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Very strong anionic homoaromaticity in (*deloc*-1,3,4)-1-sila-3,4-diboracyclopentane-1-ides, the importance of the energy of the reference system for homoaromatic stabilization energies

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Abstract

(*deloc*-1,3,4)-1-Sila-3,4-diboracyclopentane-1-ide (**3a**) was prepared as solvent separated ion pair $[Li(Et_2O)(thf)_3]$[**3a**] and as contact ion pair $[Li(Et_2O)]$[**3a**]. Both were fully characterized by NMR spectroscopy as well as by X-ray structure analyses. Their five-membered rings are strongly distorted as seen from short transannular Si···B distances of 206 and 208 pm as compared with 276 pm in the undistorted 1-sila-3,4-diboracyclopentane (**4c**). This distortion is also found in the unsubstituted prototype **3u** by geometry optimizations at the MP2/6-311 + G** level of theory. In addition, computations show that a three-center-two-electron (3c2e) bond between the silicon and the two boron atoms is present in the distorted **3u**. The planar classical reference molecule **3u*** with a 2c2e π bond between the boron atoms is not accessible by computations. Therefore, the energy difference between **3u** and **3u*** was estimated by isodesmic equations to be about 80 kcal mol^{-1} (at MP4/6-311 + G**), considerably larger than any homoaromatic stabilization energy (HSE) ever discussed. The origin of this huge HSE of **3u** is strong electrostatic destabilization of the reference system **3u*** due to intramolecular charge separation. The series of bishomoaromatic systems is thus extended by a borderline case of very large HSE. The very small HSE of **1u** at the other end of the series is also due to the energy of the reference: **1u*** is strongly stabilized by hyperconjugation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ab initio calculations; Anions; Boron; Homoaromaticity; Silicon

1. Introduction

Homoaromaticity [1] has long been regarded as a weak effect [2]. This conclusion is based on the small energy difference of only 5.1 kcal mol^{-1} between bishomoaromatic **1u** (Scheme 1), with a cyclic three-center-two-electron (3c2e) bond, and reference **1u*** having these two electrons in a 2c2e π bond. The energy difference between homoaromatic species and classical isomers (like **1u** and **1u***) is called homoaromatic stabilization energy, HSE. Experimentally known bishomoaromatic cations of type **1** all have bicyclic structures [3].

'Homoaromatic stabilization of anions' has been reported to be 'either quite insignificant or non-existent altogether' [4]. Recently, we have presented bishomoaromatic dianions **2** [5] and the HSE of **2u** was shown to be considerably larger than that of the isoelectronic cation **1u**. Here we extend this series by (*deloc*-1,3,4)-1-sila-3,4-diboracyclopentane-1-ides (**3**) and show the HSE of **3u** to be larger than any other ever discussed for homoaromatic species.

The origin of the extraordinarily strong homoaromaticity of **3u** is revealed to be due to the unfavorable

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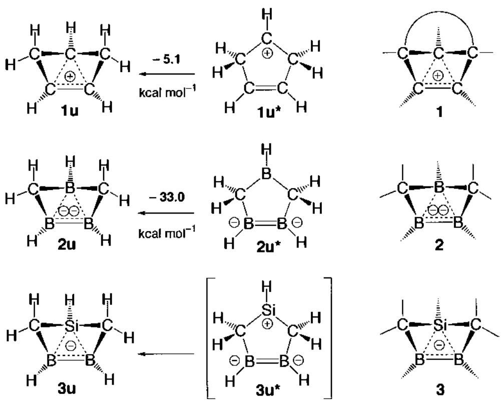
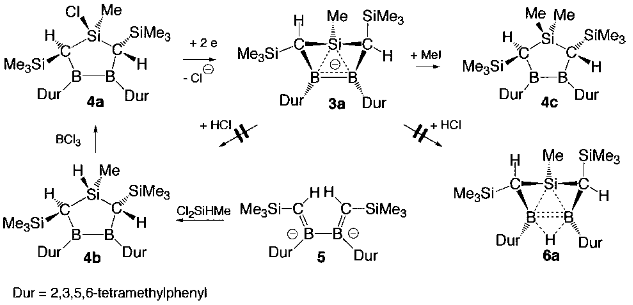
energy of its reference system **3u*** which is strongly *destabilized* by charge separation. The small homoaromaticity of the archaic **1u** is also due to the energy of its reference, **1u***, which is strongly *stabilized* by hyperconjugation.



Scheme 1. Homoaromatic stabilization energies as calculated for the prototype bishomoaromatic cation **1u** and the isoelectronic dianion **2u** at the MP4/6-311 + G** level. Representations **1** and **2** show the skeletons of experimentally known bicyclic and monocyclic derivatives, a derivative of **3** is described in this paper.



Scheme 2. Synthesis of the dianion **3a** from **5** and transformation of **3a**–**4c**.

2. Results and discussion

2.1. Synthesis and reactivity

The solvent separated ion pair [Li(Et_2O)(thf)$_3$][**3a**] is obtained by reaction of **4a** with two equivalents of lithium naphthalenide in thf at – 78 °C and by subsequent crystallization from diethyl ether (Scheme 2). Compound **4a** is accessible from BCl_3 and **4b**, which was synthesized from 2,3-diborata-1,3-butadiene (**5**) [5] and dichloromethylsilane. The contact ion pair [Li(Et_2O)][**3a**] was prepared by reaction of **4a** with lithium powder in Et_2O. Both ion pairs of **3a** react with methyl iodide at – 100 °C to yield **4c**. Reaction of **3a** with HCl, however, does not lead back to **4b** nor to the nonclassical **6a** with a B–H–B bridge, which could be expected considering the products [6] obtained by protonation of dianions of type **2**.

The proposed structures of the new compounds are based on their ^{1}H-, ^{13}C-, ^{11}B- and ^{29}Si-NMR spectra (Table 1). The ^{11}B-NMR chemical shifts of **4a**–**c** near 97 ppm are characteristic for tetraorganyl-diboranes(4). The boron centers of **3a**, however, are considerably shielded ($\delta^{11}B = 20–23$) resembling those of dianions of type **2** ($\delta^{11}B = 7–21$). The ring silicon of **3a** is similarly shielded ($\delta^{29}Si = -68$) as compared with that of **4b** ($\delta^{29}Si = 5$ ppm). The signals for the carbon atoms of the five-membered rings of **3a** appear at 9.1 and 5.0 ppm in contrast to those of **4a**–**c** at 41.9–47.5 ppm. These high field shifts indicate increased coordination numbers at boron and silicon of the ring of **3a** and a distortion similar to that in dianions of type **2**. The ring carbon atoms of the latter are shielded by about 40 ppm relative to those of their uncharged and undistorted precursors. Final support for the distorted structure of **3a** was obtained by X-ray crystal structure analyses of both ion pairs.

2.2. Crystal structures

Single crystals of [Li(Et_2O)(thf)$_3$][**3a**] and [Li(Et_2O)]-

Table 1
Comparison of characteristic distances and angles of [Li(Et_2O)(thf)$_3$][**3a**]·1/2Et_2O, [Li(Et_2O)][**3a**], and **4c** as well as of **3u** and **4u**

	[Li(Et_2O)(thf)$_3$][**3a**]]·1/2Et_2O	[Li(Et_2O)][**3a**]	**3u** [a]	**4c**	**4u** [a]
Bond lengths					
Si1···B1	207.3(5)	208.3(3)	206.3	275.2(2)	268.5
Si1···B2	204.9(5)	207.9(3)	206.3	276.2(2)	268.5
Bond angles					
C1–B1–B2–C2/C1–Si1–C2 [b]	90.8(2)	92.8(2)	90.7	175.6(2)	[c]
Si1–C–B1	72.3(3)	72.7(1)	71.5	105.0(1)	100.1
Si1–C–B2	71.0(3)	72.5(1)	71.5	105.8(1)	100.1

[a] Computed at the MP2(fc)/6-311 + G** level.

[b] Interplanar angle.

[c] Angle not defined since C–B–B–C are not in the same plane in the C_2 conformation of **4u**. The torsional angle Si–C–C–B amounts to 162.1°.

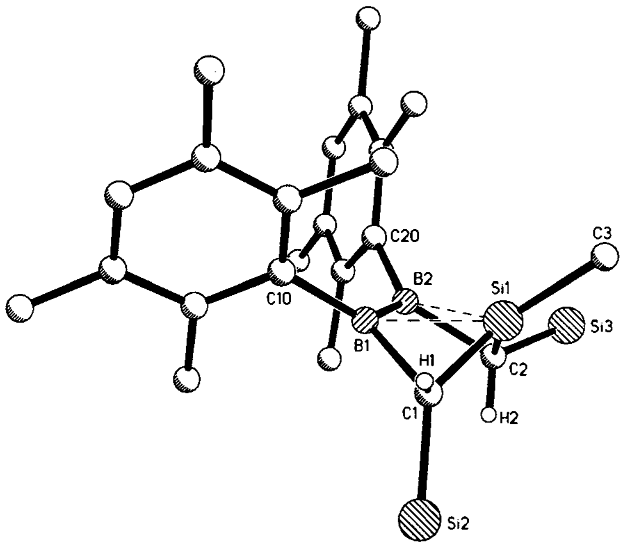


Fig. 1. Structure of $[Li(Et_2O)(thf)_3][\mathbf{3a}]\cdot 1/2Et_2O$ in the crystal; selected bond lengths (pm) and angles (°) (completing Table 1). The gegenion of **3a** as well as the non-coordinated ether molecule of this salt, the methyl substituents at Si2 and Si3 and most of the hydrogen atoms have been omitted for clarity. C1–B1 166.9(6), B1–B2 165.3(7), B2–C2 168.1(6), C2–Si1 184.0(5), Si1–C1 183.8(5); C1,Si1,C2 108.4(2), C1,B1,B2 113.1(4), B1,B2,C2 113.7(4).

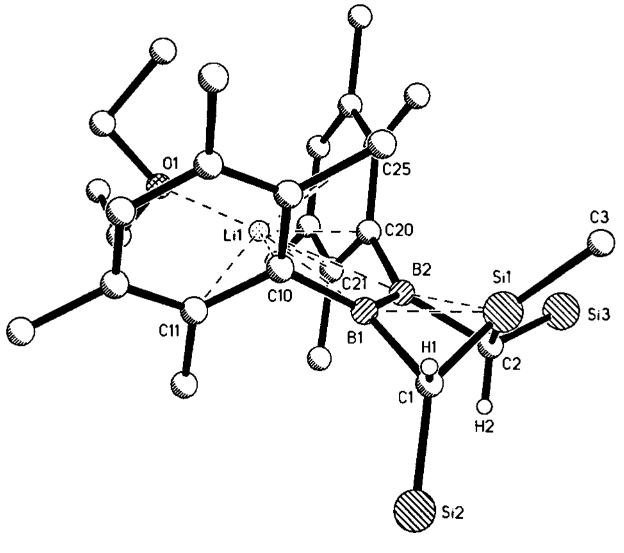


Fig. 2. Structure of $[Li(Et_2O)][\mathbf{3a}]$ in the crystal; selected bond lengths (pm) and angles (°) (average values, labels from first molecule, completing Table 1). The methyl substituents at Si2 and Si3 and most of the hydrogen atoms have been omitted for clarity: C1–B1 166.7(4), B1–B2 166.6(4), B2–C2 167.4(4), C2–Si1 183.4(3), Si1–C1 183.9(3), B1–Li 246.8(5), B2–Li 243.8(6), Li–O 192.7(12), Li–C10 233.3(5), Li–C11 247.7(6), Li–C20 219.9(6), Li–C21 274.2(6), Li–C25 276.5(6); C1,Si1,C2 109.3(1), C1,B1,B2 113.2(2), B1,B2,C2 113.7(2).

3a] were grown from diethyl ether solutions at −30 °C, those of **4c** from pentane at −30 °C. Figs. 1–3 show the corresponding structures in the crystal. Characteristic distances and angles are compared in Table 1 with corresponding data obtained for model compounds **3u** and **4u** by ab initio calculations (see below).

In the *contact ion pair* (c.i.p.) $[Li(Et_2O)][\mathbf{3a}]$, the Li ion shows approximately planar pentacoordination to both boron atoms, both *ipso*-C atoms of the duryl moieties, and an ether–O-atom (Fig. 2). The duryl rings are rotated around the B–C axes so that one of their *ortho*-C atoms gets an additional close contact to Li. In contrast, the structure of the *solvent separated ion pair* (s.s.i.p.) $[Li(Et_2O)(thf)_3][\mathbf{3a}]$ shows no contacts of Li to the anion **3a** shorter than 411 pm. Nevertheless, the differences in geometry of anion **3a** in both structures are surprisingly small: in the central unit B1,B2,C2,Si1,C1 there is no significant difference ($< 3\sigma$) in bond lengths and angles. Only the folding angle at the C1···C2 axis is somewhat more narrow (90.8(2)°) in the s.s.i.p. than in the c.i.p. (92.8(2)°). In addition, the angles at the B–B bond towards the *ipso*-C-atoms of the duryl rings are a little widened in the c.i.p. (131.2(2)° in average, as compared with 129.1(4)°). The differences in the torsional angles at the B–*ipso*-C axes characterizing the rotational position of the duryl rings are even larger within the two independent molecules of $[Li(Et_2O)][\mathbf{3a}]$ (range of 98.0(3)–112.7(3)°) than between c.i.p. and s.s.i.p. ($[Li(Et_2O)(thf)_3][\mathbf{3a}]$: 100.4(6) and 113.3(5)°). The coordination of Li to the anion **3a** apparently has only little influence on its structure in the crystal.

The five-membered ring of **4c** is nearly planar, the transannular distances Si···B are long (276 pm) and the B–C–Si angles (105 and 106°) in the order to be expected for a normal five membered ring [7]. The central rings of $[Li(Et_2O)(thf)_3][\mathbf{3a}]$ and $[Li(Et_2O)][\mathbf{3a}]$, however,

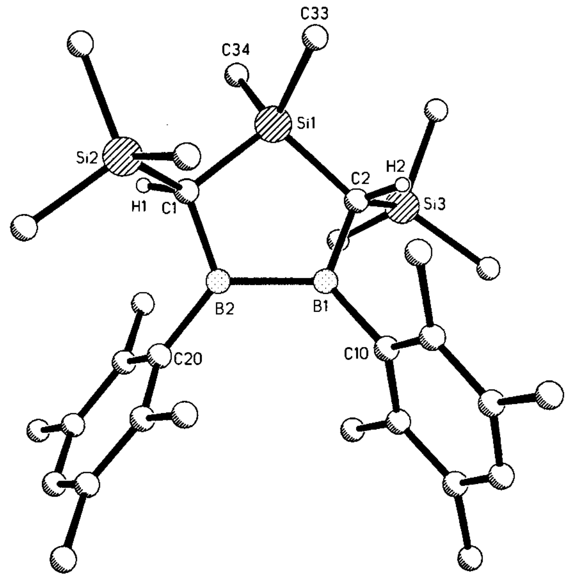
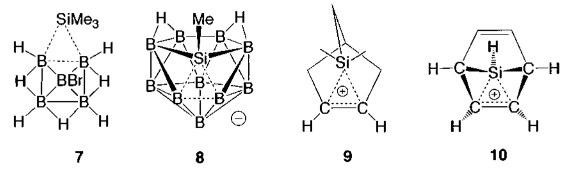
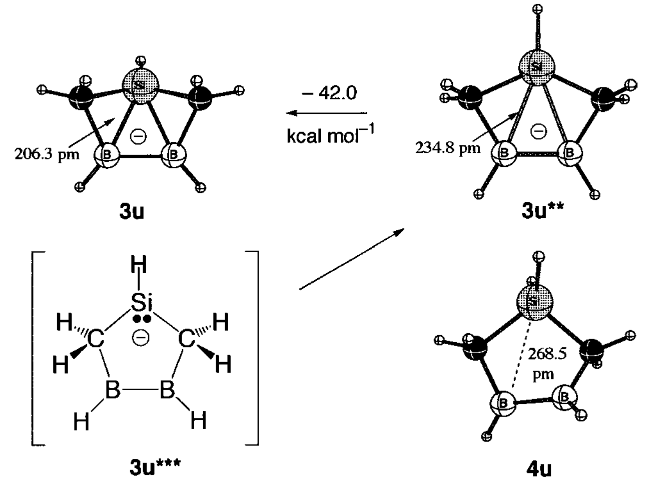


Fig. 3. Structure of **4c** in the crystal; selected bond lengths (pm) and angles (°) (completing Table 1): C1–B2 156.7(3), B2–B1 173.6(3), B1–C2 157.4(3), C2–Si1 188.7(2), Si1–C1 188.6(2), C1,Si1,C2 101.2(1), C2,B1,B2 110.0(2), B1,B2,C1 109.4(2).



Scheme 3. Reference molecules with 3c2e bonds containing a silicon center.



Scheme 4. Computed structures of prototypes **3u** and **4u**. Structure **3u****, a planar conformer of **3u**, still has a 3c2e bond instead of the 2c2e bond of **3u*** required as the reference for determination of the HSE of **3u**.

are strongly distorted: the interplanar angles between planes C1–B1–B2–C2 and C1–Si–C2 are 91 and 93°, respectively, the transannular distances Si···B (206 and 208 pm) considerably shorter and the B–C–Si angles distinctly smaller (71.0–73.0°) than in **4c**. All these distortions are characteristic for bishomoaromatic species [3,5,6].

The separations of Si and B involved in a 3c2e B–Si–B bond of the anion **3a** are considerably shorter compared with those of the uncharged **7** (232(2) pm) [8] and resemble those of anion **8** (205 and 207 pm) [9] (Scheme 3). The computed Si···C distances connected with the 3c2e C–Si–C bond in cations **9** (241 pm, B3LYP/6-31G*) [10] and **10** (212.6 pm, MP2/6-31G*) [11] are longer than the Si···B distances discussed above, despite of the fact that the covalent radius of carbon is somewhat smaller than that of boron (77 vs. 80 pm).

2.3. Ab initio calculations

The geometry of model compounds **3u** and **4u** have been computed at the MP2/6-311 + G** level [12]. Bond lengths and angles obtained are in nice agreement (Table 1) with corresponding data from the X-ray structure determinations for derivatives.

The computed energies of **3u** and reference molecules expected to have *no* 3c2e bonds were compared to gain insight into the strength of homoaromaticity of **3u**. In analogy to planar **1u*** and **2u***, we first considered the C_{2v} symmetric form of **3u**, i.e. **3u** forced to planarity. The geometry optimization converged to **3u****, which was characterized as a third order stationary point 42.0 kcal mol^{-1} higher in energy than **3u** (Scheme 4). However, the transannular Si···B distance in **3u**** of 234.8 pm is remarkably short compared to that of a five-membered ring *without* cyclic delocalization (**4u**: 268.5 pm). An NBO analysis performed on **3u**** localized a 3c2e bond occupied by 1.86 electrons, to which the Si atom contributes 45% and the two boron atoms contribute 28% each [13]. In contrast, for **2u*** the NBO analysis localizes 1.87 electrons in a B–B π bond and 0.10 electrons in a formally empty p-orbital at the boron between two carbon atoms. Hence, a Lewis structure as drawn for **3u*** in Scheme 1 is not an appropriate representation of the electronic structure of **3u**** (Scheme 4).

Even if the transannular Si···B distance is arbitrarily elongated to 268.5 pm (the value computed for **4u**), cyclic delocalization does not vanish [14]. Structure **3u**** is also obtained when a hypothetical species **3u***** with an uncharged B–B moiety and the two additional electrons located at the silicon center is used as starting point for a geometry optimization. Since **3u**** still has a 3c2e bond, its energy difference of 42.0 kcal mol^{-1} relative to **3u** cannot be taken as a measure, but only as a lower limit for the HSE of **3u**.

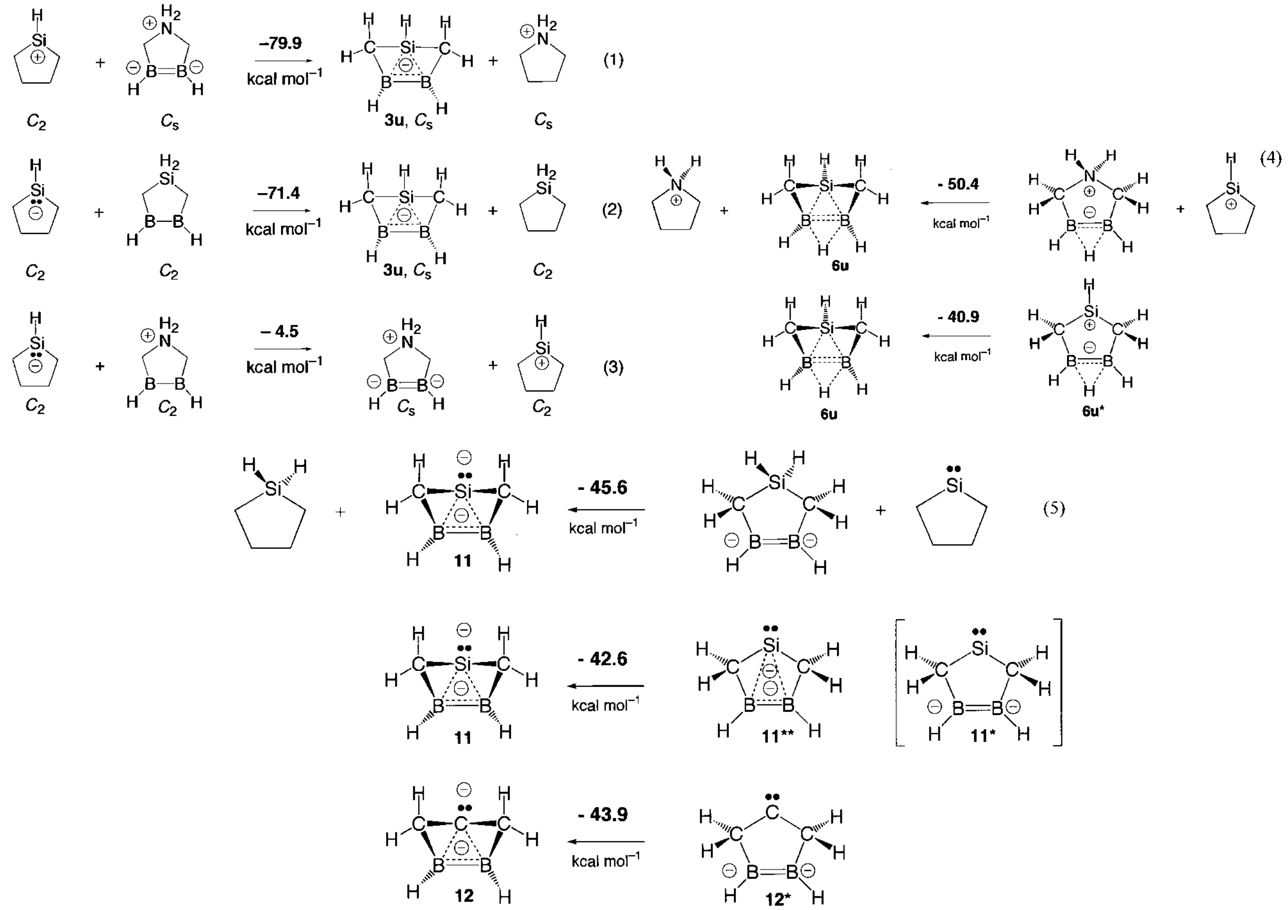
The stabilization in reference system **3u**** may be ‘switched of by separating the Si–H and HB–BH moieties in an isodesmic equation. Splitting the 3c2e bond of **3u** into a silyl cation and a diborane(4) dianion (left hand side of Eq. (1), Scheme 5), i.e. modeling species **3u***, [15] gives a HSE of 79.9 kcal mol^{-1}.

A similarly strong stabilization is computed when the 3c2e bond of **3u** is split into a silyl anion and a neutral diborane(4) moiety (left hand side of Eq. (2)), i. e. modeling species **3u***** of Scheme 4. Conserving the trigonal planar Si atom coordination geometry, which is present in **3u** [16] and **3u****, leads to an energy value of 71.4 kcal mol^{-1} [17]. However, now the 3c2e bond is *not* compared with a 2c2e bond, as is generally done to estimate HSE's (e.g. in the case of **1u** and **2u**), but with an electron pair localized at *one* center (*1*c2e). Hence, the localization of the electrons of the 3c2e bond in **3u** at *one* Si center requires about as much energy as localization to a B=B π bond [18]. This surprising fact can be rationalized by the considerable amount of energy needed for the intramolecular *separation of one positive charge from two negative charges*, which inevitably accompanies the formation of a B=B π bond. Eq. (3) is nearly thermoneutral, which confirms the energetic compensation of a B=B π bond formation from an electron pair localized at Si by a corresponding charge separation.

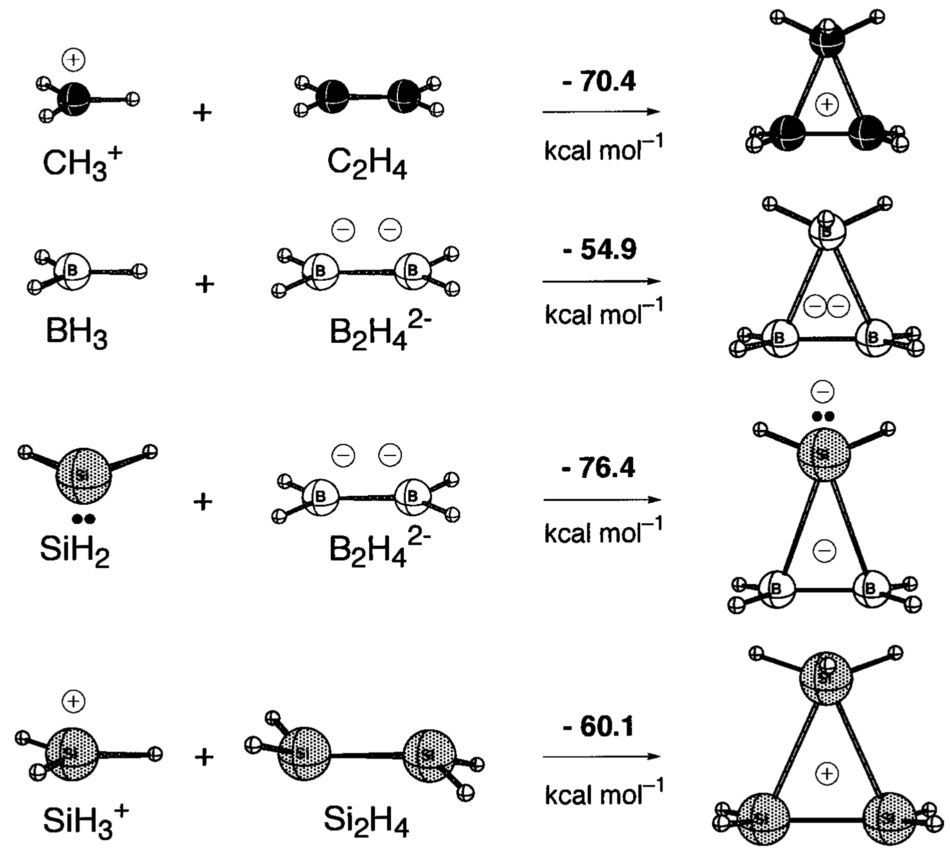
Charge separation, which did not occur in any of the reference molecules for homoaromatic species known so far, is the major factor for the huge HSE of **3u**. This is demonstrated by the isodesmic Eq. (4), modeling reference system **6u***, where a positive charge at a silicon center is separated from *only one* negative charge on two boron atoms. The HSE is reduced by nearly 30–50.4 kcal mol^{-1}. Structure **6u*** can be computed without problems and it is well described by a 2c2e bond between the two boron atoms and an essentially empty p-orbital at the silicon atom. The energy of **6u*** is 40.9 kcal mol^{-1} higher than that of **6u**, i.e. the HSE obtained by this direct comparison is of the same order of magnitude as that obtained by the isodesmic Eq. (4).

In order to eliminate any charge separation effects, we modeled silylene **11*** with an empty orbital at silicon without positive charge and a B=B double bond by the isodesmic Eq. (5). Again the HSE obtained, 45.6 kcal mol^{-1}, is considerably smaller than that from isodesmic Eq. (1). However, attempts to compute **11*** with a 2c2e bond resulted in **11**** showing a 3c2e bond: cyclic delocalization is maintained in **11**** regardless of a long transannular B···Si distance of 276.5 pm. This is reminiscent to the finding for **3u**** discussed above. Interestingly, the strong tendency to form 3c2e bonds despite of the long distances is not observed for carbene **12*** which is iso-electronic and isolobal to **11***. An NBO analysis of **12*** localizes 1.92 electrons in a 2c2e B–B π bond and only 0.15 electrons in the formally empty p-orbital at the dicoordinate carbon (in addition to 1.94 electrons for an inplane lone pair at that carbon). Since cyclic delocalization of two electrons over three centers despite of two long distances between these centers is present with silicon but *not* for its first row homologous carbon, we computed the tin analogue of **3u** forced to planarity. Its NBO analysis reveals a 3c2e B_2Sn bond despite of a Sn···B distance of 274.5 pm (compare 287.2 pm in the tin analogue of **4u**). Thus, it turns out that cyclic delocalization despite of long distances between the centers is a characteristic property of the heavier main group elements [19].

In conclusion, according to common energetic criteria, anions of type **3** show by far the biggest homoaromatic stabilization energies among all known



Scheme 5. Homoaromatic stabilization energies (HSE's) computed at the MP4/6-311 + G** level using isodesmic equations [12]. Eqs. (1), (4) and (5) model **3u***, **6u***, and **11***, respectively. Only for **6u** and **12** HSE's can be determined by direct comparison with classical isomers (**6u*** and **12***), i.e. the same way as for the HSE's of **1u** and **2u**.

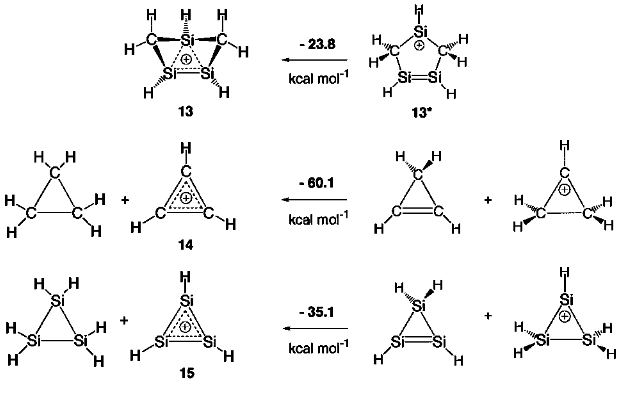


Scheme 6. Energy gain from the formation of prototypical 3c2e bonds from 2c2e-bonds and electron deficient centers as computed at the MP4/6-311 + G** level [12].

homoaromatics. To a considerable part this is due to electrostatic *destabilization of the reference molecules*. A similar answer can be given to the obvious question: why is the HSE of the archaic homoaromatic **1u** (5.1 kcal mol^{-1}, Scheme 1) so small? Does formation of a 3c2e bond between three carbon centers lead to less energy gain than between boron and silicon centers? Not at all, as seen from the energy gain upon formation of prototypes containing 3c2e bonds in Scheme 6. Formation of 3c2e bonds from 2c2e bonds yields comparable amounts of energy regardless of which kind of centers are involved.

The very small HSE of cation **1** is due to strong stabilization of the reference cation **1u*** by hyperconjugation. This is impressively shown by comparing the homoaromatic stabilization energies (HSE) of **1u** and **13** (5.1 vs. 23.8 kcal mol^{-1}) to the aromatic stabilization energies (ASE) of **14** and **15** [20] (60.1 vs. 35.1 kcal mol^{-1}) (Scheme 7).

As can be expected on grounds of weaker π bonds of heavy-atom compounds [20], the ASE of **15** is only half as big as that of **14**. The HSE of **13**, however, is almost five times larger than that of **1u**. Since formation of the 3c2e bonds between carbon and silicon centers leads to comparable stabilization (see Scheme 6), the considerably smaller HSE of **1u** as compared with **13** must be due to the energies of the reference molecules **1u*** and **13***. Carbocations (like **1u***) are considerably better stabilized by hyperconjugation than sila-cations (like **13***) as recently shown by Cremer et al. [21]. Both, the extreme big as well as the very small homoaromatic stabilization energies discussed here, thus, are consequences of destabilization and stabilization, respec-



Scheme 7. Homoaromatic and aromatic stabilization energies (HSE and ASE) of **13**, **14** and **15**, respectively, as computed at the MP4/6-311 + G** level [12]. Note that the ASE of the silicon cation **15** is about half that of the carbocation **14**, the HSE of the silicon cation **13**, however, is about five times bigger than that of the carbocation **1u**.

tively, of the reference molecules. In retrospective, the first representatives of homoaromatic species, **1**, were rather unsuited to demonstrate the full power of homoaromaticity.

3. Experimental

3.1. General

Reactions were carried out under dry argon, using standard Schlenk techniques. Solvents were dried, distilled, and saturated with argon. Glassware was dried with a heatgun in high vacuum—^{1}H-, ^{13}C-NMR: Bruker DRX 200 and AC 300 spectrometer; ^{11}B-NMR: Bruker AC 300 and AMX 500 spectrometer; ^{29}Si-NMR: Bruker AM 400, NMR references are $(CH_3)_4Si$ and $BF_3 \cdot Et_2O$. Melting points (m.p.) (uncorrected) were measured under argon.

3.1.1. [(Diethylether)tris(tetrahydrofurane)lithium]-[(deloc-1,3,4)-1-methyl-3,4-bis(2,3,5,6-tetramethylphenyl)-trans-2,5-bis(trimethylsilyl)-1-sila-3,4-diboracyclopentane-1-ide ([Li(Et$_2$O)(thf)$_3$][3a])

Twenty milliliters (20 mmol) of a 1 M solution of lithium naphthalenide in thf were added to a solution of 5.39 g (10.0 mmol) of **4a** in 100 ml of Et$_2$O at −78 °C. The solution was allowed to warm to ambient temperature during 1 h and stirred for an additional hour. All volatiles were removed in vacuo and the red viscous residue dissolved in 100 ml Et$_2$O. The insoluble salts were removed by filtration. Cooling to −30 °C for ca. 24 h led to the deposition of light-yellow crystals. Yield: 3.60 g of [Li(Et$_2$O)(thf)$_3$][**3a**] (45%), m.p.: 93 °C—^{1}H-NMR (200 MHz, [D$_8$]-thf, 25 °C) $\delta = 6.25$, 6.23 (each s, 2H, Dur-H), 3.58 (thf), 3.34 (Et$_2$O), 2.33, 2.21, 2.19, 2.03, 1.89 (each s, total 24H, Dur-Me), 1.73 (thf), 1.07 (Et$_2$O), 0.68 (s, 3H, SiMe) 0.17, −0.52 (each s, each 1H, CHSi), −0.04, −0.43 (each s, each 9H, SiMe$_3$)—^{13}C-NMR (50 MHz, [D$_8$]-thf, 25 °C) $\delta = 158.5$, 157.0 (each br. s, *i*-C), 137.8, 136.6, 134.6, 133.2, 130.1, 129.8, 129.53, 129.48 (each s, *o*- and *m*-C), 126.4, 125.8 (each d, *p*-C), 68.2 (thf), 66.1 (Et$_2$O), 26.2 (thf), 21.5, 21.4, 21.3, 21.0, 20.8, 20.7, 20.5, 20.3 (each q, Dur-Me), 15.6 (Et$_2$O), 9.1, 5.0 (each d, ^{1}J(C,H) = 119, respectively, 118 Hz, CHSi), 3.7, 2.3 (each q, SiMe$_3$), −3.5 (q, SiMe)—^{11}B-NMR (96 MHz, [D$_8$]-thf, 25 °C) $\delta = 23$, 20—^{29}Si-NMR (79 MHz, [D$_8$]-thf, 25 °C) $\delta = -1$, −4, −68.

3.1.2. [(Diethylether)lithium][(deloc-1,3,4)-1-methyl-3,4-bis(2,3,5,6-tetramethylphenyl)-trans-2,5-bis-(trimethylsilyl)-1-sila-3,4-diboracyclopentane-l-ide] ([Li(Et$_2$O)][3a])

Lithium powder (0.32 g, 46.1 mmol) was added to a solution of 2.0 g (3.7 mmol) of **4a** in 30 ml of Et$_2$O at room temperature (r.t.) and stirred for 2 h while the mixture turned red. The excess Li and LiCl were removed and the solution was reduced in vacuo to a volume of ca. 10 ml. Cooling to −30 °C for ca. 24 h led to the deposition of light-yellow crystals. Yield: 1.32 g of **3a** Li·Et$_2$O (67%), m.p.: 158 °C—^{1}H-NMR (300 MHz, C$_6$D$_6$, 25 °C) $\delta = 6.65$, 6.63 (each s, each 1H, Dur-H), 2.28 (Et$_2$O), 2.65, 2.55, 2.47, 2.44, 2.11, 2.09, 2.05, 2.01 (each s, each 3H, Dur-Me), 1.05 (s, SiMe), 0.77, −0.08 (each s, each 1H, CHSi), 0.51, 0.07 (each s, each 9H, SiMe$_3$), 0.31 (Et$_2$O)—^{13}C-NMR (75 MHz, C$_6$D$_6$, 25 °C) $\delta = 150.4$, 148.5 (each br. s, *i*-C), 138.9, 136.3, 135.5, 135.0, 134.8, 134.3, 134.01, 133.97 (each s, *o*- and *m*-C), 130.3, 130.2 (each d, *p*-C), 64.6 (Et$_2$O), 22.4, 21.1, 20.9, 20.8, 20.6, 20.5, 20.4, 20.0 (each q, Dur-Me), 13.4 (Et$_2$O), 11.0, 5.3 (each d,^{1}J(C,H) = 120 Hz, CHSi), 3.6, 2.2 (each q, SiMe$_3$), −4.7 (q, SiMe)—^{11}B-NMR (160 MHz, C$_6$D$_6$, 25 °C) $\delta = 21$, 13.

3.1.3. 1-Chloro-l-methyl-3,4-bis(2,3,5,6-tetramethylphenyl)-trans-2,5-bis(trimethylsilyl)-1-sila-3,4-diboracyclopentane (4a)

Fifteen grams (128 mmol) of BCl$_3$ were added by syringe to a solution of 7.60 g (15.0 mmol) of **4b** in 100 ml of pentane at −78 °C. The mixture was allowed to warm to r.t. during 4 h and then kept at −30 °C for at least 16 h. After 1 h at r.t. the solvent and all volatiles were removed in vacuo and the deep yellow residue digested with 100 ml pentane. Insoluble material was separated by a reversed G4-frit and washed two times with each 10 ml of pentane. The pentane solution was evaporated to dryness in vacuo and the solid obtained crystallized from pentane at −30 °C. Yield: 7.68 g of deep yellow **4a** (95%), m.p.: 137 °C—^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C) $\delta = 6.79$ (s, 2H, Dur-H), 2.43, 2.31 (each s, each 1H, CHSi), 2.19, 2.17, 2.09, 1.99, 1.49, 1.45 (each s, total 24H, Dur-Me), 0.86 (s, 3H, SiMe), 0.08, 0.05 (each s, each 9H, SiMe$_3$)—^{13}C-NMR (75 MHz, CDCl$_3$, 25 °C) $\delta = 149.5$ (br. s, *i*-C), 133.3, 133.1, 132.9, 132.6, 130.5, 130.3, 129.8, 129.6 (each s, *o*- and *m*-C), 130.1, 130.0 (each d, *p*-C), 47.5, 47.4 (each d,^{1}J(C,H) = each about 106 Hz, CHSi), 20.7, 20.6, 20.2, 19.5, 19.1, 18.7 (each q, Dur-Me), 7.7 (q, SiMe), 2.5, 2.4 (each q, SiMe$_3$)—^{11}B-NMR (96 MHz, CDCl$_3$, 25 °C) $\delta = 97$.

3.1.4. 1-Methyl-3,4-bis(2,3,5,6-tetramethylphenyl)-trans-2,5-bis(trimethylsilyl)-1-sila-3,4-diboracyclopentane (4b)

Cl$_2$SiHMe (4.60 g, 40 mmol) was added by syringe to a suspension of 12.45 g (20.0 mmol) of **5**·2Li·2Et$_2$O in 150 ml of Et$_2$O at −110 °C. The mixture turned yellow during stirring at this temperature for 4 h and was then allowed to warm to r.t. The solvent and all volatiles were removed in vacuo and the deep yellow residue digested with 100 ml pentane. Insoluble material was separated by a reversed G4-frit and washed two times with each 20 ml of pentane. The pentane solution was evaporated to dryness in vacuo and the solid obtained crystallized from pentane at −30 °C. Yield: 9.60 g (95%) deep yellow **4b**, m.p.: 135 °C—^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C) $\delta = 6.79$ (s, 2H, Dur-H), 4.93 (pseudo-sextet, 1H, ^3J(H,H) = 3.0–3.5 Hz, SiH), 2.24, 2.08 (each d, each 1H, ^3J(H,H) = 3.5, respectively, 2.9 Hz, CHSi), 2.20, 2.15, 1.88, 1.47 (each s, each 6H, Dur-Me), 0.57 (d, ^3J(H,H) = 3.9 Hz, 3H, SiMe), 0.05, 0.04 (each s, each 9H, $SiMe_3$)—^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C) $\delta = 150.8$, 150.3 (each br. s, *i*-C), 133.0, 132.9, 132.6, 130.2, 130.0, 129.9 (each s, *o*- and *m*-C), 129.8, 129.7 (each d, *p*-C), 42.7, 40.9 (each d, ^1J(C,H) = 106, respectively, 102 Hz, CHSi), 20.6, 20.5, 20.1, 19.9, 19.5, 18.8 (each q, Dur-Me), 2.8, 1.6 (each q, $SiMe_3$), 0.5 (q, SiMe)—^{11}B-NMR (96 MHz, $CDCl_3$, 25 °C) $\delta = 97$—^{29}Si-NMR (79 MHz, $CDCl_3$, 25 °C) $\delta = 5.3$ (d, J(Si–H) = 180 Hz, SiH), 0.1, −0.1 (each s, $SiMe_3$).

3.1.5. 1,1-Dimethyl-3,4-bis(2,3,5,6-tetramethylphenyl)-trans-2,5-bis(trimethylsilyl)-1-sila-3,4-dibora-cyclopentane (4c)

A threefold excess of MeI (2.3 g, 15.6 mmol) was added at −110 °C to a solution of 4.2 g (5.2 mmol) $[Li(Et_2O)(thf)_3]$[**3a**] in 50 ml of Et_2O. The solution was kept at −110 °C for 2 h and then allowed to reach r.t. during another 2 h. All volatiles were removed in vacuo and the yellow residue digested with 50 ml of pentane. Salts were filtered off and the clear solution reduced to ca. 10 ml. Cooling to −30 °C led to deposition of yellow crystals.

Yield: 0.80 g (29%) deep yellow **4c**, m.p.: 146 °C—^{1}H-NMR (200 MHz, $CDCl_3$, 25 °C) $\delta = 6.79$ (s, 2H, Dur-H), 1.93 (s, 2H, CHSi), 2.20, 2.07, 2.05, 1.60 (each s, each 6H, Dur-Me), 0.54 (s, 6H, $SiMe_2$), 0.03 (s, 18H, $SiMe_3$)—^{13}C-NMR (50 MHz, $CDCl_3$, 25 °C) $\delta = 150.6$ (br. s, *i*-C), 132.8, 132.5, 129.6, 129.5 (each s, *o*- and *m*-C), 129.4 (d, *p*-C), 42.6 (d, ^1J(C,H) = 101 Hz, CHSi), 20.3, 20.1, 19.4, 18.8 (each q, Dur-Me), 4.5 (q, $SiMe_2$), 2.5 (q, $SiMe_3$)—^{11}B-NMR (96 MHz, $CDCl_3$, 25 °C) $\delta = 95$.

3.1.6. X-ray crystal structure analyses of $[Li(Et_2O)(thf)_3]$[3a]·1/2Et_2O, $[Li(Et_2O)]$ [3a], and 4c

Single crystals were investigated on an image plate system (IPDS Stoe) using graphite monochromatized Mo–K_α radiation at 193 K (Table 2). The space groups were determined from the systematic absences and intensity statistics, no absorption corrections were applied. The structures were solved by direct methods and refined against all F^2 data using full-matrix least-squares and difference Fourier techniques (SHELX programs [22,23]). Most hydrogen atoms were kept riding on calculated positions with isotropic displacement factors taken as 1.2 times (1.5 times for CH_3) the U_{eq} value of the corresponding C atom. The hydrogen atoms at C1 and C2 of the central ring were located and refined with individual isotropic displacement factors. For all heavier atoms, anisotropic displacement parameters were used. Details of the experimental and crystal data

Table 2
Crystallographic and experimental data for $[Li(Et_2O)(thf)_3]$[**3a**]·1/2Et_2O, $[Li(Et_2O)]$[**3a**], and **4c**

	$[Li(Et_2O)(thf)_3]$[**3a**]·1/2Et_2O	$[Li(Et_2O)]$[**3a**]	**4c**
Empirical formula	$C_{47}H_{88}B_2LiO_{4.5}Si_3$	$C_{33}H_{57}B_2LiOSi_3$	$C_{30}H_{52}B_2Si_3$
Formula weight (g mol^{-1})	838.00	582.62	518.61
Color, habit	Bright-yellow block	Colorless, irregular	Yellow rhombus
Crystal size (mm)	0.30 × 0.20 × 0.10	0.40 × 0.30 × 0.25	0.40 × 0.20 × 0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$I2/a$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a (Å)	16.975(1)	17.406(1)	11.930(1)
b (Å)	17.178(1)	26.876(1)	14.594(1)
c (Å)	37.230(2)	17.492(1)	19.754(1)
β (°)	97.69(1)	113.46(1)	102.46(1)
V (Å^3)	10758.5(11)	7506.4(7)	3358.3(4)
Z	8	8	4
Calculated density (mg m^{-3})	1.035	1.031	1.026
Absorption coefficient (mm^{-1})	0.125	0.148	0.157
Temperature (K)	193(2)	193(2)	193(2)
λ (Mo–K_α) (Å)	0.71073	0.71073	0.71073
Diffractometer	IPDS (Stoe)	IPDS (Stoe)	IPDS (Stoe)
θ range (°)	1.93–24.04	1.98–26.00	2.11–25.97
Reflections: total, unique	29 545, 8451	58 889, 14 619	22 254, 6534
Observed [$>4\sigma(F)$]	2560	7440	3479
Number of parameters	542	812	340
R ($F>4\sigma(F)$)	0.0526	0.0464	0.0383
wR_2 (all reflections)	0.1417	0.1143	0.0866
GOF, S	0.719	0.819	0.811
Residual electron density (e Å^{-3})	0.21, −0.21	0.36, −0.34	0.19, −0.18

are summarized in Table 1. In [Li(Et$_2$O)(thf)$_3$][**3a**]·1/2Et$_2$O, the thf and ether molecules show partially high and strong anisotropic displacement parameters indicating high mobility or/and disorder. In the structure of [Li(Et$_2$OA)][**3a**], two crystallographically independent ion pairs are found with similar geometry. The given bond lengths and angles are average values. In one of the ion pairs, the ether molecule is disordered.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-143677, 143678, 167879. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[13] For comparison: according to an NBO analysis, the 3c2e-bond in **3u** is occupied by 1.93 electrons, 40% assigned to Si and 30% each to B.

[14] Fixing the Si···B distance to 268.5 pm and optimization of the remaining geometric parameters in C_{2v} symmetry results in an energy of + 43.9 kcal mol^{-1} relative to **3u**. An NBO analysis reveals a 3c2e bond occupancy of 1.86 electrons which are assigned to Si (57%) and B (22% each). The C_2 structure has two imaginary frequencies, a relative energy of 41.1 kcal mol^{-1} and a 3c2e bond with 1.82 electrons (54% at Si, 23% at each B).

[15] The number of charged species must not alter otherwise electrostatics govern the energetic balance of the equation. The ammonium group models the formal positive charge at the Si center of **3u***, but does not allow for cyclic delocalization which is present in **3u****.

[16] In **3a** the angle sum at Si1 is 355.5°, in **3u** it is 358.2°.

[17] Employing the C_1 minimum structure of the silacyclopentyl anion which is strongly pyramidalized at the Si center, 32.8 kcal mol^{-1} are obtained instead. Due to the big energy required for planarization of silyl anions, this value is even smaller than 42.0 kcal mol^{-1}, the lower limit determined for the stabilization of **3u** by cyclic delocalization.

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[19] The tin analogue of **3u**** is 60.6 kcal mol^{-1} higher in energy than the global minimum which, however, does not possess a 3c2e B$_2$Sn bond. Instead, there are a lone pair at Sn (with 75% s character) and to *two* 3c2e BCSn bonds. The latter can be understood as the consequence of very strong C–Sn-hyperconjugation due to the negative charge at tin. Reluctance to decrease the s character of a lone pair at a heavy main group center explains why the tin analogue of silaanion **3u** shows no homoaromatic stabilization, which requires a planar tin center.

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