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A Triatomic Silicon(0) Cluster Stabilized by a Cyclic Alkyl(amino) Carbene

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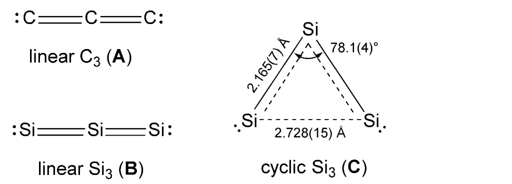
Dedicated to Dr. Richard Weidner

Abstract: *Reduction of the neutral carbene tetrachlorosilane adduct (cAAC)$SiCl_4$ (cAAC = cyclic alkyl(amino) carbene :$C(CMe_2)_2(CH_2)N(2,6\text{-}iPr_2C_6H_3)$ with potassium graphite produces stable (cAAC)$_3Si_3$, a carbene-stabilized triatomic silicon(0) molecule. The Si–Si bond lengths in (cAAC)$_3Si_3$ are 2.399(8), 2.369(8) and 2.398(8) Å, which are in the range of Si–Si single bonds. Each trigonal pyramidal silicon atom of the triangular molecule (cAAC)$_3Si_3$ possesses a lone pair of electrons. Its bonding, stability, and electron density distributions were studied by quantum chemical calculations.*

The major component (90%) of the earth's crust is made of silicates consisting of silicon(IV), which is the preferred oxidation state of silicon.[1] Reduction of silicon(IV) compounds (such as SiO_2 with charcoal at high temperature) or high-temperature chemical decomposition of $SiCl_4$ or $HSiCl_3$ leads to crystalline silicon(0), which is used for silicon chips in almost all electronic equipments.[2,3] Monocrystalline silicon has an extended diamondlike cubic crystal structure.[4] The optical and electronic properties of silicon-containing semiconductors originate from the molecular to macroscopic size regimes, and hence studies of silicon clusters are very important.[3,5] Small clusters consisting only of silicon atoms, which are generated in different ways for short periods of time, are of huge importance for numerous reasons. To date, these low-nuclearity silicon clusters have been characterized only by spectroscopic methods and studied by theoretical calculations. Silicon clusters ranging from Si_2 to Si_7 are prepared by vapor deposition of amorphous silicon and were observed in the gas phase by mass spectrometry[6] or studied in neon and argon matrices.[7–8] They were also characterized by electronic absorption spectra in neon matrices at 5 K.[9] Larger ionic silicon clusters of up to 43 silicon atoms were generated by pulsed laser vaporization and detected by mass spectrometry studies.[10] In addition, small silicon clusters play an important role in the photochemistry of some silicon-rich evolved stars.[11] The Si_3 molecule is one of the most important-silicon based clusters. The most recent study on the Si_3 cluster was an investigation on a trapped sample in an inert gas matrix. On the basis of infrared spectroscopy, optical studies, and ab initio calculations, the molecule was found to be asymmetric with C_{2v} symmetry.[12,13] Importantly, Si_3 is suspected to be an interstellar species[14,15] along with interstellar molecules C_3, SiC_2, SiC_3, SiCN, and SiNC in space,[16,17] which were generally detected and studied by infrared, microwave, and radio wave spectroscopy. Molecular Si_3 was discovered among the reaction products when SiH_4 was discharged during an experiment to characterize new silicon hydrides.[12,13] Ab initio calculations predict that silicon-containing clusters are significantly different in structure and bonding from the analogous lighter carbon compounds.[7,18,19] For example, linear C_3 (**A**) is more stable than cyclic C_3.[20] In contrast, bent Si_3 (**C**) is more stable by 9.5 kcal mol^{-1} than its linear Si_3 (**B**) molecule (Scheme 1) with an extremely shallow bending potential.[12,13] All these reported species are not stable at room temperature and are not formed selectively. A C_3 molecule that is stable at room temperature and is stabilized by a neutral ligand has not been isolated to date.[20,21]

Singlet carbenes are a class of compounds which have a pair of electrons on a sp^2-hybridized orbital of a divalent carbon atom.[22] They have become powerful tools for stabilization and isolation of extremely reactive unusual



Scheme 1. Linear and cyclic isomers of C_3 (**A**), and Si_3 (**B**, **C**) clusters.

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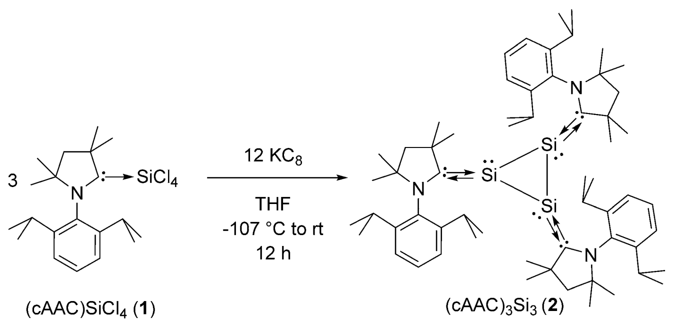
Supporting information for this article (including UV/Vis spectrum, structural determination, and computational details for **2**) is available on the WWW under http://dx.doi.org/10.1002/anie.201511019.



Scheme 2. Synthesis of compound **2**.

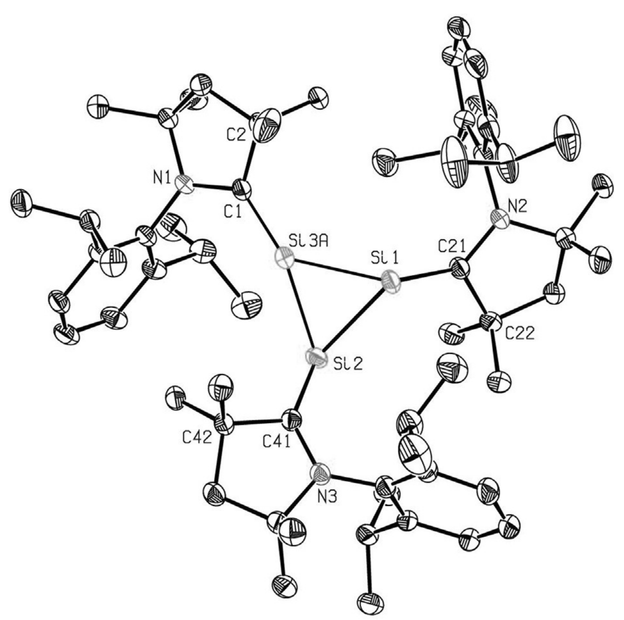


Figure 1. Molecular (ORTEP) view of carbene-stabilized triatomic silicon(0) (**2**) in the solid state (H atoms are omitted for clarity). Thermal ellipsoids represent 50% probability. Selected experimental bond distances [Å] and angles [°] [calculated at BP86/def2-SVP level] for **2** are Si1–Si2 2.399(8) Å [2.398], Si1–Si3A 2.369(8) Å [2.365], Si2–Si3A 2.398(8) Å [2.399], Si1–C21 1.854(7) Å [1.855], Si2–C41 1.878(7) Å [1.892], Si3A–C1 1.834(7) Å [1.850], N1–C1 1.392(6) Å [1.392], N2–C21 1.385(6) Å [1.388], N3–C41 1.378(5) Å [1.373]; Si2-Si1-Si3A 60.4(3)° [60.5], Si1-Si2-Si3A 59.2(3)° [59.1], Si1-Si3A-Si2 60.4(3)° [60.4], N1-C1-C2 107.3(3)° [107.1], N2-C21-C22 107.3(3)° [107.9], N3-C41-C42 107.2-(3)° [107.6].

chemical species.[23] Monoatomic and diatomic silicon(0)[24,25] have been stabilized by carbenes such as *N*-heterocyclic carbenes and cyclic alkyl(amino) carbenes. Cyclic alkyl-(amino) carbenes are inherently stronger σ-donors and better π-acceptors because of the presence of only one adjacent nitrogen atom in the molecule.[22] This property prompted us to utilize cyclic alkyl(amino) carbene (cAAC) stabilized (cAAC)$SiCl_4$[26] as a precursor for the synthesis of a triatomic silicon(0) compound (cAAC)$_3Si_3$ (**2**; where cAAC = :C$(CMe_2)_2(CH_2)$N(2,6-$i$$Pr_2C_6H_3$)). Herein, we report on the preparation, synchrotron single-crystal X-ray diffraction study, and theoretical calculations of tris(cyclic alkyl(amino) carbene)trisilicon(0) (**2**; Scheme 2). This compound is stable, isolable, and storable at room temperature. Results on this Si_3 molecule should also provide a fundamental route for selectively preparing small single-cluster species, which will allow further synthetic endeavors at room temperature.

The ^{29}Si NMR spectrum of **2** in C_6D_6 shows a singlet at +7.20 ppm which is downfield-shifted compared with that of precursor **1** (−103.5 ppm). However, it is upfield-shifted compared with those of cAAC-stabilized monoatomic ((cAAC)$_2$Si; +66.71 ppm) and diatomic ((cAAC)$_2Si_2$; +254.60 ppm) silicon(0) compounds. The ^{29}Si NMR resonance of **2** is close to the value of +14.6 ppm reported for [PhC(NtBu)$_2$]SiCl[27] but is observed at a considerably lower field than the value of +38.4 ppm reported for (NHC)$_2Si_2Cl_2$[25] and the value of +78.3 ppm reported for [C(H)N(tBu)]$_2$Si:.[28] The resonance of the carbene carbon atom of **2** appears at +207.4 ppm. which is close to that of precursor **1** (+206.1 ppm).[26]

Single-crystal structural determination with synchrotron radiation,[29] followed by aspherical-atom least-squares refinement[30] and subsequent structural analysis of **2** showed that the triangular Si_3 unit is sterically well-shielded by three cAAC ligands. Each silicon atom is bonded to two adjacent silicon atoms and further bound to the carbene carbon atom of a cAAC ligand. Three cAAC ligands in **2** are oriented in a propeller fashion with respect to the center of the triangular Si_3 unit (Figure 1). None of the cAAC ligands is in the plane of the Si_3 unit. The Si–Si bond distances of **2** are 2.399(8) Å, 2.369(8) Å, and 2.398(8) Å, which are longer by about 0.04 Å than the sum of the Si covalent radii (2.34 Å)[31] and about 0.02 Å longer than the Si–Si single bond length in α-silicon (2.36 Å).[32] Each silicon atom of **2** is in the formal oxidation state zero and adopts a three-coordinate trigonal pyramidal structure. The sums of the bond angles of silicon atoms in **2** are 320.1°, 333.6°, and 292.0° (mean value of 315.2°). One of the silicon atoms (Si3) is slightly disordered. The pyramidal geometry at each silicon atom in **2** results from a lone pair of electrons (distances from Si atoms to corresponding triangular planes; Si1–Si2Si3AC21 0.663 Å, Si2–Si1Si3AC41 0.966 Å, Si3A–Si1Si2C1 0.541 Å). Two lone pairs of electrons of two silicon atoms (Si3A, Si1) are on the same side while the third one (Si2) is on the opposite side. Thus, **2** can be considered as a triangular trisilylene having 6 π electrons. The triangular Si_3 unit of **2** is comparable to the graphene-like two-dimensional silicene[33] which has an extended nonplanar Si_6 unit (Si–Si distance 2.32 Å) with a Si_3 fragment over three silver atoms of the silver(111) substrate. The silicon–carbon distances are 1.854(7), 1.878(7), and 1.834(7) Å which are comparable to those of cAAC-stabilized monoatomic and diatomic silicon-(0) compounds.[24–25] The average silicon–carbon bond length of **2** is shorter than that of precursor **1** (about 1.94 Å). The average carbon–nitrogen bond length of **2** is 1.38 Å, which is longer by about 0.08 Å than that of **1**, thus suggesting significant π back-donation from each silicon atom to carbene carbon atom.

We carried out quantum chemical calculations using density functional theory at the BP86/def2-SVP level in order to analyze the bonding situation in **2**. The calculated bond lengths and angles are in excellent agreement with the experimental data (Figure 1). The natural bond orbital (NBO) analysis suggests a rather uncomplicated picture of the core bonds in $(cAAC)_3Si_3$. The relevant bond orbitals are shown in Figure S4 in the Supporting Information. The cyclic Si_3 moiety features three Si–Si σ-bond orbitals that are slightly polar with degrees varying between 45–55 % because of the asymmetry of the three Si(cAAC) moieties. The dative bonds of the ligands exhibit three cAAC→Si σ-donor bond orbitals that are polarized with 68–71 % toward the carbon end. The π-type bond orbitals that arise from the cAAC←Si π back-donation are almost nonpolar (between 40–54 % at Si) which indicates quite large π back-donation. This effect can be explained by the strong repulsion between the three formally lone-pair orbitals, which comes from the exchange (Pauli) repulsion, in the Si_3 ring. Pyramidalization and strong π back-donation relieve the Pauli repulsion.[34] Compound **2** could thus also be depicted with Si=C double bonds. The ^{15}N NMR resonance of **2** is observed at −233.0 ppm (see the Supporting Information), which is upfield-shifted when compared to that of precursor **1** (−164.1 ppm) but close to the value recorded for silylone [24] $(cAAC)_2Si$ (−230.0 ppm). These values suggest that the π back-donation from silicon atom to carbene carbon atom (C_{cAAC}←Si) of **2** is similar in magnitude to that of $(cAAC)_2Si$. However, the dissociation of the cAAC ligands smoothly leads to the fragments Si_3 and 3 cAAC in the singlet states, which supports the description with coordinate bonds.[35] The NBO calculations gave positive partial charges at Si between 0.20–0.33 *e*. The Wiberg bond order for the Si–C bonds is in between 1.13 and 1.25, which indicates some double-bond character. The calculation of the electronic excitation of **2** using time-dependent DFT at the B3LYP/def2-TZVP level where the solvent influence was estimated with the polarized continuum model (PCM) produced a simulated UV/Vis spectrum (Figure S6 in the Supporting Information) which shows peaks at 406 and 497 nm. The signal at 497 nm comes from the π→π* (HOMO-1→LUMO and HOMO→LUMO + 1, Figure 2) excitation of the exocyclic Si–C orbitals. The signal at 406 nm is a mixture of excitations from the Si–Si bonding orbitals into vacant orbitals of the cAAC ligands (Table S4 and Figure S7 in the Supporting Information).

We also calculated the related carbene complex $(NHC^{Ph})_3Si_3$ in which silicon and NHC^{Ph} should be more weakly bonded, because the cAAC is a stronger σ donor and a better π acceptor than NHC^{Ph}. The geometry of the latter is shown in Figure S5 in the Supporting information. The calculated Si–C bonds in $(NHC^{Ph})_3Si_3$ are longer (1.947, 1.941, and 1.927 Å) than in **2** and the ligand-exchange reaction $(cAAC)_3Si_3 + 3\,NHC^{Ph} \rightarrow (NHC^{Ph})_3Si_3 + 3\,cAAC$ is endergonic by $\Delta G = 20.9$ kcal mol^{-1}. The bond dissociation energy (BDE) for loss of the cAAC ligands $(cAAC)_3Si_3 \rightarrow Si_3 + 3\,cAAC$ is 115.7 kcal mol^{-1} at BP86/def2-SVP. A recalculation at M06-2X/def2-TZVPP//BP86/def2-SVP gives a value of 130.4 kcal mol^{-1} which suggests an average BDE of $D_e = 43.5$ kcal mol^{-1} for each ligand.

In conclusion, more than six decades after spectroscopic detection of the Si_3 cluster by Honig, the stable and isolable carbene-stabilized triatomic silicon(0) **2** has been synthesized in a simple synthetic procedure by controlling the reaction conditions. The employment of cAAC carbene as a π-accepting ligand is crucial. Compound **2** is stable and isolable at room temperature under an inert atmosphere. It possesses a triangular Si_3 unit with a lone pair of electrons on each silicon atom, and hence it can be also considered as a triangular trisilylene. The lone pair of electrons of each silicon atom is polarized toward carbene carbon atom because of the significant π-accepting properties of the cAAC ligand. This tris(cyclic alkyl(amino) carbene)trisilicon(0) might serve as a model for a better understanding of the formation of suspected silicon clusters in the interstellar medium. Additionally, the isolation of this molecule paves the way for the possible synthesis of other stable silicon(0) clusters which were previously thought to be unisolable under normal laboratory conditions and could be, until now, detected by mass spectrometry and characterized by correlating the spectroscopic data with theoretically calculated values.

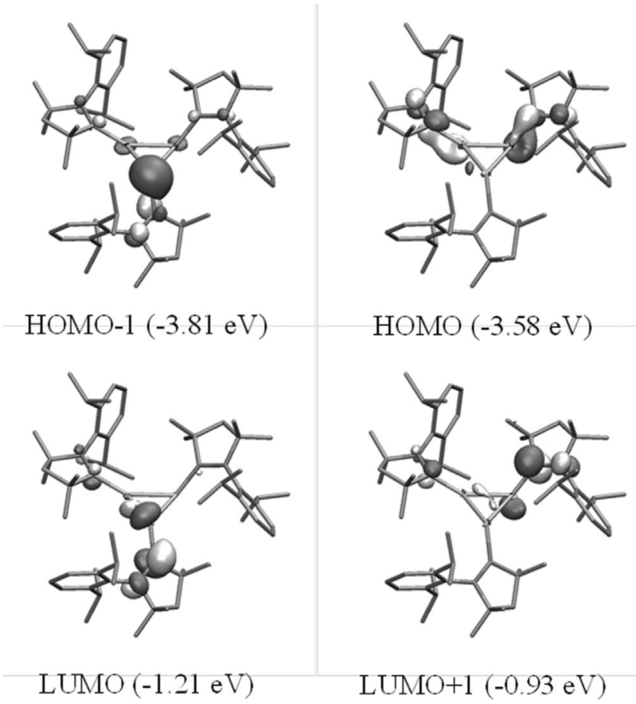


Figure 2. Frontier molecular orbitals of **2** (B3LYP/def2-TZVP//BP86/def2-SVP). Hydrogen atoms are omitted for clarity.

Experimental Section

Synthesis of **2**: The adduct $(cAAC)SiCl_4$ (**1**) was placed in a flask and dissolved in THF at room temperature. THF was added to another flask containing four equivalents of potassium graphite (KC_8). Both of these flasks were cooled to −107 °C by using THF/liquid nitrogen baths. The solution containing **1** was then added to a continuously stirred slurry of KC_8 by cannula. The temperature of the mixture was slowly raised to −78 °C over 15 minutes and the resultant mixture was stirred at this temperature for another 30 minutes to obtain a dark-green solution. The temperature of this solution was slowly raised to −20 °C over two hours to produce a greenish-red solution which slowly changed to dark-red. Finally the solution was stirred for 9 hours at room temperature to obtain an air- and moisture-sensitive dark red-purple solution of **2**. The graphite was separated by filtration and the product **2** was extracted with *n*-hexane which was stored at −32 °C in a freezer to form the dark rods of **2** in 25 % yield. The dark red-purple crystals of **2** decompose above 165 °C under an inert atmosphere. The UV/Vis spectrum of **2** (in *n*-hexane) shows absorption bands at 418 and 540 nm.. Elemental analysis (%) found (calcd) for $C_{60}H_{93}N_3Si_3$: C, 76.72 (76.61); H, 9.79 (9.96); N, 4.52 (4.46). ^{1}H NMR (500 MHz, 298 K, C_6D_6): $\delta = 7.13$ (m, 9H), 3.34–3.23 (m, 6H), 1.76 (s, 6H), 1.74 (d, $J = 6.7$ Hz, 18H), 1.23 (d, $J = 6.9$ Hz, 36H), 1.16 ppm (s, 18H). ^{13}C NMR (126 MHz, 298 K, C_6D_6): $\delta = 207.08$, 149.17, 137.98, 128.42, 128.29, 125.67, 69.57, 56.19, 50.81, 34.56, 31.92, 29.02, 28.47, 27.91, 25.38 ppm; ^{29}Si NMR (99.395 MHz, 298 K, C_6D_6): $\delta = 7.20$ ppm; ^{15}N NMR (50.709 MHz, 298 K, C_6D_6): $\delta = -233.0$ ppm. See reference [29] for the synchrotron radiation method, and the Supporting Information for theoretical calculations.

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[1] W. A. Deer, R. A. Howie, J. Zussman, *An Introduction to the Rock-Forming Minerals*, 2nd ed., Prentice Hall, Englewood, NJ, **1996**.
[2] T. I. Williams, *History of Invention: From Stone Axes to Silicon Chips, Revised Edition*, Checkmark Books, New York, **2000**.
[3] T. Kamins, *Polycrystalline Silicon for Integrated Circuits and Displays*, 2nd ed., Kluwer Academic Publishers, Norwell, MA, **1998**.
[4] W. C. O'Mara, R. B. Herring, L. P. Hunt, *Handbook of Semiconductor Silicon Technology*, Noyes Publications, Park Ridge, NJ, **1990**.
[5] A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J. P. Mondia, G. A. Ozin, O. Toader, H. M. van Driel, *Nature* **2000**, *405*, 437.
[6] R. E. Honig, *J. Chem. Phys.* **1954**, *22*, 1610.
[7] K. Raghavachari, V. Logovinsky, *Phys. Rev. Lett.* **1985**, *55*, 2853.
[8] S. Li, R. J. V. Zee, W. Weltner, Jr., K. Raghavachari, *Chem. Phys. Lett.* **1995**, *243*, 275.
[9] J. Fulara, P. Freivogel, M. Grutter, J. P. Maier, *J. Phys. Chem.* **1996**, *100*, 18042.
[10] M. F. Jarrold, *Science* **1991**, *252*, 1085.
[11] A. E. Glassgold, G. A. Mamon, *Chemistry and Spectroscopy of Interstellar Molecules* (Eds.: D. K. Bohme, E. Herbst, N. Kaifu, S. Saito), University of Toyko Press, Tokyo, **1992**, p. 261.
[12] M. C. McCarthy, P. Thaddeus, *Phys. Rev. Lett.* **2003**, *90*, 213003.
[13] M. C. McCarthy, P. Thaddeus, *Astrophys. J.* **2003**, *592*, L91.
[14] E. B. Jenkins, *Interstellar Processes* (Eds.: D. J. Hollenbach, H. A. Thronson, Jr.), Dordrecht, Reidel, **1987**, p. 533.
[15] S. Pfalzner, C. Kramer, C. Straubmeier, A. Heithausen, *The Dense Interstellar Medium in Galaxies*: Proceedings of the 4th Cologne–Bonn–Zermatt Symposium "The Dense Interstellar Medium in Galaxies", Zermatt, 22–26 September, **2003**.
[16] R. Naghma, B. Antony, *Mol. Phys.* **2013**, *111*, 269.
[17] K. W. Hinkle, J. J. Keady, P. F. Bernath, *Science* **1988**, *241*, 1319.
[18] I. Vasiliev, S. Öğüt, J. R. Chelikowsky, *Phys. Rev. Lett.* **1997**, *78*, 4805.
[19] N. Binggeli, J. R. Chelikowsky, *Phys. Rev. Lett.* **1995**, *75*, 493.
[20] C. Nicolas, J. Shu, D. S. Peterka, M. Hochlaf, L. Poisson, S. R. Leone, M. Ahmed, *J. Am. Chem. Soc.* **2006**, *128*, 220.
[21] V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2006**, *312*, 722.
[22] M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810; *Angew. Chem.* **2010**, *122*, 8992.
[23] M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485.
[24] a) K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, B. Niepötter, H. Wolf, R. Herbst-Irmer, D. Stalke, *Angew. Chem. Int. Ed.* **2013**, *52*, 2963; *Angew. Chem.* **2013**, *125*, 3036; b) K. C. Mondal, P. P. Samuel, M. Tretiakov, A. P. Singh, H. W. Roesky, A. C. Stückl, B. Niepötter, E. Carl, H. Wolf, R. Herbst-Irmer, D. Stalke, *Inorg. Chem.* **2013**, *52*, 4736; c) B. Niepötter, R. Herbst-Irmer, D. Kratzert, P. P. Samuel, K. C. Mondal, H. W. Roesky, P. Jerabek, G. Frenking, D. Stalke, *Angew. Chem. Int. Ed.* **2014**, *53*, 2766; *Angew. Chem.* **2014**, *126*, 2806.
[25] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. von R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069.
[26] K. C. Mondal, H. W. Roesky, A. C. Stückl, F. Ihret, W. Kaim, B. Dittrich, B. Maity, D. Koley, *Angew. Chem. Int. Ed.* **2013**, *52*, 11804; *Angew. Chem.* **2013**, *125*, 12020.
[27] C.-W. So, H. W. Roesky, J. Magull, R. B. Oswald, *Angew. Chem. Int. Ed.* **2006**, *45*, 3948; *Angew. Chem.* **2006**, *118*, 4052.
[28] M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Balyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691.
[29] Synchrotron radiation was required for structural analysis because of the weak scattering power of the sample, probably arising from rapid crystal decay upon reaction with oxygen. A wavelength of 0.6525 Å was chosen on beamline P11 at the Petra III, storage ring at DESY (Hamburg); two out of eight datasets (crystals) were chosen and merged to a) minimize systematic errors and b) allow full coverage of reciprocal space in space group $P\bar{1}$. Lattice constants: $a = 13.883(2)$, $b = 14.089(3)$, $c = 17.70(6)$, $\alpha = 95.7(3)$, $\beta = 98{,}62(4)$, $\gamma = 119.28(10)°$, unit cell volume 2924(10) Å^3, 62798 refl. measured, 10437 unique, $8650 > 4\sigma(F)$, $R_1(F) = 4.6\,\%$. CCDC 1420696 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
[30] a) B. Dittrich, C. B. Hübschle, K. Pröpper, F. Dietrich, T. Stolper, J. J. Holstein, *Acta Crystallogr. Sect. B* **2013**, *69*, 91; b) B. Dittrich, C. M. Wandtke, A. Meents, K. Pröpper, K. C. Mondal, P. P. Samuel, N. A. SK, A. P. Singh, H. W. Roesky, N. Sidhu, *ChemPhysChem* **2015**, *16*, 412.
[31] J. Y. Corey, *The Chemistry of Organic Silicon Compounds, Vol. 1* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, UK, **1989**, Chapter 1.
[32] R. Nesper, A. Currao, S. Wengert, *Organosilicon Chemistry II: From Molecules to Materials* (Eds.: N. Auner, J. Weis), VCH, Weinheim, **1996**, p. 469.
[33] P. Vogt, P. D. Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet, G. L. Lay, *Phys. Rev. Lett.* **2012**, *108*, 155501.
[34] For the role of Pauli repulsion see: A. Krapp, F. M. Bickelhaupt, G. Frenking, *Chem. Eur. J.* **2006**, *12*, 9196.
[35] G. Frenking, *Angew. Chem. Int. Ed.* **2014**, *53*, 6040; *Angew. Chem.* **2014**, *126*, 6152.

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