹Si{H} NMR (C₆D₆, 60 MHz): δ = -22.0 (s, *SiP*h), 22.8 (s, *SiC*l) ppm. IR \tilde{v} = 3068(w), 2955(w), 2895(w), 1486(m), 1427(w), 1248(s), 1106(s), 1053(w), 999(w), 831(s), 814(s), 786(vs), 768(s), 729(s), 696(vs), 670(m), 644(m), 618(m), 495(s), 465(s), 419(m).

 $O(Si_2Me_4Ph)_2$ (5): To 0.94 g (4.1 mmol) of 4 in 20 mL of *n*-pentane, 5 mL of 1M HCl_{aq} was added at ambient temperature. The solution was stirred for 2 h. The aqueous phase was was extracted with 20 mL *n*-pentane twice. The combined organic phases were dried over MgSO₄ for 4 h and subsequently filtered. The solvent was evaporated *in vacuo* and the resulting colourless oil was purified using column chromatography (silicagel; heptane : di*iso*propyl ether = 3:1) yielding 0.66 g (81%) of **5** as colourless oil.

¹H NMR (C_6D_6 , 300 MHz): $\delta = 0.19$ (s, CH_3 , 12H), 0.34 (s, CH_3 , 12H), 7.18-7.26 (m, $H_{arom.}$, 6H), 7.48-7.51 (m, $H_{arom.}$, 4H) ppm; ; ¹³C NMR (C_6D_6 , 75 MHz): $\delta = -3.8$ (s, CH_3), 2.4 (s, CH_3), 128.2 (s, $C_{arom.}$), 128.9 (s, $C_{arom.}$), 134.3 (s, $C_{arom.}$), 139.2 (s, $C_{arom.}$) ppm; ²⁹Si{H} NMR (C_6D_6 , 60 MHz): $\delta = -25.8$ (s, *SiPh*), 4.9 (s, *SiO*) ppm. IR $\tilde{\nu} = 3068$ (w), 2951(m), 2894(w), 1427(m), 1403(w), 1246(s), 1105(m), 1036(s), 825(s), 793(s), 768(vs), 729(s), 695(vs), 658(m), 638(s), 470(m), 441(w). **1,2,4,5-Tetrasila[12]crown-4** (6): At room temperature, 1.0 mL (1.09 g, 3.4 mmol, 1eq.) of **5** diluted in 50 mL of Et_2O and 0.23 mL (0.36 g, 3.4 mmol, 1eq.) of dihydroxydiethylether, 0.95 mL (0.69 g, 6.8 mmol, 2eq.) of NEt₃ in 50 mL of Et_2O were simultaneously dropped into 50 mL of Et_2O . The solution was stirred for 12 h. Subsequently, the solvent was removed at reduced pressure and 50 mL of *n*-pentane was added to the residue, followed by filtration. The solvent from the resulting clear solution was evaporated under reduced pressure and 1.13 g (94%) of compound **6** was obtained as a viscous colourless oil.

¹H NMR (CD₂Cl₂, 300 MHz): $\delta = 0.19$ (s, CH₃, 12H), 0.22 (s, CH₃, 12H), 3.55-3.58 (m, CH₂, 4H), 3.76-3.79 (m, CH₂, 4H) ppm; ¹³C NMR (CD₂Cl₂, 75 MHz): $\delta = -0.17$ (s, CH₃), 3.1 (s, CH₃), 64.4 (s, CH₂), 73.4 (s, CH₂) ppm; ²⁹Si{H} NMR (CD₂Cl₂, 60 MHz): $\delta = 0.9$ (s, SiO_{Si}), 10.9 (s, SiO_C) ppm. IR $\tilde{v} = 2950$ (w), 2866(w), 1245(s), 1143(m), 1094(m), 1032(s), 940(m), 854(m), 825(m), 798(s), 759(vs), 716(m), 680(m), 658(m), 634(m). MS (ESI⁺): m/z (%) 353.1451 [*M*H]⁺ (45).

[Li(1,2,4,5-tetrasila[12]crown-4)OTf] (7): To 1.13 g (3.2 mmol, 1eq.) of **6** diluted in 50 mL of dichloromethane, 0.65 g (4.2 mmol, 1eq.) of lithium triflate was added at ambient temperature and stirred for 18 h. In the case of an excess of the lithium salt, the resulting suspension was filtered and the solvent of the resulting clear solution was evaporated *in vacuo*. The remaining white powder was washed twice with 20 mL of *n*-pentane and subsequently dried under reduced pressure. 0.95 g (57%) of **7** was obtained as an amorphous colourless powder. Single crystals in form of colourless rods were grown after 4 d in a mixture of dichloromethane and cyclopentane (2:1) at -35 °C.

¹H NMR (CD₂Cl₂, 300 MHz): δ = 0.37 (s, CH₃, 12H), 0.40 (s, CH₃, 12H), 3.69-3.72 (m, CH₂, 4H), 3.84-3.87 (m, CH₂, 4H) ppm; ¹³C NMR (CD₂Cl₂, 75 MHz): δ = -1.3 (s, CH₃), 2.9 (s, CH₃), 61.4 (s, CH₂), 71.4 (s, CH₂) ppm; ²⁹Si{H} NMR (CD₂Cl₂, 60 MHz): δ = 9.4 (s, SiO_{Si}), 15.9 (s, SiO_C) ppm; ⁷Li NMR (CD₂Cl₂, 194 MHz): δ = -0.9 (s) ppm; ¹⁹F NMR (CD₂Cl₂, 283 MHz): δ = -78.8 (s) ppm. IR \tilde{v} = 2955(w), 2874(w), 2834(w), 2791(w), 1572(w), 1548(w), 1523(w), 1478(w), 1349(m), 1254(s), 1157(s), 1131(m), 1042(s), 950(m), 928(s), 855(s), 829(s), 800(m), 766(m), 729(s), 696(vs), 637(s), 598(m), 571(vs), 524(w), 514(w), 493(w), 476(w), 449(w), 410(w). MS (ESI⁺): *m/z* 359.1533 (%) [*M*]⁺-OTf (100).

[Li([12]crown-4)OTf] (8): To 0.52 g (2.9 mmol, 1eq.) of [12]crown-4 and 0.46 g (2.9 mmol, 1eq.) of lithium triflate, 15 mL of dichloromethane was added. The suspension was stirred for 18 h resulting in a clear solution. The quantity of the solvent was reduced until saturation. After 7 d at room temperature, crystals of 8 (0.72 g, 75%) were obtained as colourless needles. ¹H NMR (CD₂Cl₂, 300 MHz): δ = 3.77 (s, *CH*₂, 16H) ppm; ¹³C NMR (CD₂Cl₂, 75 MHz): δ = 67.8 (s, *CH*₂) ppm; ⁷Li NMR (CD₂Cl₂, 194 MHz): δ = -0.7 (s) ppm; ¹⁹F NMR (CD₂Cl₂, 283 MHz): δ = -79.2 (s) ppm. IR \tilde{v} = 2940.3(w), 1492.8(w), 1449(w), 1363(w), 1290(s), 1255(s), 1226(s), 1138(s), 1082(vs), 1037(s), 1018(s), 928(s), 862(m), 757(w), 638(vs), 589(w), 572(w), 530(w), 516(m), 448(m). MS (ESI⁺): *m/z* 183.1203 (%) [*M*]⁺-OTf (60). **Crystal Structure** Data collection was performed using a BRUKER D8 QUEST diffractometer at 100(2) K with MoK_{α} radiation and graphite monochromatization (λ = 0.71073). Structure solution was realized by direct methods, refinement with full-matrix-least-squares against F^2 using SHELXL-14 and Olex2 software.^[5,6] The presentation of crystal structures was done with DIAMOND4.2.2^[7]

Table S1. X-Ray measurement, structure solution and refinement details of 7.

Empirical formula	$C_{13}H_{32}F_3Li_1O_7S_1Si_4\cdotCH_2Cl_2$
Formula weight ∕g∙mol⁻¹	593.67
Crystal color, shape	colourless plate
Crystal size /mm ³	0.525 x 0.225 x 0.214
Crystal system	orthorhombic
Space group	Pbca
<i>a</i> / Å	14.6745(7)
b / Å	24.0048(11)
<i>c</i> / Å	32.5952 (14)
V /Å ³	11481.9(9)
Z	16
$\rho_{calc}/g \cdot cm^{-3}$	1.374
μ (Mo _{K$lpha$}) /mm ⁻¹	0.515
2 ϑ range /°	2.52 – 25.19
Reflections measured	146908
Independent reflections	10456, <i>R</i> _{int} = 0.0774
$R_1\left(l>2\sigma(l)\right)$	0.0534
wR ₂ (all data)	0.1273
GooF (all data)	1.040
Largest diff. peak and hole /e.Å ⁻³	2.079 and -0.982

Table S2. X-Ray measurement, structure solution and refinement details of 8.

Empirical formula	$C_9H_{16F_3Li_1O_7S_1}$
Formula weight ∕g∙mol ⁻¹	332.22
Crystal color, shape	colourless needle
Crystal size /mm ³	0.543 x 0.216 x 0.201
Crystal system	monoclinic
Space group	P2 ₁ /n
<i>a</i> / Å	7.0179(3)
<i>b</i> / Å	13.5605(6)
<i>c</i> / Å	14.8661(7)
в /°	96.427(2)°
V/Å ³	1405.86(11)
Z	4
$\rho_{calc}/g\cdot cm^{-3}$	1.570
μ (Mo _{K$lpha$}) /mm ⁻¹	0.293
2 ϑ range /°	2.76 - 28.48
Reflections measured	45249
Independent reflections	3538, <i>R</i> _{int} = 0.0258
$R_1\left(l>2\sigma(l)\right)$	0.0259
wR_2 (all data)	0.0663
GooF (all data)	1.087
Largest diff. peak and hole /e.Å ⁻³	0.376 and -0.495



Figure S1: Molecular structure of **8** in the crystal. Thermal ellipsoids represent the 50% probability level.

Computational Details. Calculations were performed with the program system TURBOMOLE V7.0.1.^[8,9] The RI approximation^[10], and dispersion corrections^[11,12] were applied throughout. For all calculations the BP86 functional^[13,14] was chosen, utilizing a def2-TZVP basis set.^[15-17]

Table S3. XYZ-Data of calculated [12]crown-4.

C 0.6580504 6.3036040 7.4297272 O 3.5041127 8.0329490 9.7956205 O 1.9110279 6.9543463 7.6030028 O -0.5146714 7.5291689 9.1149147 O 1.0812992 8.6028858 11.3124479 H 0.7896435 5.2829991 7.0169361 H 0.1143625 6.9068114 6.6889837 C -0.1710307 6.2167912 8.7034908 С 3.9673535 7.1139726 8.8134944 C 3.2539380 7.4586710 11.0675579 С 2.8867524 6.1822236 8.2833703 C -0.9355723 7.6314505 10.4696854 C 0.1975921 7.5066482 11.4790138 C 2.3755900 8.4087109 11.8695370 H -1.0826082 5.6160129 8.5002794 Н 0.3942727 5.6839992 9.4903056 Н 4.8086452 6.5041417 9.2007737 4.3432798 7.7334549 7.9869955 Н 4.2035608 7.2933280 11.6188571 Н H 2.7616658 6.4730187 10.9741594 H 3.3521505 5.4432082 7.5977409 H 2.4372470 5.6086790 9.1146374 H -1.7110760 6.8752628 10.7062666 H -1.3883501 8.6289507 10.5613174 н -0.2318272 7.4991169 12.5028706 0.7227740 6.5433353 11.3446466 Н н 2.3116862 8.0431177 12.9142570 H 2.8420116 9.4038815 11.8808800

Table S4. XYZ-Data of calculated [Li([12]crown-4)]⁺.

Li	1.4662440	8.3819177	9.1793385
С	0.6370139	6.2956097	7.4279934
0	3.3747203	7.9775398	9.7650136
0	1.8613156	6.9889305	7.7514396
0	-0.3813237	7.5242773	9.1717896
0	1.1336798	8.5171759	11.1860279
Н	0.8467394	5.3036260	7.0005166
Н	0.1414259	6.9093283	6.6643608
С	-0.2386716	6.1841757	8.6629443
С	3.9768918	7.0871570	8.8022467
С	3.3219841	7.4732885	11.1131270
С	2.9269528	6.1489303	8.2360688
С	-0.9433563	7.6202632	10.4980100
С	0.1572408	7.5189961	11.5385836
С	2.3974238	8.4057837	11.8745029
Н	-1.2251627	5.7664888	8.4031095
Н	0.2247390	5.5308962	9.4240204
Н	4.8096194	6.5252426	9.2511025
Н	4.3769188	7.7337160	8.0100784
Н	4.3290702	7.4735878	11.5614483
Н	2.9392777	6.4369985	11.1210600
Н	3.3457219	5.5492623	7.4113935
Н	2.5491576	5.4581178	9.0103481
Н	-1.7108367	6.8485282	10.6578388
Н	-1.4221544	8.6071764	10.5454149
Н	-0.2434034	7.7154285	12.5467364
Н	0.6164327	6.5145583	11.5378641
Н	2.2537721	8.0628121	12.9099368
Н	2.8144974	9.4211567	11.8953847

Table S5. XYZ-Data of calculated 6.

С	5.0565995	-0.4640374	-0.6600938
Si	4.4634216	0.3471104	0.9305700
с	4.0804727	-0.9701214	2.2208096
Si	2.5372537	1.6312398	0.4982458
с	2.8500613	2.9527291	-0.8019207
0	5.7200192	1.2961656	1.4699969
Si	6.0803214	2.4159955	2.6492472
с	4.8712560	2.2890788	4.0810969
с	1.1187391	0.5326822	-0.0972168
0	2.1485536	2.2833963	1.9934172
с	1.0127634	3.0926638	2.2831665
С	1.4021899	4.5342774	2.5399274
0	1.6037111	5.2070417	1.2957041
С	2.4359932	6.3599203	1.3882890
с	3.8560455	6.0704322	0.9292403
0	4.4167916	5.0458257	1.7402662
Si	6.0178484	4.5457703	1.6482312
C	6.5825151	4.4377018	-0.1487559
c	7.8313505	2.0467238	3.2334745
C	7.1111000	5.7975206	2.5453744
н	0.5354335	2.6904147	3.1927082
н	0.2647936	3.0565149	1.4702913
н	2 3239932	4 5497999	3 1418875
н	0.5922369	5.0358130	3.1080909
н	2 0046757	7 1387301	0 7367807
н	2.0010737	6 7489671	2 4215424
н	3 8371470	5 7512548	-0 1276969
н	4 4449537	7 0068979	0.9900166
н	5 9934484	3 7000555	-0 7103974
н	6 5163903	5 4054641	-0 6681401
н	7 6336899	4 1138432	-0 1834575
н	7.0556145	6 7924194	2 0774502
н	6 8131763	5 9011434	3 5984895
н	8 1635856	5 4775860	2 5219892
н	8 1470032	2 7662206	4 0036660
н	7 8897271	1 0366898	3 6661/109
н	8 5/195577	2 1006532	2 1029509
н	3 8422707	2.1000552	3 7059530
н	4 9702400	1 3251410	4 6026022
н	5 0503680	3 0010812	4.0020022
н	3 6902211	-0 5133422	3 1405893
н	3 3224478	-1 6752575	1 8479916
н	1 98/3859	-1 5//1951	2 /7///59
н	5 9577415	-1 0682326	-0 4762848
н	4 2822778	-1 1257309	-1 0759447
н	5 30324/8	0.20031/10	-1 // 203/07
н	0 2060850	1 1172850	-0 2805270
н	1 3895710	0 0303082	-1 0383012
н	0.8765202	-0 2422428	0 6424425
н	1 9891924	3 6789521	-0 8000031
н	3.72039324	3.5603874	-0.525335/
н	3.0458430	2.4866478	-1.7794324

Table S6. XYZ-Data of calculated [Li(1,2,4,5-tetrasila[12]crown-4]+.

H 2.4593820 11.7850633 16.9155223 С 1.9745866 12.1921653 16.0149641 Si 2.7297672 11.4082212 14.4897142 H 2.1186544 13.2811152 16.0241515 0.8991218 11.9830922 16.1039512 н Si 5.0193276 11.9346495 14.2779264 2.0682816 12.0994386 13.0745470 0 С 2.4344791 9.5592688 14.4528380 5.0660835 12.1050212 12.5736684 0 С 5.4927732 13.5671150 15.0688795 C 6.1836842 10.5656466 14.8045809 Si 0.4433081 12.4970356 12.7283927 Li 3.3887558 12.4881096 11.6013983 2.9585959 9.0745858 15.2898992 н 1.3664522 9.3171386 14.5439694 н н 2.8101218 9.1132615 13.5213931 6.2432923 12.5049504 11.8469688 C H 5.3791296 13.5033617 16.1612947 H 6.5412731 13.8313338 14.8667072 н 4.8555914 14.3902993 14.7164680 5.9636635 9.6247841 14.2815005 н Н 7.2372405 10.8256549 14.6240255 6.0792943 10.3801345 15.8842063 н Si 0.4279300 12.5667960 10.3682634 С 0.0756664 14.1768014 13.4710412 C -0.7164073 11.1867759 13.3987805 0 2.1191584 12.6624461 10.1120869 0 4.7326504 12.9015347 10.0813261 С 2.7185231 13.0619473 8.8656404 н 6.4379949 13.5748708 12.0228125 7.1231584 11.9267558 12.1697977 н С 5.9745905 12.2488414 10.3791594 C -0.3980879 14.0934675 9.6632506 C -0.2201871 11.0098053 9.5526488 H -0.9326647 14.5089120 13.1829380 н 0.1162112 14.1491988 14.5693192 H 0.7891750 14.9365951 13.1220227 H -0.4891019 10.1930374 12.9893835 H -0.6918367 11.1243156 14.4958014 H -1.7494889 11.4350700 13.1110388 С 4.1286669 12.5100124 8.8411246 Н 2.1542088 12.6693610 8.0048690 H 2.7304372 14.1613632 8.8069517 5.8766264 11.1650216 10.1891034 Н 6.7909720 12.6482620 9.7543729 н н 0.0211553 15.0172825 10.0853767 H -0.3090410 14.1404397 8.5679259 H -1.4727608 14.0790987 9.8991692 H -1.2924624 10.8869709 9.7667691 -0.1088577 11.0443390 8.4586740 н 0.2996516 10.1154658 9.9230967 н Н 4.6917212 12.9116272 7.9818763 H 4.1122188 11.4072585 8.7720323

- [1] W. Uhlig, Prog. Polym. Sci. 2002, 27, 255.
- [1] M. R. Willcott, J. Am. Chem. Soc. **2009**, 131, 13180.
- [2] C. Ackerhans, P. Böttcher, P. Müller, H. W. Roesky, I. Usón, H.-G. Schmidt, M. Noltemeyer, *Inorg. Chem.* **2001**, *40*, 3766.
- [3] H. Gilman, K. Shiina, D. Aoki, B. J. Gaj, D. Wittenberg, T. Brennan, J. Organomet. Chem. 1968, 13, 323.
- [4] G. M. Sheldrick, SHELXL14, Program for the Refinement of Crystal Structures, Universität Göttingen, 2014.
- [5] O. V. Dolomanov, L. J. Bourhis, R. J. Hildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339-341.
- [6] H. Putz, K. Brandenburg, Diamond Crystal and Molecular Structure Visualization, Crystal Impact, Kreuzherrenstr. 102, 53227 Bonn, Germany.
- [7] TURBOMOLE Version 7.0.1, TURBOMOLE GmbH 2016.TURBOMOLE is a development of University of Karlsruhe and Forschungszentrum Karlsruhe 1989–2007, TURBOMOLE GmbH since 2007.
- [8] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, WIREs Comput. Mol. Sci. 2014, 4, 91-100.
- [9] F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057-1065.
- [10] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. **2010**, *132*, 154104.
- [11] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 2011, 32, 1456.
- [12] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100.
- [13] J. P. Perdew, *Phys. Rev. B* **1996**, *33*, 8822-8824.
- [14] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, 7, 3297.
- [15] F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057.
- [16] M. Dolg, H. Stoll, A. Savin, H. Preuss, *Theor. Chim. Acta* **1989**, *75*, 173.
- [17] H. Stoll, B. Metz, M. Dolg, J. Comput. Chem., 2002, 23, 767.