DOI: 10.1002/anie.201208307

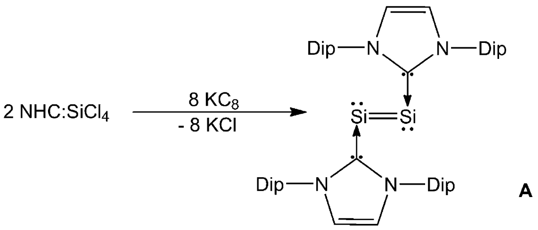
Low-Valent Silicon

A Stable Singlet Biradicaloid Siladicarbene: $(L\mathbf{:})_2Si$**

Kartik Chandra Mondal, Herbert W. Roesky, Martin C. Schwarzer, Gernot Frenking,*
Benedikt Niepötter, Hilke Wolf, Regine Herbst-Irmer, and Dietmar Stalke**

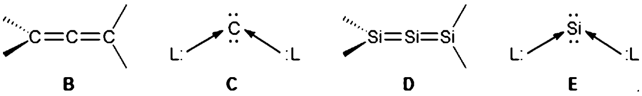
Dedicated to Professor Cameron Jones on the occasion of his 50th birthday

Silicon, the congener of carbon, frequently shows different chemistry than that of its sister element. It has been realized that silicon prefers a positive charge if bonded to a more electronegative atom. Compounds with silicon in lower oxidation states are very important, since they can activate small organic molecules which cannot be activated by transition metals. In 2008 Robinson et al.[1] reported on the adduct of two N-heterocyclic carbene (NHC) molecules with disilicon **A** (Scheme 1). This unusual compound was prepared from the N-heterocyclic carbene and $SiCl_4$ by reduction with KC_8. The silicon atoms of compound **A** exist in the formal oxidation state zero and the structure was determined by single-crystal X-ray analysis. The C→Si=Si←C backbone of **A** has Si=Si←C angles of 93.37(5)° and long Si–C bonds of 1.9271(15) Å (Scheme 1). These bonding characteristics were taken as confirmation of the zero valent state of the silicon atoms in **A**. Kira et al.[2,3] prepared a compound which was introduced as the first trisilaallene with a Si=Si=Si angle between 135.46(5)° and 136.49(6) and mentioned that compounds of this type are highly flexible. The X-ray analysis exhibits dynamic disorder even at low temperatures.[4] These trisilaallenes have a bent structure and distinctly differ from the carbon analogues. The differences were explained by Frenking et al.[5,6]



Scheme 1. Synthesis of NHC:Si=Si:NHC (**A**). NHC = N-heterocyclic carbene. Dip = 2,6-diisopropylphenyl.

However, in recent papers of Bertrand et al.,[7,8] Fürstner et al.,[9] and Frenking et al.[10–12] it was shown experimentally and by DFT calculations that the allene type molecule **B** can also be rationalized along a structure of type **C** in Scheme 2 when the central C atom is bonded to the ligands L, which act as donor ligands, such as phosphoranes or N-heterocyclic carbenes (NHCs). Compounds **C** with the general formula $C(L\mathbf{:})_2$ and two electron lone pairs have been termed carbones[10–12] whereas carbenes CR_2 have only one lone pair. When L is a carbene ligand in $C(L\mathbf{:})_2$, the compound is termed a carbodicarbene.[10,11] A related situation may be envisaged for the silicon homologue of allene **D**. Theoretical studies by Frenking et al.[5,6] suggested that the trisilaallene that was synthesized by Kira et al.[3] should rather be considered as a silylone $Si(L\mathbf{:})_2$ **E** which explains why the compound has a rather acute bonding angle Si-Si-Si and why the substituents at the terminal silicon atoms are not orthogonal to each other, whereas in the typical allene structure they would be.



Scheme 2. Schematic representation of an allene (**B**), a carbone (**C**), a trisilaallene (**D**), and a silylone (**E**).

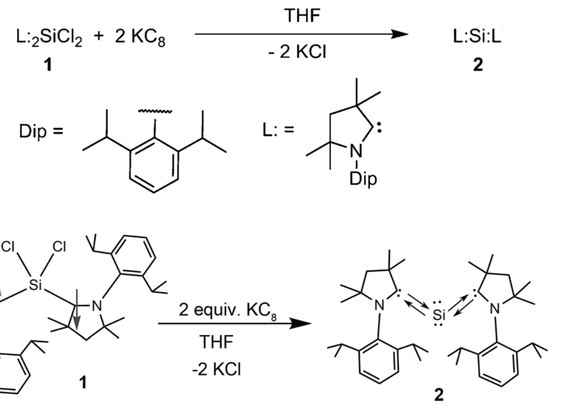
According to these interesting results we wanted to prepare a compound with an alternating C-Si-C backbone, in which the silicon is the central atom of an allene type unit. As a precursor we selected $(L\mathbf{:})_2SiCl_2$ (**1** in Scheme 3).[13] It was characterized by X-ray structure analysis and X-band EPR and found to exist as two polymorphs with paired and two unpaired electrons located at the carbene carbon atoms.[13] L**:** is a cyclic alkyl amino carbene (cAAC).[7,8] The silicon atom in **1** adopts a distorted tetrahedral geometry. In the course of the reaction it was reduced with two equivalents of KC_8 to yield compound **2**, which contains a silicon atom with only two cAAC L**:** carbene ligands coordinated to it. To

---

[*] Dr. K. C. Mondal, Prof. H. W. Roesky, B. Niepötter, H. Wolf, Dr. R. Herbst-Irmer, Prof. D. Stalke
Institut für Anorganische Chemie, Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
E-mail: hroesky@gwdg.de
dstalke@chemie.uni-goettingen
M. C. Schwarzer, Prof. G. Frenking
Fachbereich Chemie, Philipps-Universität Marburg
Hans-Meerweinstrasse, 35032 Marburg (Germany)
E-mail: frenking@chemie.uni-marburg.de

[**] H.W.R. thanks the Deutsche Forschungsgemeinschaft (DFG RO 224/60-I) for support. We are grateful to Prof. Dr. Marina Bennati, Dr. Igor Tkach, Dr. Claudia Stückl for EPR and Felix Klinke for UV/Vis measurements. D.S. is grateful for funding from the DFG Priority Programme 1178, the DNRF-funded Center for Materials Crystallography (CMC) for support, and the Land Niedersachsen for providing a fellowship in the Catalysis for Sustainable Synthesis (CaSuS) Ph.D. program.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201208307.



Scheme 3. Synthetic route for the preparation of **2** from **1** under KC$_8$ reduction.

our knowledge there are no reports on a single silicon atom coordinated by two carbene carbon atoms such as found in **2**.[14] Synthesis of **2** is thus quite interesting (Scheme 3). A related siladicarbene with NHC ligands in Si(L:)$_2$ has been theoretically postulated and calculated by Frenking et al.[5,6]

[(L:)$_2$Si]·0.5(*n*-hexane) (**2**) was prepared from a 1:2 molar ratio of (L:)$_2$SiCl$_2$ (**1**)[13] and KC$_8$ in tetrahydrofuran. This mixture was slowly warmed to room temperature and filtered. The royal-blue filtrate was evaporated to dryness and extracted with *n*-hexane. The concentrated dark blue solution gave blue–black rods of compound **2** in a 95% yield, when it was stored at 0°C in a refrigerator.

The crystals of **2** are stable in air for one day. Compound **2** melts at 194–195°C and decomposes at 202–203°C. It shows UV absorption bands at 270, 327, 392, 570, and 611 nm which are comparable to those found for L:$_2$SiCl$_2$ (**1**; 321, 350, 400, and 570 nm). The trisilaallene (R$_2$Si=Si=SiR$_2$) of Kira et al.[2,3] has similar thermal stability while the UV/Vis spectrum has absorptions at 390 and 584 nm.[2] The ^{29}Si NMR spectrum of **2** has a singlet at $\delta = 66.71$ ppm which is downfield of that of the starting material (L:)$_2$SiCl$_2$ ($\delta = 4.13$ ppm).[13] The chemical shift of the central silicon atom of trisilaallene[2,3] was reported at $\delta = 157$ ppm. This shift indicates that the 3D orientation of the electron density in **2** and in R$_2$Si=Si=SiR$_2$[2] is different. The broadening of three ^{13}C NMR resonances ($\delta = 68.7$, 57.7 and 48.5 ppm) was not observed for **2** unlike **1**.[13] The ^{13}C NMR spectrum of **1** shows broadening of three resonances ($\delta = 73$, 67, and 58 ppm) of the five-membered ring skeleton (the corresponding resonances of L: are $\delta = 82.5$, 57.7, 50.3 ppm).[8]

Compound **2** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains two nearly identical molecules of **2** and one *n*-hexane lattice solvent molecule. The molecular structure of **2** consists of one two-coordinate silicon atom (Figure 1) at the center coordinated to the carbene carbon atoms of the two cAAC ligands (L:).[7,8] This silicon atom adopts a bent geometry. The C-Si-C bond angles of the two symmetry independent molecules are 117.18(8)° (C41-Si2-C61) and 117.70(8)° (C1-Si1-C21), respectively, which are smaller by about 5° than those of the precursor **1** (122.99(7)°). The Si=Si=Si[2,3] and C:→C←:C[11c] bond angles of allene type molecules are larger, close to 135°.

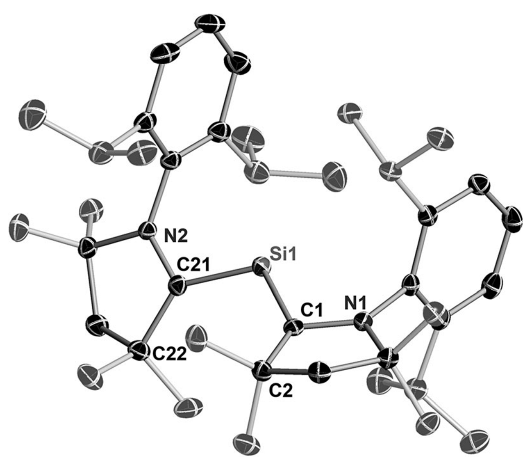


Figure 1. One molecule of the molecular structure of compound **2**. H atoms and solvent molecule are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected experimental [calculated at M05-2X/SVP singlet; triplet] bond lengths [Å] and angles [°]: Si1–C1 1.8411(18) [1.849; 1.886], Si1–C21 1.8417(17) [1.850; 1.877], N1–C1 1.378(2) [1.367; 1.398], N2–C21 1.378(2) [1.368; 1.378]; C1-Si1-C21 117.70(8) [117.9; 115.8].

The sum of angles around the carbene carbon atoms of **2** are on average 357.7° (358.1°, **1**) implying slight deviation from trigonal-planar geometry. The carbene Si–C bonds in **2** (Si1–C1 1.8411(18), Si1–C21 1.8417(17) Å) are very close to those in **1** (1.8455(16) and 1.8482(17) Å)[13] which are distinctly shorter (ca. 0.14 to 0.1 Å) than that in tricoordinate NHC:SiCl$_2$ (Si–C 1.985(4) Å).[15] The Si–C bonds in **2** are shorter than typical Si–C$_{aryl}$ single bonds (1.879 Å)[16a] but slightly longer than those in some recently prepared Si–C$_{sp^3}$ systems (1.8174(14) Å)[16b] and much longer than Si=C double bonds (1.702–1.775 Å).[16c] The Si–C bonds in **2** are slightly shorter than the calculated value for the silylone Si(NHC)$_2$ (1.869 Å).[5,6] The carbene C–N distances in **2** are similar to those found in **1** while the orientation of the carbene ligands in **2** is completely different to that in **1**. The average N-Si-N angle in **2** is about 170° which is considerably wider than in **1** (ca. 132°). Superposition of the two molecules in the asymmetric unit is shown in Figure S3 in the Supporting Information.

The X-band EPR spectrum of **2** showed no EPR resonance. This suggests a singlet ground state of **2**. However, the dark blue color of the compound suggests a rather small HOMO–LUMO gap which could introduce a biradicaloid character.

We optimized the geometry of **2** in the singlet and triplet states at the M05-2X/SVP level of theory.[17–19] The calculated bond lengths and angles, given in Figure 1, show that the values for the singlet state are in very good agreement with the experiment and in better agreement than those of the triplet state. The superposition of the X-ray structure with the calculated singlet and triplet forms shows a nearly perfect alignment between the singlet form and the experimental structure while the calculated triplet exhibits a significantly greater deviation from the experiment (Figure S1, Supporting Information).

Calculations at various levels of theory using the M05-2X/SVP optimized geometries predict that the triplet form is between 17.2 kcal mol^{-1} (M05-2X/TZVPP) and 18.5 kcal mol^{-1} (B3LYP/TZVPP//M05-2X/SVP) higher in energy than the singlet. Thus, the calculations agree with the analysis of the EPR spectrum that **2** is not in a triplet state.

Figure 2 shows the shapes of the HOMO and HOMO−1 of the singlet form of **2** which exhibit the typical features of a silylone SiL_2.[10–12] The HOMO−1 is a σ lone-pair orbital at Si while the HOMO is a π-type orbital which has the largest extension at Si but exhibits significant Si–C π bonding. This situation is in agreement with the calculated Si–C bond lengths for **2** (1.849 Å and 1.850 Å) which are slightly shorter than in $Si(NHC)_2$ (1.869 Å).[10–12] The ligand cAAC in **2** is a better π-acceptor than NHC,[8] because the divalent carbon donor atom in the NHC ligand is attached to two nitrogen atoms whereas there is only one nitrogen atom available for N→C π donation in the cAAC ligand.

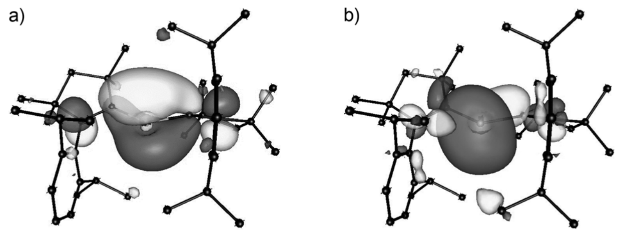
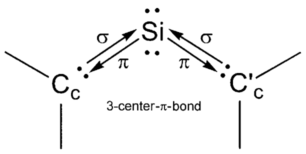


Figure 2. Plots of the HOMO (a) and HOMO−1 (b) of **2**.

The NBO analysis of **2** which was carried out with the option of multicenter bonding gives one σ lone-pair orbital and a three-center C-Si-C π orbital of which 40 % is at Si and 30 % is at each C atom. The best representation of the bonding situation of the siladicarbene **2** is shown in Scheme 4.



Scheme 4. Schematic representation of the bonding situation in **2**.

As a further probe for the classification of **2** as a silylone, we calculated the first and the second proton affinities (PAs) which have been suggested as indicator of the ylidone character of EL_2 compounds.[5] The theoretically predicted values at RI-BP86/SVP are $PA(1) = 272.2$ kcal mol^{-1} and $PA(2) = 186.7$ kcal mol^{-1}. The very large value for the second PA(2) clearly supports the assignment of **2** as a genuine silylone.

We carried out CASSCF(2,2)/SVP calculations using the M05-2X/SVP optimized geometry to see if **2** may have a biradical character. The calculation gave coefficients of 0.96 for the closed-shell 2,0 configuration, −0.28 for the 1,1 configuration, and 0.0 for the 0,2 configuration. Thus, compound **2** is a closed-shell singlet which has a non-negligible contribution from the singly excited state which indicates that the molecule has some biradicaloid character and low electronic excitation energy. Calculations at TDDFT-B3LYP/SVP//M05-2X/SVP level give the lowest excitation at 550 nm with an oscillator strength of 0.157 while the second band is calculated at 543 nm with an oscillator strength of 0.066. This result is in reasonable agreement with the experimentally observed bands at 611 and 570 nm.

In comparison, the theoretical analysis on $R_2Si{=}Si{=}SiR_2$[2,3] suggested a zwitterionic nature of the corresponding energy-minimized conformation. The HOMO of $R_2Si{=}Si{=}SiR_2$ is a π-type orbital and the HOMO−1 is a σ lone pair orbital, these orbitals are very similar to the HOMO and HOMO−1 of **2**.[2] Thus, the bonding situation in **2** and in Kira's compound[2] is very much the same, therefore $R_2Si{=}Si{=}SiR_2$ should be classified as a siladisilylene instead of a trisilaallene.[5b]

Keeping in mind the biradical electronic structure of precursor **1** it is intriguing whether compound **2** can possibly be better described as a silylene (i.e., Si^{II} compound) which carries two radical substituents in which the two unpaired electrons give the π HOMO (Figure 2). Computational evidence supports the assignment of **2** as a Si^0 species, however. We calculated $Si(Me)_2$ as a model silylene and compared it with **2**. The equilibrium bond angle C-Si-C of $Si(Me)_2$ (91.1°) is much more acute than in **2** (117.9°). The most striking difference between the two compounds comes from the proton affinities. Compound **2** strongly binds two protons at Si but $Si(Me)_2$ binds only one proton at Si ($PA(1) = 224.1$ kcal mol^{-1}). A second proton binds to one methyl group ($PA(2) = 151.1$ kcal mol^{-1}). NBO calculations show that the electron density at Si in **2** ($q = 0.55$ e) is larger than in $Si(Me)_2$ ($q = 0.91$). The positive partial charge at Si which agrees with the electronegativities of silicon and carbon indicates that the Si→C π back-donation is larger than the Si←C σ donation.[25] Finally, the largest coefficient of the π HOMO of **2** is at the central Si atom which makes it more reasonable to discuss the π orbital at the central moiety in terms of C←Si→C donation rather than C→Si←C interactions. Therefore, we think that the bonding situation in **2** is better described as silylone rather than silylene.

In conclusion, we have prepared royal-blue, two coordinate, singlet biradicaloid siladicarbene $(L\!:)_2Si$, which is stable under an inert gas atmosphere. This is the first example of a silicon atom in the formal oxidation state of zero, stabilized by two carbene molecules. The amorphous powder of $(L\!:)_2Si$ is stable for an hour while its crystals are stable in air for about a day. The preparation of such unique species provides the roadmap for biradicaloids that show unexpected stability. The calculated bond lengths and angles match fairly well with the singlet state and are also in a good agreement with those of the experimental data, and better than those of the triplet state. Calculations at various levels of theory show that the triplet form is 17.2 to 18.5 kcal mol^{-1} higher in energy than the singlet. This result has also been supported by X-band EPR experiments. The ligand cAAC in **2** is a better π-acceptor than NHC,[8] because the divalent carbon donor atom in the NHC ligand is attached to two nitrogen atoms while there is only one nitrogen atom available for the N→C π donation in the cAAC ligand. This difference explains the slightly shorter Si–C bonds in **2** than in Si(NHC)$_2$. The NBO analysis of **2** gives one σ lone-pair orbital and a three-center C-Si-C π orbital with 40 % at Si and 30 % at each C. The bonding situation in **2** is shown in Scheme 4. Further calculations to see if **2** may have a biradical character showed that compound **2** is a closed-shell singlet which has a non-negligible contribution from the singly excited state which indicates that the molecule has a biradicaloid character and low electronic excitation energy. Calculations at TDDFT-B3LYP/SVP//M05-2X/SVP level produce the lowest excitation at 550 nm with an oscillator strength of 0.157, while the second band is calculated at 543 nm with an oscillator strength of 0.066.

Experimental Section

2: THF (85 mL) was cooled to $-78\,^{\circ}\mathrm{C}$ and added to an 1:2 mixture of (L**:**)$_2$SiCl$_2$ (**1**; 3 mmol, 2007 mg) and KC$_8$ (6 mmol, 810 mg). Then the mixture was warmed to room temperature in 15–20 min and stirred for 14 h and filtered. The royal-blue filtrate was evacuated to dryness and extracted with *n*-hexane (90 mL) and the resulting volume was reduced to 20–30 mL under vacuum. The concentrated dark blue solution produced blue–black rods of compound **2** in 95 % yield when it was stored at 0 °C in a refrigerator. The crystals of **2** are stable in air for one day. M.p. 194–195 °C, decomp.202–203 °C; UV/Vis bands at 570 and 611 nm. ^{1}H NMR (C$_6$D$_6$, 298 °C, 500.133 MHz): $\delta = 7.31$–7.19 (d, 2H$_{ar}$, *m*-H), 7.14–7.06 (d, 2H$_{ar}$, *m*-H), 7.07–7.04 (m, 2H$_{ar}$, *p*-H), 3.17 (m, 2H, CHMe$_2$), 2.68 (m, 2H, CHMe$_2$), 1.91 (s, 2H, CH$_2$), 1.86 (s, 2H, CH$_2$), 1.75 (s, 6H, NCMe$_2$), 1.74 (s, 6H, NCMe$_2$), 1.50 (d, 6H, CHMe$_2$), 1.31 (d, 6H, CHMe$_2$), 1.25 (d, 6H, CHMe$_2$), 1.07 (d, 6H, CHMe$_2$), 1.0 (s, 6H, CMe$_2$), 0.90 ppm (s, 6H, CMe$_2$); ^{13}C NMR: $\delta =$ 210.9 (carbene), 136.2, 128.9, 125.4, 124.8, 68.7, 57.7, 48.5, 36.0, 31.9, 31.3, 30.1, 29.8, 29.4, 28.3, 27.9, 25.1 ppm; ^{29}Si NMR: $\delta = 66.71$ ppm.

Crystal data for **2**: L**:**$_2$Si (L**:** = **:**C(CH$_2$)(CMe$_2$)$_2$N-2,6-*i*Pr$_2$C$_6$H$_3$) $M_r = 642.09\ \mathrm{g\,mol^{-1}}$, triclinic, space group $P\bar{1}$, $a = 9.145(2)$, $b = 19.347(3)$, $c = 24.566(3)$ Å, $\alpha = 112.00(3)$, $\beta = 98.33(2)$, $\gamma = 91.71(2)^{\circ}$, $V = 3970.6(12)$ Å^3, $Z = 4$, $\mu(\mathrm{Mo\text{-}K_{\alpha}}) = 0.089\ \mathrm{mm^{-1}}$, $T = 101(2)$ K, 87462 reflections measured, 16274 unique reflections, $R_{\mathrm{int}} = 0.0629$, 916 parameters refined, $R1$ (all data) $= 0.0728$, $R1\ [I > 2\sigma(I)] = 0.0457$, $wR2$ (all data) $= 0.1108$, $wR2[I>2\sigma(I)] = 0.0980$, GOF $= 1.020$, largest diff. peak and hole 0.379 and $-0.304\ \mathrm{e\,Å^{-3}}$. CCDC 896896 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: Geometry optimizations of **2** were carried out using the DFT functional BP86[17] and M05-2X[18] with def2-SVP basis sets.[19] The RI-Approximation was applied whenever possible.[20] The optimized geometry was verified as a minimum on the potential-energy surface by calculation of the vibrational frequencies analytically at the RI-BP86/SVP level of theory (AOFORCE).[21] Improved energies were calculated at M05-2X and RI-B3LYP with the larger basis sets def2-TZVPP[22] using M05-2X/SVP optimized geometries. Calculations were carried out with the program package Gaussian 09[23] for M05-2X and TurboMole 6.3[24] for other functionals.

Received: October 16, 2012
Published online: January 10, 2013

Keywords: biradicals · DFT calculation · low oxidation state · silicon · X-ray structure

---

[1] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069–1071.

[2] S. Ishida, T. Iwamoto, C. Kabuto, M. A. Kira, *Nature* **2003**, *421*, 725–727.

[3] M. Kira, *Chem. Comunm.* **2010**, *46*, 2893–2903.

[4] M. Kira, T. Iwamoto, S. Ishida, T. Abe, C. Kabuto, *J. Am. Chem. Soc.* **2009**, *131*, 17135–17144.

[5] a) N. Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.* **2009**, *15*, 8593–8604; b) N. Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.* **2009**, *15*, 3448–3456.

[6] N. Takagi, R. Tonner, G. Frenking, *Chem. Eur. J.* **2012**, *18*, 1772–1780.

[7] D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389–399.

[8] V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5851–5855; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709.

[9] M. Alcarazo, C. W. Lehmann, A. Anoop, W. Thiel, A. Fürstner, *Nat. Chem.* **2009**, *1*, 295–301.

[10] R. Tonner, G. Frenking, *Angew. Chem.* **2007**, *119*, 8850–8853; *Angew. Chem. Int. Ed.* **2007**, *46*, 8695–8698.

[11] a) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260–3272; b) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3273–3289; c) C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2008**, *120*, 3250–3253; *Angew. Chem. Int. Ed.* **2008**, *47*, 3206–3209.

[12] R. Tonner, G. Frenking, *Pure Appl. Chem.* **2009**, *81*, 597–614.

[13] K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, I. Tkach, H. Wolf, D. Kratzert, R. Herbst-Irmer, B. Niepötter, D. Stalke, *Angew. Chem.* **2013**, DOI: 10.1002/ange.201204487; *Angew. Chem. Int. Ed.* **2013**, DOI: 10.1002/anie.201204487.

[14] a) G. Fritz, E. Matern, H. Bock, G. Brähler, *Z. Anorg. Allg. Chem.* **1978**, *439*, 173–182; b) H. Grützmacher, F. Breher, *Angew. Chem.* **2002**, *114*, 4178–4184; *Angew. Chem. Int. Ed.* **2002**, *41*, 4006–4011; c) C. Riplinger, J. P. Y. Kao, G. M. Rosen, V. Kathirvelu, G. R. Eaton, S. S. Eaton, A. Kutateladze, F. Neese, *J. Am. Chem. Soc.* **2009**, *131*, 10092–10106.

[15] a) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem.* **2009**, *121*, 5793–5796; *Angew. Chem. Int. Ed.* **2009**, *48*, 5683–5686; b) S. S. Sen, S. Khan, P. P. Samuel, H. W. Roesky, *Chem. Sci.* **2012**, *3*, 659–682; c) S. K. Mandal, H. W. Roesky, *Chem. Commun.* **2010**, *46*, 6016–6041; d) R. S. Ghadwal, H. W. Roesky, K. Pröpper, B. Dittrich, S. Klein, G. A. Frenking, *Angew. Chem.* **2011**, *123*, 5486–5490; *Angew. Chem. Int. Ed.* **2011**, *50*, 5374–5378.

[16] a) M. Kaftory, M. Kapon, M. Botoshansky in *The Chemistry of Organic Silicon Compounds*, *Vol. 2*, *Part 1* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1989**, chap. 5; b) T. Nozawa, M. Nagata, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2011**, *133*, 5773–5775; c) Ya. V. Lee, A. Sekiguchi, *Organometallic Compounds of Low-coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*, Wiley, Chichester, **2010**, chap. 5.

[17] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.

[18] Y. Zhao, N. E. Schultz, D. G. Truhlar, *J. Chem. Phys.* **2005**, *123*, 161103–161107.

[19] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577.

[20] R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2004**, *6*, 5119–5121.

[21] a) P. Deglmann, F. Furche, *J. Chem. Phys.* **2002**, *117*, 9535–9538; b) P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2002**, *362*, 511–518; c) P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2004**, *384*, 103–107.

[22] F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143–152.

[23] Gaussian 09, Revision C.1, M. J. Frisch et al. Gaussian, Inc., Wallingford CT, **2010**. For full reference see Supporting Information.

[24] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165 – 169.

[25] A similar situation has been reported for the related complex(BH)(cAAC)$_2$ where the partial charge q(BH) = 0.05 e suggests that the (BH)→C π back-donation is slightly larger than the (BH)←C σ donation and where the borane (BH)(Me)$_2$ carries a larger partial charge of q(BH) = 0.61 e: R. Kinjo, B. Donnadieu, M. A. Celik, G. Frenking, G. Bertrand, *Science* **2011**, *333*, 610 – 613.