Check for updates

■ **Cluster Compounds** |*Very Important Paper*|

VIP

Chalcogen-Expanded Unsaturated Silicon Clusters: Thia-, Selena-, and Tellurasiliconoids

Nadine E. Poitiers, Volker Huch, Michael Zimmer, and David Scheschkewitz*[a]

Abstract: Reactions of silylenes with heavier chalcogens (E) typically result in Si=E double bonds or their π-addition products. In contrast, the oxidation of a silylene-function-alized unsaturated silicon cluster (siliconoid) with Group 16 elements selectively yields cluster expanded siliconoids Si_7E (E = S, Se, Te) fully preserving the unsaturated nature of the cluster scaffold as evident from the NMR signatures of the products. Mechanistic considerations by DFT calculations suggest the intermediacy of a Si_6 siliconoid with exohedral Si=E functionality. The reaction thus may serve as model system for the oxidation of surface-bonded silylenes at Si(100) by chalcogens and their diffusion into the silicon bulk.

The synthesis of unsaturated silicon clusters (siliconoids)[1] as well as the corresponding hetero derivatives[2] draws increasing attention due to their role as presumed intermediates during chemical vapor deposition[3] or heterogeneous catalysis.[4] In addition, the unsubstituted vertices share important features of native silicon surfaces, in particular the presence of free valencies, the so-called "dangling bonds".[5]

A variety of neutral and anionic stable siliconoids has been reported during the last decades.[2, 6, 7–16] The manipulation of stable representatives under retention of the unsaturated character is mostly limited to the shell of stabilizing ligands. A notable exception is the deliberate core expansion from Si_6 via Si_7 and Si_8 using silicocene $SiCp*_2$ as a source of atomic silicon.[13d] In general, reactions of siliconoids with oxidizing reagents result in the saturation of the free valencies and thus the loss of siliconoid character according to the definition.[17] More particularly, while saturated silicon clusters are well-known to undergo cluster expansion with chalcogens[12, 18] the related chemistry of neutral siliconoids is completely unexplored, pre-

sumably due to the facile oxidation of the "naked" vertices. In view of the tremendous importance of chalcogen-containing silicon materials,[19] including sub-valent varieties such as the famous "silicon monoxide",[20] we contemplated the possibility of the incorporation of Group 16 elements as heteroatoms into the cluster core without compromising the siliconoid characteristics. A large variety of molecular model systems for silicon subchalcogenides has been described in recent years, which are strictly electron-precise without exception and thus do not reflect the widely accepted assumption of nanoscalar cluster domains in these composite materials.[18a–c] N-heterocyclic silylenes, for instance, are well-known to readily undergo oxidation to the corresponding silanones and heavier versions thereof.[21–24]

We therefore envisaged that chalcogens may initially attack the pending silylene center of our recently reported siliconoid/silylene hybrid species[13g] instead of the unsubstituted vertices of the Si_6 scaffold. In the same communication we had shown that the $Fe(CO)_4$ fragment coordinates to the silylene moiety exclusively.[13g] We now report that this strategy indeed leaves the "naked" vertices untouched in the reaction with chalcogens as well, while the pronounced electrophilicity of the plausibly formed Si=E moiety (E = S, Se, Te) expands the cluster core to incorporate two additional vertices: a pentacoordinate silicon and the heavier chalcogen.
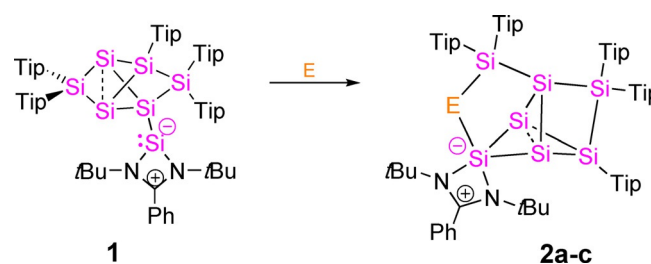
Simple stirring of a benzene suspension of the silylene-functionalized siliconoid **1** with an excess of the chalcogen at room temperature (**2a**: E = S, 2.5 equiv, 4 h; **2b**: E = Se, 2.5 equiv, 16 h; **2c**: E = Te, 7 equiv, 72 h) results in the uniform conversion to the chalcogen-expanded siliconoids **2a–c** (Scheme 1).

The longest wavelength absorptions in the UV/Vis spectra are at $\lambda_{max} = 394$ nm (**2a**), 396 nm (**2b**), 404 nm (**2c**) and thus within the range observed for previously reported siliconoids ($\lambda_{max} = 364$ to 477 nm).[13c,d] The chalcogen-expanded ESi_7 siliconoids **2a–c** exhibit a high thermal stability, showing almost no

[a] N. E. Poitiers, Dr. V. Huch, Dr. M. Zimmer, Prof. Dr. D. Scheschkewitz
Krupp-Chair of Inorganic and General Chemistry
Saarland University
Campus Saarbrücken C4.1, 66123 Saarbrücken (Germany)
E-mail: scheschkewitz@mx.uni-saarland.de

Supporting information and the ORCID identification numbers for the authors of this article can be found under:
*https://doi.org/10.1002/chem.202003180.*

Scheme 1. Synthesis of chalcogen-expanded Si_7 siliconoids **2a–c** (**2a**: E = S, **2b**: E = Se, **2c**: E = Te).

Chemistry–A European Journal

Communication
doi.org/10.1002/chem.202003180

Chemistry Europe
European Chemical
Societies Publishing

decomposition at their melting points up to 380 °C. In the solid state, crystals can be exposed to air for a few minutes without apparent decomposition. This is remarkably reminiscent of the stability of selenium and other heavier chalcogens bonded to silicon surfaces, which require temperatures of up to 1000 K for desorption.[22]

The structures of siliconoids Si_7E **2a–c** in the solid state were determined by X-ray diffraction on bright yellow crystals obtained in 74% (**2a**), 70% (**2b**) and 75% (**2c**) yield, respectively (Figure 1). The cluster cores resemble that of the aforementioned $Si_7Tip_5Cp^*$ siliconoid and its expansion to $Si_8Tip_5Cp^*$.[13d] As in $Si_7Tip_5Cp^*$, the Si1, Si2 and Si5 vertices are arranged as a central isosceles triangle, although only the two vertices of the base (Si1 and Si2) show hemispheroidal coordination environments[1a] (**2a**: $\phi(Si1) = +1.3628$ Å, $\phi(Si2) = 1.2919$ Å, $\phi(Si5) = -0.2267$ Å; **2b**: $\phi(Si1) = +1.3603$ Å, $\phi(Si2) = +1.2850$ Å, $\phi(Si5) = -0.2120$ Å; **2c**: $\phi(Si1) = +1.3616$ Å, $\phi(Si2) = +1.2758$ Å, $\phi(Si5) = -0.2356$ Å). The Si_7E cluster is formally derived from the Si_5 propellane motif distorted by the twofold interconnection of the "propeller blades". This distortion results in a seesaw-type coordination environment at Si5 with a quasilinear arrangement towards Si6 and Si5 (Si4-Si5-Si6 162.705(4)° (**2a**); 161.951(2)° (**2b**); 158.951(3)° (**2c**) vs. 173.77° for $Si_7Tip_5Cp^{*[13d]}$). The $SiTip_2$-bridge between Si5 and the former N-heterocyclic silylene moiety Si7 is extended by the insertion of the chalcogen atom. Together with the two nitrogen centers and the two adjacent "naked" silicon vertices pentacoordination of Si7 is attained. The distance between the unsubstituted silicon atoms in **2a–c** (Si1–Si2 **2a**: 2.6583(5) Å, **2b**: 2.6483(7) Å, **2c**: 2.611(7) Å, Table 1) are comparable with those of the $Si_7Tip_5Cp^*$ (2.648 Å).[13d] The Si2–Si7 bonds are markedly longer (**2a**: 2.4967(5) Å, **2b**: 2.4904(7), **2c**: 2.5017(7) Å) than all remaining Si–Si bonds of the cluster core. The Si6–E bonds of
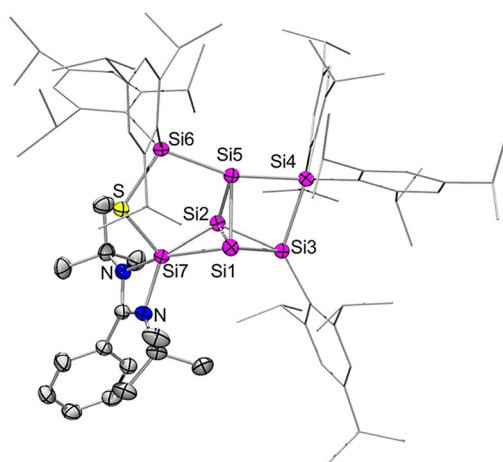
Figure 1. Representative molecular structure of siliconoid **2a** in the solid state. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50%. For structure of **2b,c** see Supporting Information. Selected bond length [Å] and angles [°]: **2a**: Si1–Si7 2.4967(5), Si1–Si2 2.6583(5), Si4–Si5 2.4067(5), Si6–S 2.2044(5), Si7–S 2.1438(5), Si7–N1 1.852(1), Si7–N2 1.909(1); **2b**: Si2–Si7 2.4904(7), Si1–Si2 2.6483(7), Si4–Si5 2.4101(8), Se–Si7 2.2923(6), Se–Si6 2.3474(6), Si7–N2 1.860(2), Si7–N1 1.924(2); **2c**: Si2–Si7 2.5017(7), Si1–Si2 2.6411(7), Si4–Si5 2.4249(7), Te–Si7 2.5120(5), Te–Si6 2.5764(5), Si7–N1 1.862(2), Si7–N2 1.928(2).

Table 1. Selected analytical data of Group 16 core-expanded siliconoids **2a–c**.

	$\delta^{29}Si5$ [ppm]	$\delta^{29}Si1/2$ [ppm]	Si1-Si2 [Å]	Si7-E [Å]	Si6-E [Å]	λ_{max} [nm]
2a (E=S)	−109.7	−251.1 −314.9	2.6583(5)	2.1438(5)	2.2044(5)	395
2b (E=Se)	−100.4	−251.5 −309.3	2.6483(7)	2.2923(6)	2.3474(6)	397
2c (E=Te)	−86.7	−250.2 −299.3	2.611(7)	2.5120(5)	2.5764(5)	405

2a–c (**2a**: 2.2044(5) Å, **2b**: 2.3474(6) Å, **2c**: 2.5764(5) Å) are significantly longer than Si7–E (**2a**: 2.1438(5) Å, **2b**: 2.2923(6) Å, **2c**: 2.5120(5) Å) and hence in the range of typical Si–E single bonds as, for example, in dichalcogenatrisilabicyclopentanes (Si–S: 2.198 Å; Si–Se: 2.339 Å; Si–Te: 2.561 Å).[25] The difference in Si–E bond lengths may be interpreted as manifestation of some residual double bond character of Si7–E and consequentially a somewhat weaker interaction Si6–E, possibly with a certain donor-acceptor character.
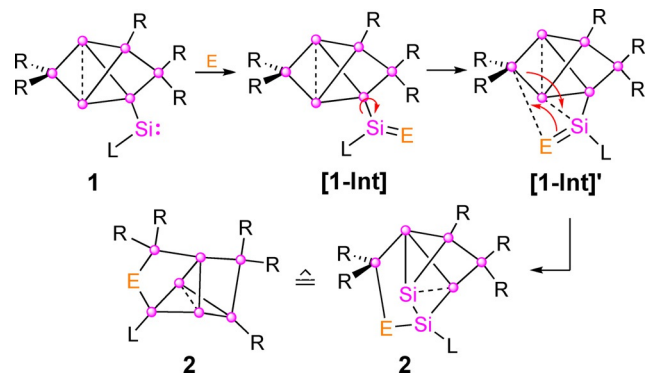
At first glance, the typical wide dispersion of ^{29}Si NMR signals of siliconoids is not retained in **2a–c**. While two of signals for the unsubstituted silicon atoms Si1 and Si2 are observed in the characteristic region between about −250 and −300 ppm, a third strongly shielded signal at −109.7 ppm (**2a**), −100.4 ppm (**2b**) and −86.7 ppm (**2c**) without a cross-peak in the 2D $^{29}Si/^1H$ correlation NMR spectra is indicative of the presence of the additional silicon vertex Si5 without substituent, similar to the observations in the hetero-atom-free Si_7 siliconoid.[13d] The resonances at 33.5 (**2a**), 26.6 (**2b**) and 2.3 ppm (**2c**) are assigned to the silicon vertex of the former N-heterocyclic silylene moiety. While siliconoids $Si_7Tip_5Cp^*$ and $Si_8Tip_5Cp^{*[13d]}$ still exhibit a similarly wide ^{29}Si NMR shift distribution as the Si_6 benzpolarenes,[13c,e] the chemical shifts of **2a–c** for Si7 may seem quite ordinary at first, but are in fact extraordinarily deshielded considering the pentacoordination of Si7. Pentacoordinate silicon atoms containing the same amidinato ligand typically give rise to signals between −124.9 and −82.9 ppm.[26] All other signals are observed at unremarkable chemical shifts and are assigned to either $SiTip_2$ or $SiTip$ vertices on the basis of the number of cross-peaks to aryl hydrogens in the 2D $^{29}Si/^1H$ NMR correlation spectra (see Supporting Information). The occurrence of two sets of signals in the ^1H NMR of **2c** suggests the presence of rotational isomers. Indeed, a VT-NMR study in toluene solution revealed an increase in intensity of the second set of signals with temperature although the barrier proved to be too high to accurately determine the coalescence temperature (> 343 K). The low solubility of **2a–c** hindered the acquisition of ^{29}Si NMR with sufficient signal-to-noise ratio and thus prevented the detection of the second set of signals for **2c**. The ^{125}Te spectrum of **2c**, however, reveals a major signal at −93.72 ppm and a second less intense signal at −22.84 ppm. The ^{77}Se spectrum of **2b** shows one sharp signal at 53.9 ppm.

In the CP-MAS ^{29}Si NMR, very similar chemical shifts are observed proving the identity of the cluster in the solid state and

the major rotational isomer in solution. The CP/MAS NMR chemical shifts of the heavier chalcogen atoms in **2b** and **2c** depend slightly on the rotation frequency of the rotors, a commonly observed phenomenon due to the heating of the sample induced by fast spinning of the rotor.[27] This effect is more pronounced in case of the ^{125}Te signals of **2c** with a downfield shift of $\Delta\delta = 9.1$ ppm upon increasing the frequency from 5 to 15 KHz. In comparison, the ^{77}Se signals of **2b** are only shifted by $\Delta\delta = 3.2$ ppm under identical conditions. The same phenomenon, albeit significantly less pronounced, is observed for the ^{29}Si CP/MAS NMR chemical shifts of **2b,c** (Supporting Information) with downfield-shifts $\Delta\delta$ between 0.2 and 0.9 ppm with increasing rotation frequency from 5 to 15 KHz.

The mechanism of chalcogen-expansion of the cluster is of particular relevance in view of the considerable interest in chalcogen and chalcogenide diffusion through silicon materials spurred by applications in micro- and optoelectronics as well as batteries.[19d, 28] The formation of heterosiliconoids **2a–c** is readily understood by an initial oxidation of the pending silylene center by the chalcogen leading to the formation of an intermediate siliconoid **[1-Int]** with Si$=$E functionality in *ligato*-position. Such a pathway may well correspond to the an initial step of the sorption of chalcogens to the deconstructed Si(100)(1×1) surface with its surface-bonded silylene centers. After rotation about the Si—Si bond between silylene and siliconoid core, the strongly polar Si$=$E moiety of **[1-Int]′** would be predisposed to attack the *privo*-vertex (which typically hosts major contributions to the LUMO of functionalized benzpolarene siliconoids)[13b] with its negatively polarized chalcogen end. In this scenario, the silicon end with its partial positive charge would accept electron density from one of the *nudo*-vertices in concert with the cleavage of the bond between the *nudo*- and the *privo*-silicon atoms (Scheme 2). We speculate that similar pathways may be active during the process of chalcogen diffusion from the silicon surface into the bulk.[28b]

In order to support our mechanistic proposal, optimization of the electronic structures of the sulfur-expanded siliconoid **2a** and the proposed intermediates **[1-Int]** and **[1-Int]′** with E$=$S were carried out at the BP86-D3(BJ)/def2-SVP level of theory (Supporting Information). Compared to **[1-Int]**, the final product **2a** is favored by $\Delta\Delta G = -9.26$ kcal mol^{-1} in free en-

thalpy, which is in line with the fast and spontaneous formation of **2a** (see Supporting Information). According to the Hammond postulate,[29] an approximate idea about the activation barrier for this process can be deduced from the free enthalpy of **[1-Int]′** as necessary intermediate, which is by $\Delta\Delta G = +4.71$ kcal mol-1 higher in free enthalpy than **[1-Int]**. The shape of the frontier orbitals of **[1-Int]** adds further support for this scenario. The HOMO and HOMO-1 represent the lone pairs at the sulfur atom, while the LUMO exhibits a major contribution at the *privo*-vertex as commonly found for hexasilabenzpolarene structures (Figure 2). The intramolecular in phase-overlap of HOMO and LUMO upon rotation of the Si$=$E moiety towards the *privo*-vertex as in **[1-Int]′** would plausibly result in relaxation to **2a** with a small barrier (Scheme 2).

In conclusion, we reported the expansion of the core structure of neutral silylene-functionalized siliconoids with chalcogens in the backbone. The heterosiliconoids of type Si$_7$E (E$=$S, Se, Te) feature three unsubstituted vertices and are shown to be thermally extremely robust. The former silylene moiety is now pentacoordinate, yet shows a chemical shift at unusually low field presumably due to the characteristic deshielding effect of the cluster current. The mechanistic scenario for cluster expansion may serve as inspiration for the consideration of alternative pathways in surface and bulk interactions of chalcogens with silicon.
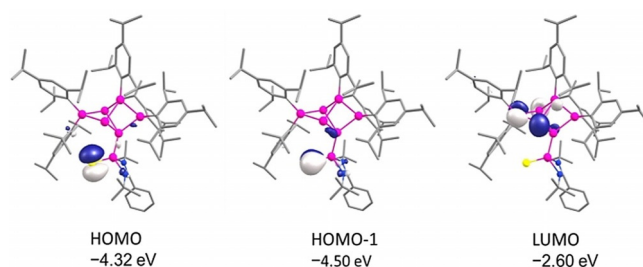
Figure 2. Selected Molecular orbitals of **[1-Int]′** at the BP86-D3(BJ)/def2-SVP level of theory (isocontour value at 0.051840).

HOMO −4.32 eV   HOMO-1 −4.50 eV   LUMO −2.60 eV

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Scheme 2. Mechanistic considerations regarding the formation of chalcogen-expanded Si$_7$E siliconoids **2a–c**.

[1] a) Y. Heider, D. Scheschkewitz, *Dalton Trans.* **2018**, *47*, 7104–7112; b) S. Kyushin in *Organosilicon Compounds: Theory and Experiment (Synthesis), Vol. 1* (Ed.: V. Y. Lee), Academic Press **2017**, pp. 69–144; c) T. Iwamoto, S. Ishida, *Chem. Lett.* **2014**, *43*, 164–170; d) F. Breher, *Coord. Chem. Rev.* **2007**, *251*, 1007–1043.

Chemistry–A European Journal

Communication
doi.org/10.1002/chem.202003180

Chemistry Europe
European Chemical
Societies Publishing

[2] a) A. Jana, V. Huch, M. Repisky, R. J. F. Berger, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2014**, *53*, 3514–3518; *Angew. Chem.* **2014**, *126*, 3583–3588; b) L. Klemmer, V. Huch, A. Jana, D. Scheschkewitz, *Chem. Commun.* **2019**, *55*, 10100–10103.

[3] a) T. M. l. Davidson, *J. Organomet. Chem.* **1970**, *24*, 97–100; b) H. Murakami, T. Kanayama, *Appl. Phys. Lett.* **1995**, *67*, 2341–2343; c) M. Watanabe, H. Murakami, T. Miyazaki, T. Kanayama, *Appl. Phys. Lett.* **1997**, *71*, 1207–1209; d) W. M. M. Kessels, M. C. M. Van De Sanden, D. C. Schram, *Appl. Phys. Lett.* **1998**, *72*, 2397–2399; e) G. A. Rechtsteiner, O. Hampe, M. F. Jarrold, *J. Phys. Chem. B* **2001**, *105*, 4188–4194.

[4] N. E. Poitiers, L. Giarrana, V. Huch, M. Zimmer, D. Scheschkewitz, *Chem. Sci.* **2020**, *11*, 7782–7788.

[5] H. Neergaard-Waltenburg, J. T. Yates, Jr., *Chem. Rev.* **1995**, *95*, 1589–1673.

[6] D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2005**, *44*, 2954–2956; *Angew. Chem.* **2005**, *117*, 3014–3016.

[7] G. Fischer, V. Huch, P. Mayer, S. K. Vasisht, M. Veith, N. Wiberg, *Angew. Chem. Int. Ed.* **2005**, *44*, 7884–7887; *Angew. Chem.* **2005**, *117*, 8096–8099.

[8] a) A. Tsurusaki, C. Iizuka, K. Otsuka, S. Kyushin, *J. Am. Chem. Soc.* **2013**, *135*, 16340–16343; b) A. Tsurusaki, J. Kamiyama, S. Kysushin, *J. Am. Chem. Soc.* **2014**, *136*, 12896–12898.

[9] T. Iwamoto, N. Akasaka, S. Ishida, *Nat. Commun.* **2014**, *5*, 5353.

[10] D. Nied, R. Köppe, W. Klopper, H. Schnöckel, F. Breher, *J. Am. Chem. Soc.* **2010**, *132*, 10264–10265.

[11] L. J. Schiegerl, A. J. Karttunen, W. Klein, T. F. Fässler, *Chem. Eur. J.* **2018**, *24*, 19171–19174.

[12] J. Keuter, K. Schwedtmann, A. Hepp, M. Bergander, O. Janka, C. Doerenkamp, H. Eckert, C. Mück-Lichtenfeld, F. Lips, *Angew. Chem. Int. Ed.* **2017**, *56*, 13866–13871; *Angew. Chem.* **2017**, *129*, 14054–14059.

[13] a) K. Abersfelder, A. J. P. White, H. S. Rzepa, D. Scheschkewitz, *Science* **2010**, *327*, 564–566; b) K. Abersfelder, A. J. P. White, R. J. F. Berger, H. S. Rzepa, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2011**, *50*, 7936–7939; *Angew. Chem.* **2011**, *123*, 8082–8086; c) P. Willmes, K. Leszczyńska, Y. Heider, K. Abersfelder, M. Zimmer, V. Huch, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2016**, *55*, 2907–2910; *Angew. Chem.* **2016**, *128*, 2959–2963; d) K. I. Leszczyńska, V. Huch, C. Präsang, J. Schwabedissen, R. J. F. Berger, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2019**, *58*, 5124–5128; *Angew. Chem.* **2019**, *131*, 5178–5182; e) Y. Heider, P. Willmes, V. Huch, M. Zimmer, D. Scheschkewitz, *J. Am. Chem. Soc.* **2019**, *141*, 19498–19504; f) Y. Heider, N. E. Poitiers, P. Willmes, K. I. Leszczyńska, V. Huch, D. Scheschkewitz, *Chem. Sci.* **2019**, *10*, 4523–4530; g) N. E. Poitiers, L. Giarrana, K. I. Leszczyńska, V. Huch, M. Zimmer, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2020**, *59*, 8532–8536; *Angew. Chem.* **2020**, *132*, 8610–8614.

[14] C. Lorenz, F. Hastreiter, K. Hioe, N. Lokesh, S. Gärtner, N. Korber, R. M. Gschwind, *Angew. Chem. Int. Ed.* **2018**, *57*, 12956–12960; *Angew. Chem.* **2018**, *130*, 13138–13142.

[15] T. Henneberger, W. Klein, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2018**, *644*, 1018–1027.

[16] F. Hastreiter, C. Lorenz, J. Hioe, S. Gärtner, N. Lokesh, N. Korber, R. M. Gschwind, *Angew. Chem. Int. Ed.* **2019**, *58*, 3133–3137; *Angew. Chem.* **2019**, *131*, 3165–3169.

[17] K. Abersfelder, A. Russell, H. S. Rzepa, A. J. P. White, R. Haycock, D. Scheschkewitz, *J. Am. Chem. Soc.* **2012**, *134*, 16008–16016.

[18] a) C. W. Carlson, R. West, *Organometallics* **1983**, *2*, 1798–1801; b) W. Wojnowski, B. Dręczewski, A. Herman, K. Peters, E.-M. Peters, H. G. von Schnering, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 992–993; *Angew. Chem.* **1985**, *97*, 978–979; c) M. Unno, N. Yamashita, H. Matsumoto, *Phosphorus Sulfur Silicon Relat. Elem.* **2011**, *186*, 1259–1262; d) L. C. Siemes, J. Keuter, A. Hepp, F. Lips, *Inorg. Chem.* **2019**, *58*, 13142–13149; e) K. Schwedtmann, A. Hepp, K. Schwedtmann, J. J. Weigand, F. Lips, *Eur. J. Inorg. Chem.* **2019**, 4719–4726.

[19] a) J. E. Carey, C. H. Crouch, M. Shen, E. Mazur, *Opt. Lett.* **2005**, *30*, 1773–1775; b) Z. Huang, J. E. Carey, M. Liu, Y. Guo, E. Mazur, J. C. Campbell, *Appl. Phys. Lett.* **2006**, *89*, 033506; c) A. J. Said, D. Recht, J. T. Sullivan, J. M. Warrender, T. Buonassisi, P. D. Persans, M. J. Aziz, *Appl. Phys. Lett.* **2011**, *99*, 073503; d) K. Eom, J. Lee, M. Oschatz, F. Wu, S. Kaskel, G. Yushin, T. F. Fuller, *Nat. Commun.* **2017**, *8*, 13888.

[20] Y. Wang, M. Chen, Y. Xie, P. Wie, H. F. Schaefer, P. von R. Schleyer, G. H. Robinson, *Nat. Chem.* **2015**, *7*, 509–513.

[21] a) A. C. Filippou, B. Baars, O. Chernov, Y. N. Lebedev, G. Schnakenburg, *Angew. Chem. Int. Ed.* **2014**, *53*, 565–570; *Angew. Chem.* **2014**, *126*, 576–581; b) S. S. Sen, *Angew. Chem. Int. Ed.* **2014**, *53*, 8820–8822; *Angew. Chem.* **2014**, *126*, 8964–8966; c) S. U. Ahmad, T. Szilvàsi, E. Irran, S. Inoue, *J. Am. Chem. Soc.* **2015**, *137*, 5828–5836.

[22] a) A. C. Papageorgopoulos, M. Kamaratos, *Surf. Sci.* **2000**, *466*, 173–182; b) M. Y. Ali, M. Tao, *J. Appl. Phys.* **2007**, *101*, 103708.

[23] a) H. Suzuki, N. Tokitoh, S. Nagase, R. Okazaki, *J. Am. Chem. Soc.* **1994**, *116*, 11578–11579; b) T. Iwamoto, K. Sato, S. Ishida, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **2006**, *128*, 16914–16920; c) S. Yao, Y. Xiong, M. Driess, *Chem. Eur. J.* **2010**, *16*, 1281–1288; d) S.-H. Zhang, H. -Xian, C.-W. So, *Chem. Eur. J.* **2011**, *17*, 3490–3499; e) Y. Xiong, S. Yao, M. Driess, *Angew. Chem. Int. Ed.* **2013**, *52*, 4302–4311; *Angew. Chem.* **2013**, *125*, 4398–4407; f) R. Tacke, C. Kobelt, J. A. Baus, R. Bertemann, C. Burschka, *Dalton Trans.* **2015**, *44*, 14959–14974; g) N. Parvin, S. Pal, S. Khan, S. Das, S. K. Pati, H. W. Roesky, *Inorg. Chem.* **2017**, *56*, 1706–1712; h) M. K. Bisai, V. S. V. S. N. Swamy, T. Das, K. Vanka, R. G. Gonnade, S. S. Sen, *Inorg. Chem.* **2019**, *58*, 10536–10542; i) D. Sarkar, V. Nesterov, T. Szilvàsi, P. J. Altmann, S. Inoue, *Chem. Eur. J.* **2019**, *25*, 1198–1202; j) R. Kobayashi, S. Ishida, T. Iwamoto, *Angew. Chem. Int. Ed.* **2019**, *58*, 9425–9428; *Angew. Chem.* **2019**, *131*, 9525–9528; k) M.-P. Luecke, E. Pens, S. Yao, M. Driess, *Chem. Eur. J.* **2020**, *26*, 4500–4504.

[24] Heavier analogues: a) N. Tokitoh, T. Matsumoto, R. Okazaki, *Tetrahedron Lett.* **1992**, *33*, 2531–2534; b) N. Tokitoh, T. Matsumoto, K. Manmaru, R. Okazaki, *J. Am. Chem. Soc.* **1993**, *115*, 8855–8856; c) T. Matsumoto, N. Tokitoh, R. Okazaki, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2316–2317; *Angew. Chem.* **1994**, *106*, 2418–2420; d) M. Saito, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.* **1997**, *119*, 11124–11125; e) N. Tokitoh, *Phosphorus Sulfur Silicon Relat. Elem.* **1998**, *136*, 123–138; f) R. Okazaki, N. Tokitoh, *Acc. Chem. Res.* **2000**, *33*, 625–630; g) W.-P. Leung, W.-H. Kwok, Z.-Y. Zhou, T. C. Mak, *Organometallics* **2000**, *19*, 296–303.

[25] H. Zhao, L. Klemmer, M. J. Cowley, V. Huch, M. Zimmer, D. Scheschkewitz, *Z. Anorg. Allg. Chem.* **2018**, *644*, 999–1005.

[26] a) C.-W- So, H. W. Roesky, J. Magull, R. B. Oswald, *Angew. Chem. Int. Ed.* **2006**, *45*, 3948–3950; *Angew. Chem.* **2006**, *118*, 4052–4054; b) R. S. Ghadwal, S. S. Sen, H. W. Roesky, M. Granitzka, D. Kratzert, S. Merkel, D. Stalke, *Angew. Chem. Int. Ed.* **2010**, *49*, 3952–3955; *Angew. Chem.* **2010**, *122*, 4044–4047; c) R. S. Ghadwal, K. Pröpper, B. Dittrich, P. G. Hones, H. W. Roesky, *Inorg. Chem.* **2011**, *50*, 358–364; d) K. Junold, M. Nutz, J. A. Baus, C. Burschka, C. Fonseca Guerra, F. M. Bickelhaupt, R. Tacke, *Chem. Eur. J.* **2014**, *20*, 9319–9329; e) F. M. Mück, J. A. Baus, M. Nutz, C. Burschka, J. Poater, F. M. Bickelhaupt, R. Tacke, *Chem. Eur. J.* **2015**, *21*, 16665–16672.

[27] J. Brus, *Solid State Nucl. Magn. Reson.* **2000**, *16*, 151–160.

[28] a) L. Du, Z. Wu, F. Tang, R. Li, Y. Jiang, *Proc. SPIE* **2016**, *9686*, 96860Y; b) S. Hu, P. Han, Y. Mi, Y. Xing, P. Liang, Y. Fan, *Mater. Sci. Semicond. Process.* **2013**, *16*, 987–991.

[29] G. S. Hammond, *J. Am. Chem. Soc.* **1955**, *77*, 334–338.