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Silaborates with an Unprecedented Cluster Geometry

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The reaction of *o*-silaborane with a series of carbanions is presented. Adducts of *o*-silaborane were prepared in reaction with Grignard reagents (RMgBr R = Me, Ph, benzyl, allyl, vinyl, and ethinyl) (**3a**−**f**). The salts were isolated in high yield and characterized by elemental analyses and NMR spectroscopy. In the case of the benzylide adduct the structure in the solid state was determined by X-ray single-crystal structure analysis. Ab initio calculations were carried out on the methylide derivative $[Me_3Si_2B_{10}H_{10}]^-$, and results of the geometry optimizations together with calculated NMR chemical shifts are discussed. The first substitution reaction at a silicon vertex of the *o*-silaborane skeleton is presented with the synthesis of $[MeSiPhSiB_{10}H_{10}]$, which is characterized by X-ray crystal structure analysis.

Introduction

The geometry of a polyborane or heteroborane cluster is usually elucidated with respect to Williams[1] geometrical systematics and the skeletal electron counting rules invented by Wade[2] and elaborated by Mingos.[3] By counting the cluster with respect to the number of electrons and skeleton atoms, the geometry of a cluster can be predicted. Following these systematics, an increase in the number of cluster electrons is tantamount to a cluster-opening reaction. Thus, the reduction of the most prominent heteroborane, *o*-carborane $[C_2B_{10}H_{12}]$, results in a dramatic change of the icosahedral geometry.[4] The reduction product $[C_2B_{10}H_{13}]^-$ exhibits a geometry that is derived from the deltahedral shape of the 13-vertex *closo* cluster by removal of one vertex (geometry A in Figure 1).[5] Another cluster-opening reaction of an icosahedral cluster skeleton is known for aza-*closo*-dodecaborane(12). The icosahedral azaborane $[RNB_{11}H_{11}]$ reacts with a variety of nucleophiles to yield adducts comprising a 12-vertex *nido* cluster geometry (geometry B in Figure 1).[6] Both geometries A and B were described by Williams as primary fragments resulting from removal of one vertex from the 13-vertex deltahedron.[1]

Twelve-vertex *nido* clusters with other than the primary fragment geometries are very common. Especially in the case of the tetracarborane $R_4C_4B_8H_8$ a variety of cluster geometries were determined either by crystal structure analysis or by NMR spectroscopical investigations.[7] A relationship between these geometries and the primary fragments was shown by Williams after breaking and reintroduction of various edge connections.[1]

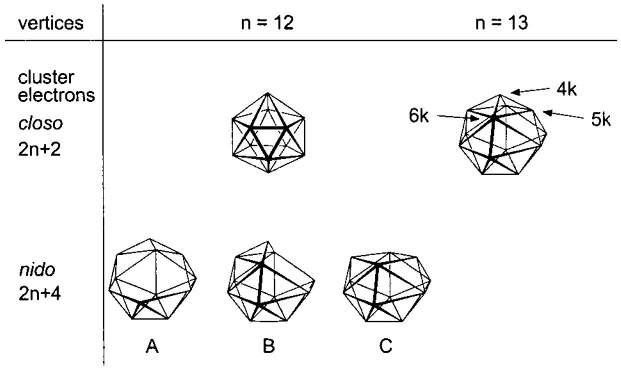

Figure 1. *closo* and *nido* cluster geometries for 12 and 13 vertices.

Another unexpected cluster geometry is realized in the case of the dialkylamide adducts of 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12)[8] (*o*-silaborane) (anion $[Et_2N(MeSi)_2B_{10}H_{10}]^-$, **2**, in Figure 2).[9] Whereas Wade's cluster rules predict an *arachno* cluster, the *closo* geometry of *o*-silaborane remains almost unchanged after adduct formation. Ab initio calculations of *o*-silaborane and the amide adduct gave further insight

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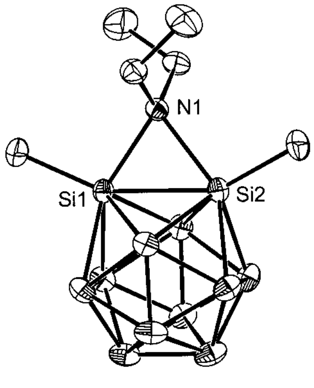

$[(Et_2N)(MeSi)_2B_{10}H_{10}]^-$

2

Figure 2. Diethylamide adduct of *o*-silaborane.

into the acceptor abilities of the icosahedral silaborane and proved the LUMO to be essentially concentrated on the two silicon centers.

The interesting structure of the amide adduct prompted us to study carbanions as another type of nucleophile in this reaction.

Results and Discussion

The carbanion adducts of *o*-silaborane (**1**) can be obtained straightforwardly in high yield from the reaction with the respective Grignard reagent (Scheme 2). Crown ether (12-C-4) was added in stoichiometric amounts to a thf solution of the magnesium salts, and crystalline substances result from slow diffusion of a less polar solvent into these solutions. The very moisture-sensitive colorless crystalline adducts were characterized by heteronuclear and two-dimensional NMR spectroscopy as well as by elemental analyses. However, due to the high sensitivity toward small amounts of moisture, the results of the elemental analyses for **3a** and **3d** show relatively large deviations from theory. In the case of the benzylide adduct the structure in the solid state was determined by X-ray single-crystal structure analysis.

NMR Spectroscopical Investigations. The number of ^{11}B NMR resonances for the cluster skeleton is a good indicator of the symmetry of the anionic adducts in solution. Six signals with an intensity ratio of 2:2:2:2:1:1 for the methylide adduct **3a** give evidence for C_s symmetry of these species in solution. For the other also C_s symmetrical clusters **3b**−**f** only five signals are visible. The resonances for B9 and B12 are accidentally isochronic (Figure 3). Due to the different chemical environments for the MeSi groups, two resonances were detected in the ^{1}H NMR as well as in the ^{29}Si NMR spectra.

In contrast to the C_s symmetrical carbanion adducts, the amide adduct shows C_{2v} symmetry in solution (Figure 2). For the anions of type **2** one resonance for the MeSi groups in the ^{1}H NMR as well as in the ^{29}Si NMR and only four signals in the ^{11}B NMR spectrum for 10 boron atoms were detected. Obviously the number of electron pairs at the donor atom of the attacking nucleophile determines the symmetry and structure of the adduct.

X-ray Structural Analysis of the Benzylide Adduct. To further elucidate the cluster geometry of the carbanion adducts, an X-ray structure analysis was carried out in the case of the benzylide adduct **3c**. Crystal, data collection, and refinement parameters are given in Table 2. Atomic coordinates and equivalent isotropic displacement parameters are given in the Supporting Information. The molecular structure of the silaborate **3c** is depicted in Figure 4.

Selected interatomic distances are compiled in Table 1. On the basis of the interatomic distances between Si2 and the boron atoms the incorporation of Si2 in the cluster skeleton remains nearly unchanged with respect to *o*-silaborane. As expected, for the attacked cluster vertex Si1 the Si1−B distances exhibit a substantial geometrical change. Surprisingly the distances toward B3 and B6 are symmetrically elongated, resulting in the formation of two quadrangles in the cluster skeleton. This skeleton can be compared with that of the $R_4C_4B_8H_8$ cluster geometries determined by crystal structure analysis.[10] As in **3c**, the carborane skeleton features (Figure 5) two neighboring quadrangles.

Adducts of the *closo* clusters $MC_2R_2B_4H_4$ and $MC_2R_2B_9H_9$ (M = RGa, RAl, Ge, Sn) exhibit opened cluster geometries that were described as highly slip distorted with respect to the central atom.[11] Interestingly the *commo*-cluster $Si(C_2B_9H_{11})_2$ reacts with pyridine under almost complete removal of the silicon atom from the cluster framework.[12] Obviously the *nido* 12-vertex compounds can adopt a variety of structures.

In the special case of *o*-silaborane two different nucleophiles react under the formation of adducts with different cluster geometries. In the case of the symmetrically bridged dialkylamide almost no change of the cluster geometry is detectable (Table 1), and for carbanion adducts an opening of the skeleton takes place.

Ab Initio Calculation. To achieve a better understanding of the chemistry of the silaboranes, we conducted ab initio calculations[13] on the methylide adduct $[Me_3Si_2B_{10}H_{10}]^-$. The results of the geometry optimization are compiled in Table 3, and the calculated NMR chemical shifts are listed in Table 4. Due to the lack of an X-ray crystal structure analysis of the methylide adduct, we compare the results of the geometry optimization with the structure of the benzylide derivative. An indicator of the good correspondence between experiment and theory is the largest variation between the geometrical data of only 0.043 Å (Si1−B4). The NMR chemical shifts were calculated with the GIAO method[14] at the B3LYP/6-311+G(d, p) level[15] of theory based on the B3LYP/6-31G(d) geometries.[16] In contrast to the relatively small deviations between the calculated and

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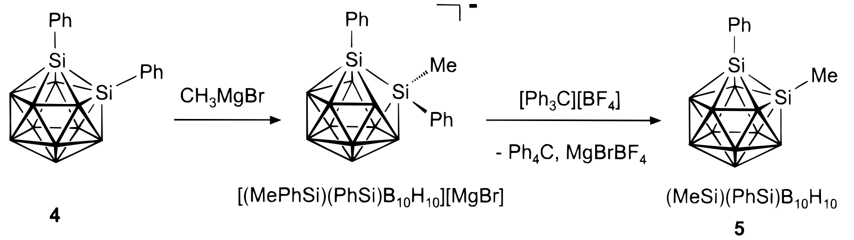
Scheme 1



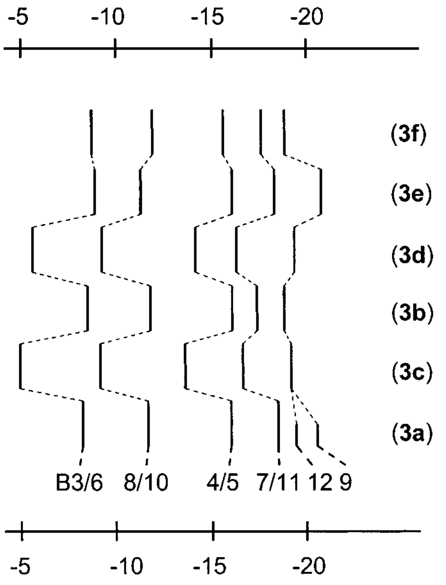
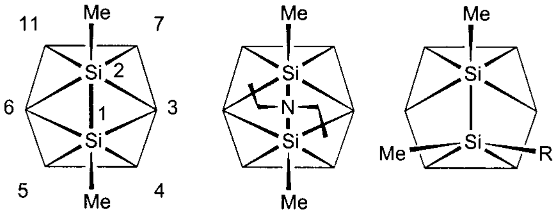


Figure 3. $^{11}B\{^{1}H\}$ NMR spectra of the carbanion adducts of *o*-silaborane.

Table 1. Selected Interatomic Distances in *o*-Silaborane and the Adducts of *o*-Silaborane ([Å], Standard Deviations in Parentheses)



Si-Si	2.308(2)	2.331(1)	2.371(2)
Si1-B3	2.116(3)	2.091(3)	2.374(6)
Si1-B6		2.103(3)	2.371(6)
Si2-B3	2.116(3)	2.108(3)	2.073(6)
Si2-B6		2.114(3)	2.110(6)
Si1-B4	2.014(3)	2.082(3)	2.105(6)
Si1-B5		2.091(3)	2.169(7)
Si2-B7	2.014(3)	2.089(3)	2.065(6)
Si2-B11		2.079(3)	2.055(7)

measured ^{11}B NMR chemical shifts the values for the silicon nucleus show only the same tendency but not a satisfactory correspondence.

So far adducts of *o*-silaborane were isolated in the case of dialkylamides and carbanions (Table 1). In both cases the attack of the nucleophile at the silicon vertices can be understood as an interaction of the incoming anions with the LUMO, which is mainly concentrated on the silicon atoms.

Table 2. Crystal Data, Data Collection Parameters, and Convergence Results for 3c and 5

	3c	5
formula	$C_{42}H_{94}B_{20}MgO_{10}Si_4$	$C_7H_{18}B_{10}Si_2$
fw	1112.1	266.5
system	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
a, Å	16.122(6)	7.356(1)
b, Å	16.968(6)	23.692(3)
c, Å	23.43(1)	8.942(2)
β, deg	106.55(4)	97.10(1)
U, Å^3	6144(1)	1546.4(4)
Z	4	4
d_{calc}, g cm^{-3}	1.202	1.146
μ, cm^{-1}	1.51	18.33
θ_{max}, deg	26.0	70
temperature, K	203	293
λ, Å,	0.71073	1.54184
crystal dimens, mm^3	0.6 × 0.4 × 0.15	0.6 × 0.2 × 0.2
no reflns	6421	4156
indep obs reflns	3872	1859
$I > n\sigma(I)$	($n = 1.5$)	($n = 1$)
no vars	337	203
R^a	0.091	0.093
$R_w{}^b$	0.084	0.078
GOF^c	1.770	1.281
res el dens, e Å^{-3}	0.53	0.42

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. $w^{-1} = \sigma^2(F_o)$. ^{c} GOF $= [\Sigma w(|F_o| - |F_c|)^2/n_{obs} - n_{var}]^{1/2}$, n_{obs} no. of observations, n_{var} no. of variables refined.

Substitution Reaction at Diphenyl-*o*-silaborane. The substitution of an alkyl or phenyl group at a silicon atom in a common organosilicon compound is carried out by electrophilic catalysis. So far all standard procedures for the substitution of the organic substituent at the silaborane clusters [$Me_2Si_2B_{10}H_{10}$, $Ph_2Si_2B_{10}H_{10}$] failed. Nevertheless in this publication we present the first example of the successful substitution of a phenyl group in place of a methyl group at the 1,2-diphenyl-1,2-disila-*closo*-dodecaborane(12) cluster. We took advantage of the carbanion adduct formation of diphenyldisilaborane with methylgrignard (MeMgBr). In a one-pot procedure the methylide adduct of the silaborane **4** was formed by reaction with a small excess of methylmagesium bromide. Without purification the silaborate $[(MePhSi)(PhSi)B_{10}H_{10}]^-$ was treated with the trityl

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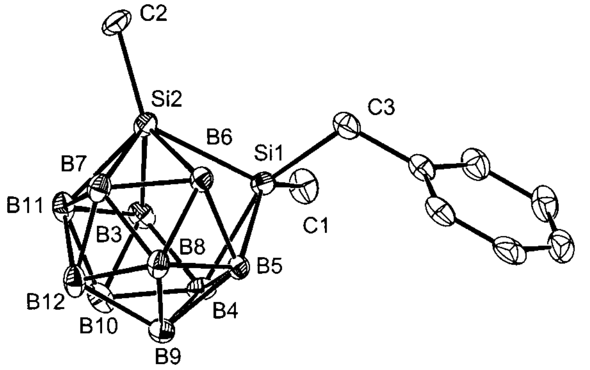
(16) All calculations were conducted with Gaussian 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, P. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.



$[(PhCH_2)(MeSi)_2B_{10}H_{10}]^-$

Figure 4. Structure of the anion of **3c** in the crystal (PLATON representation,[17] ellipsoids at 30% probability level). Selected angles [deg], standard deviations in parentheses: Si2−Si1−C1 123.4(2), Si2−Si1−C3 109.9(1), C1−Si1−C3 95.8(2), Si1−Si2−C2 127.9(2), Si1−Si2−B3 64.1(1), Si1−Si2−B6 63.5(2).

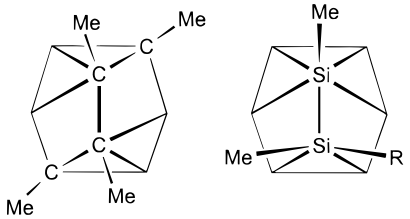


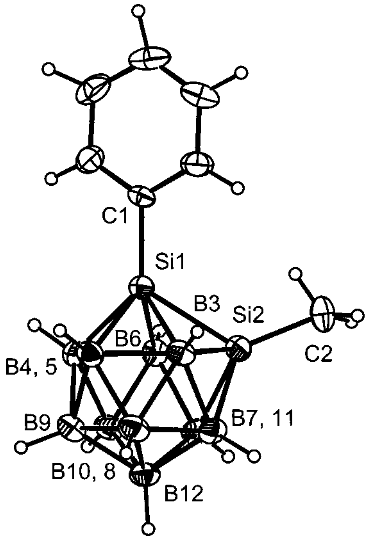
Figure 5. Top view on the $Me_4C_4B_8H_8$ cluster and carbanion adduct of *o*-silaborane.

Table 3. Selected Interatomic Distances [Å] of the Anion of 3a Calculated at B3LYP/6-31G(d) and HF/6-31G(d) (in parentheses)

Si1−Si2	2.365 (2.362)
Si1−B3	2.398 (2.397)
Si1−B6	2.409 (2.397)
Si2−B3	2.097 (2.107)
Si2−B6	2.093 (2.107)
Si1−B4	2.148 (2.154)
Si1−B5	2.147 (2.154)

Table 4. Calculated (B3LYP-GIAO/6-311+G(d,p)// B3LYP/6-31G(d))[8−10] and Observed NMR Chemical Shifts [ppm] of $[Me_3Si_2B_{10}H_{10}]^-$ Anion of 3a

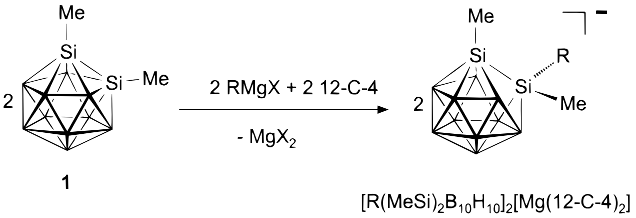
	calcd	exptl
Si1	−105.4	−85.3
Si2	−73.6	−61.2
B3/B6	−5.9/−6.0	−8.3
B4/B5	−18.3/−18.3	−16.0
B7/B11	−20.3/−19.3	−18.5
B8/B10	−12.8/−13.1	−11.4
B9	−22.1	−21.2
B12	−19.2	−19.4



$[PhSiMeSiB_{10}H_{10}]$

Figure 6. Structure of **5** in the crystal (PLATON representation,[17] ellipsoids at 30% probability level). Selected interatomic distances [Å] and angles [deg], standard deviations in parentheses: Si1−Si2 2.304(2), Si1−C1 1.828(5), Si2−C2 1.842(6), Si1−B3 2.108(7), Si1−B4 2.019(7), Si1−B5 2.019(7), Si1−B6 2.099(7), Si2−B3 2.105(6), Si2−B6 2.125(7), Si2−B7 2.026(8), Si2−B11 2.015(7), Si2−Si1−C1 121.9(2), Si1−Si2−C2 126.4(2), Si2−Si1−B3 56.8(2), Si2−Si1−B6 57.5(2).

Scheme 2



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$[R(MeSi)_2B_{10}H_{10}]_2[Mg(12\text{-}C\text{-}4)_2]$

3	R	X
a	Me	Cl
b	Ph	Br
c	benzyl	Br
d	allyl	Br
e	vinyl	Br
f	ethinyl	Br

Table 5. ^{11}B NMR Chemical Shifts of *o*-Silaboranes

	1	4	5
B3/6	−13.9	−14.7	−14.1
B4/5/7/11	−14.8	−14.7	−14.8
B8/10	−11.5	−11.8	−11.5
B9/12	−12.9	−12.8	−12.9

electrophile $[Ph_3C][BF_4]$ (Scheme 1). Work up by sublimation resulted in the isolation of a new silaborane **5** in 35% yield.

The new silaborane was characterized by NMR spectroscopy, mass spectrometry, and X-ray single-crystal structure analysis. Six signals were expected to appear in the ^{11}B NMR spectrum for the C_s symmetrical *closo*-borane **5**. Due to the small substituent effect on the boron atoms of the cluster cage, the ^{11}B NMR spectrum indicates with four resonances a higher symmetry (Table 5). The molecular structure of the silaborane is depicted in Figure 6. Crystal, data collection, and refinement parameters are given in Table 2. Atomic coordinates and equivalents isotropic displacement coefficients are given in the Supporting Information. The geometrical data of the icosahedral cluster reveal almost no difference in comparison to the structures of **1**[8] and **4**.[9b]

This nucleophilic substitution runs presumably via a bimolecular two-step mechanism. The carbanion adduct of the silaborane is the intermediate in this reaction.

In summary, we have demonstrated that *o*-silaborane forms adducts with carbanions. In the case of diphenyl-*o*-silaborane we were able to use the adduct formation in order to substitute a phenyl group by a methyl group.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were distilled from sodium and benzophenone (THF, diethyl ether) or from potassium (hexane) and stored under nitrogen. Elemental analyses were done by Mikroanalytisches Labor Pascher in Remagen, Analytischen Laboratorien in Lindlar. Mass spectrometry was done with a Varian MAT-CH-%, EI 70 eV. Due to very high sensitivity toward moisture in the case of **3a** and **3d**, insufficient C,H analyses were obtained.

Ab Initio Calculations. The Gaussian 94 package,[16] run on a cluster of workstations (Rechenzentrum der RWTH Aachen), was applied for all ab initio calculations. The geometries for $[\mathrm{Me_3Si_2B_{10}H_{10}}]^-$ (anion of **3a**) were optimized at the HF/6-31G(d) and B3LYP/6-31G(d) levels of theory; the calculation of the vibrational frequencies at the HF/6-31G(d) level showed no imaginary frequency (ZPVE = 703.97 kJ/mol; the total energies in hartrees are −949.426462 (HF) and −953.501904 (B3LYP)). The ^{11}B and ^{29}Si NMR shifts are reported relative to $\mathrm{BF_3 \cdot OEt_2}$ and TMS, respectively. It is inconvenient to compute the magnetic shielding of $\mathrm{BF_3 \cdot OEt_2}$; therefore $\mathrm{B_2H_6}$ was calculated instead and set to 16.6 ppm.[18] The absolute chemical shieldings at the B3LYP-GIAO/6-311+G(d, p)//B3LYP/6-31G(d) level are 84.11 ppm (^{11}B of $\mathrm{B_2H_6}$) and 338.80 ppm (^{29}Si of TMS).

Preparation of $\mathbf{[Mg(12\text{-}C\text{-}4)_2][B_{10}H_{10}Si_2Me_3]_2}$ (3a). A 0.7 mL sample of a solution of methylmagnesium chloride in thf (3 M, thf, 1.07 equiv) was added to a solution of *o*-silaborane (431.2 mg, 2.11 mmol) in 25 mL of the same solvent at room temperature. The reaction mixture yellowed and thickened instantly. It was stirred for 1 h. Then 60 μL of $\mathrm{Me_3SiCl}$ (1/4 equiv) was added in order to dispose of any excess of the Grignard reagent, the mixture was stirred for another 15 min, and 2.0 mL of a 1 M solution of 12-crown-4 in thf was added. Fine colorless crystal needles and leafs formed upon filtration and slow diffusion of hexane into the solution at 4 °C and were recrystallized from thf/$\mathrm{Et_2O}$ for removal of remaining magnesium chloride. Yield: 0,765 g (M = 815.67 g mol^{-1}, 89%). ^{1}H{^{11}B} NMR (thf-d_8, 500 MHz, TMS, *J* (Hz)): 0.56 (s, 3H, $\mathrm{SiC}H_3$), 0.60 (s, 6H, $\mathrm{SiC}H_3$), 0.87 (s, 1H, H9), 1.27 (s, 2H, H7/11), 1.40 (s, 1H, H12), 1.42 (s, 2H, H4/5), 1.75 (s, 2H, H8/10), 1.92 (s, 2H, H3/6), 4.07 (mult, 16H, 12-K-4). ^{11}B NMR (thf-d_8, 160 MHz, $\mathrm{Et_2O \cdot BF_3}$, *J* (Hz) −8.3 (d, ^1J = 134, B3/6), −11.4 (d, ^1J = 147, B8/10), −16.0 (d, ^1J = 134, B4/5), −18.5 (d, ^1J = 140, 7/11), −19.4 (d, ^1J = 140, B12), −21.2 (d, ^1J = 134, B9). ^{3}C{^{1}H} NMR (thf-d_8, 125 MHz): −10.0 (MeSi), 1.1 (MeSi), 25.1 (thf), 66.9 (12-K-4), 67.2 (thf). ^{29}Si NMR (thf-d_8, 100 MHz): −61.2 (Si2), −85.3 (Si1). C, H ([%], calcd in parenth): C 31.18 (32.40), H 8.65 (8.65).

Preparation of $\mathbf{[Mg(12\text{-}C\text{-}4)_2][B_{10}H_{10}Si_2Me_2Ph]_2}$ (3b). To a solution of 221.2 mg (1.08 mmol) of *o*-silaborane in 20 mL of thf was added 370 μL of a solution of phenylmagnesium bromide in $\mathrm{Et_2O}$ (3 M, 1.03 equiv). The solution yellowed instantly and clouded after 15 min. After 1 h 35 μL of $\mathrm{Me_3SiBr}$ (1/4 equiv) and again 15 min later 1.2 mL of a 1 M solution of 12-crown-4 in thf were added. The same procedure as for **3a** gave beautiful colorless crystals in excellent yield. Yield: 0.462 g (M = 939.81 g mol^{-1}, 91%). ^{1}H{^{11}B} NMR (thf-d_8, 500 MHz, TMS, *J* (Hz)): 0.57 (s, 3H, $\mathrm{Si2C}H_3$), 0.78 (s, 3H, $\mathrm{Si1C}H_3$), 1.20 (s, 1H, H9 or H12), 1,40 (s, 2H, H4/5 or H7/11), 1,43 (s, 1H, H9 or 12), 1.65 (s, 2H, H4/5 or H7/11), 1.71 (s, 2H, H8/10), 1.76 (mult, thf), 1.88 (s, 2H, H3/6), 3.61 (mult, thf), 3.99 (mult, 16H, 12-K-4), 7.01 (trtr, 1H, *p*-Ph), 7.11 (mult, 2H, *o*-Ph), 7.51 (mult, 2H, *m*-Ph). ^{11}B NMR (thf-d_8, 160 MHz, $\mathrm{Et_2O \cdot BF_3}$, *J* (Hz)): −8.6 (d, ^1J = 134, B3/6), −12.1 (d, ^1J = 135, B8/10), −16.2 (d, ^1J = 134, B4/5 or 7/11), −17.5 (d, ^1J = 140, B4/5 or 7/11), −19.2 (d, ^1J = 134, B9 and B12). ^{13}C{^{1}H} NMR (thf-d_8, 125 MHz, TMS): −9.2 ($C\mathrm{H_3Si1}$), 1.4 ($C\mathrm{H_3Si2}$), 67.0 (12-K-4), 126.0 (*p*- Ph), 127.4 (*o*- Ph), 131.8 (*m*- Ph), 157.0 (*i*-Ph). ^{29}Si NMR (thf-d_8, 100 MHz): −90.0 (Si1), −57.7 (Si2). C, H ([%], calcd in parenth): C 40.36 (40.90), H 8.03 (7.94).

Preparation of $\mathbf{[Mg(12\text{-}C\text{-}4)_2][B_{10}H_{10}Si_2Me_2(CH_2Ph)]_2 \cdot 2thf}$ (3c). To a solution of 354.1 mg (1.73 mmol) of *o*-silaborane in 20 mL of thf was added 1.90 mL of a solution of benzylmagnesium bromide in $\mathrm{Et_2O}$ (1 M, 1.10 equiv). The solution yellowed and clouded instantly. After 1 h 55 μL of $\mathrm{Me_3SiCl}$ (1/4 equiv) was added. After 1 h 1.8 mL of a 1 M solution of 12-crown-4 in thf was added. The same procedure as for **3a** gave yellowish crystals that were recrystallized to gain fine colorless needles that showed poor solubility even in thf. **4c** crystallizes with one molecule of thf per asymmetric unit. Yield (before recryst): 0.781 g (M = 1112.07 g mol^{-1}, 81%). ^{1}H{^{11}B} NMR (thf-d_8, 500 MHz, TMS, *J* (Hz)): 0.28 (s, 3H, $\mathrm{Si2C}H_3$), 0.67 (s, 3H, $\mathrm{Si1C}H_3$), 0.79 (s, 1H, H9 or H12), 1.21 (s, 2H, H4/5 or H7/11), 1.45 (s, 2H, H4/5 or H7/11), 1.69 (s, 2H, H8/10), 1.77 (mult, thf), 1.93 (s, 2H, H3/6), 3.60 (mult, thf), 4.07 (mult, 16H, 12-K-4), 6.92 (trtr, ^3J = 7.3, 1H, *p*- Ph), 7.11 (mult, 2H, *m*-Ph), 7.21 (mult, 2H, *o*- Ph). ^{11}B NMR (thf-d_8, 160 MHz, $\mathrm{Et_2O \cdot BF_3}$, *J* (Hz)): −7.0 (d, ^1J = 134, B3/6), −10.8 (d, ^1J = 134, B8/10), −15.7 (d, ^1J = 134, B4/5 or 7/11), −18.3 (d, ^1J = 134, B4/5 or 7/11), −21.1 (d, ^1J = 134, B9 and 12). ^{13}C{^{1}H} NMR (thf-d_8, 125 MHz, TMS): −11.3 (MeSi1), 10.0 (MeSi2), 23.9 (thf), 51.4 ($CH_2\mathrm{Ph}$), 66.0 (thf), 67.0 (12-K-4), 127.2, 127.9 (*p*-Ph, *o*-Ph), 131.8 (*m*-Ph), 143.4 (*i*-Ph). ^{29}Si NMR (thf-d_8, 100 MHz): −90.2 (Si1), −64.0 (Si2). C, H ([%], calcd in parenth): C 44.70 (45.36), H 8.60 (8.52).

Preparation of $\mathbf{[Mg(12\text{-}C\text{-}4)_2][B_{10}H_{10}Si_2Me_2C_3H_5]_2 \cdot thf}$ (3d). To a solution of 214.7 mg (1.05 mmol) of *o*-silaborane in 20 mL of thf was added 1.05 mL of a solution of allylmagnesium bromide in $\mathrm{Et_2O}$ (1 M, 1,1 equiv). The solution yellowed instantly and clouded after 15 min. One hour later 1.8 mL of a 1 M solution of 12-crown-4 in thf was added. The same procedure as for **3a** gave slightly yellowish crystals in good yield that contained 1 equiv of thf. Yield: 0.436 g (M = 939.85 g mol^{-1}, 88%). ^{1}H{^{11}B} NMR (thf-d_8, 500 MHz, TMS, *J* (Hz)): 0.56 (s, 3H, $\mathrm{SiC}H_3$), 0.71 (s, 3H, $\mathrm{SiC}H_3$), 1.28 (s, 1H, H9 or H12), 1.43 (s, 2H, H4/5 or H7/11 a. H9 or 12), 1.76 (s, 2H, 8/10), 1.76 (mult, thf), 1.84 (s, 2H, H4/5 or H7/11), 1.95 (d, ^3J = 8.52, 2H, $CH_2\mathrm{CHCH_2}$), 3.61 (mult, thf), 2.02 (s, 2H, H3/6), 4.07 (mult, 16H, 12-K-4), 4.69 (ddtr, ^3J = 10.1, ^2J = 2.8, $^4J \approx 0.9$, 1H, $\mathrm{SiCH_2CHC}H_2$ (Z)), 4.79 (ddtr, ^3J = 17.05, ^2J =2.78, ^4J = 1.39, 1H, $\mathrm{SiCH_2CHC}H_2$ (*E*)), 6.12 (ddtr, $^3J_{(Z)}$ = 10.11, $^3J_{(E)}$ = 17.05, ^3J = 8.52, 1H, $\mathrm{SiCH_2C}H\mathrm{CH_2}$). ^{11}B NMR (thf-$d_8$, 160 MHz, $\mathrm{Et_2O \cdot BF_3}$, *J* (Hz)): −5.8 (d, ^1J = 134 Hz, B3/6), −9.3 (d, ^1J = 135, B8/10), −14.1 (d, ^1J = 134, B4/5 or 7/11), −16.6 (d, ^1J = 140, B4/5 or 7/11 and B9 or B12), −19.3 (d, ^1J = 134, B9 or 12). ^{13}C{^{1}H} NMR (thf-d_8, 125 MHz): −9.8 (MeSi1), −21.6 (MeSi2), 51.3 ($\mathrm{Si}CH_2\mathrm{CHCH_2}$), 67.0 (12-K-4), 110.4 ($\mathrm{SiCH_2CH}CH_2$), 139.3 ($\mathrm{SiCH_2}CH\mathrm{CH_2}$). ^{29}Si NMR (thf-$d_8$, 100 MHz): −62.5 (Si2), −90.6 (Si1). C, H ([%], calcd in parenth): C 39.35 (38.34), H 8.14 (8.79).

Preparation of $\mathbf{[Mg(12\text{-}C\text{-}4)_2][B_{10}H_{10}Si_2Me_2C_2H_3]_2}$ (3e). To a solution of 285.3 mg (1.40 mmol) of *o*-silaborane in 20 mL of thf was added 1.40 mL of a solution of vinylmagnesium bromide in $\mathrm{Et_2O}$ (1 M, 1.00 equiv). The solution yellowed and clouded in the course of 15 min. After 1 h and subsequent addition of 1.6 mL of a 1 M solution of 12-crown-4 in thf the reaction mixture was filtrated. Slow diffusion of hexane and refrigerating gave yellowish leaf-shaped crystals in acceptable yield. Yield: 0.385 g (M = 839.69 g mol^{-1}, 66%). ^{1}H{^{11}B} NMR (thf-d_8, 500 MHz, TMS, *J* (Hz)): 0.54 (s, 3H, $\mathrm{SiC}H_3$), 0.79 (s, 3H, $\mathrm{SiC}H_3$), 0.93 (s, 1H, H9 or H12), 1.30(s, 3H, H4/5 or H7/11 a. H9 or 12), 1.43 (s, 2H, H4/5 or H7/11), 1.78 (s, 2H, H8/10), 1.77 (mult, thf), 2.00 (s, 2H, H3/6), 3.62 (mult, thf), 4.07 (mult, 16H, 12-K-4), 5.32 (dd, ^3J = 19.8, ^2J = 3.1, 1H, $\mathrm{SiCHC}H_2$ (Z)), 5.51 (dd, ^3J = 13.7, ^2J = 3.1, 1H, $\mathrm{SiCHC}H_2$ (E)), 6.09 (dd, $^3J_{(Z(H))}$ = 13.7, $^3J_{(E(H))}$ = 19.8, 1H, $\mathrm{SiC}H\mathrm{CH_2}$). ^{11}B NMR (thf-$d_8$,

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160 MHz, $Et_2O\cdot BF_3$, J (Hz)): −9.0 (d, $^1J = 134$, B3/6), −11.4 (d, $^1J = 134$, B8/10), −16.1 (d, $^1J = 122$, B4/5 or 7/11), −18.4 (d, $^1J = 134$, B4/5 or 7/11 and B9 or B12), −20.8 (d, $^1J = 147$, B9 or 12). $^{13}C\{^1H\}$ NMR (thf-d_8, 125 MHz): −9.9 (CH_3Si1), 20.5 (CH_3Si2), 66.9 (12-K-4), −125.5 ($SiCHCH_2$), 158.7 ($SiCHCH_2$). ^{29}Si NMR (thf-d_8, 100 MHz): −59.1 (Si2), −95.4 (Si1). C, H ([%], calcd in parenth): C 34.54 (34.33), H 7.93 (8.40).

Preparation of $[Mg(12\text{-}C\text{-}4)_2][B_{10}H_{10}Si_2Me_2(C_2H)]_2\cdot thf$ (3f). To a solution of 334.3 mg (1.64 mmol) of *o*-silaborane in 20 mL of thf was added 3.50 mL of a solution of ethynylmagnesium bromide in the same solvent (0.5 M, 1.07 equiv). The solution turned slightly pinkish and clouded instantly. After 1 h 22 μL of Me_3SiBr (1/10 equiv) and 4.2 mL of a 0.8 M solution of 12-crown-4 in thf were added. The same procedure as for **3a** gave colorless needles that lost thf upon evacuation. Yield: 0.395 g (M = 835.66 g mol^{-1}, 58%). $^1H\{^{11}B\}$ NMR (thf-d_8, 500 MHz, TMS, J (Hz)): 0.68 (s, 3H, $SiCH_3$), 0.87 (s, 3H, $SiCH_3$), 1.18 (s, 1H, H9 or H12), 1.34(s, 2H, H4/5 or H7/11), 1.45 (s, 1H, H9 or 12), 1.53 (s, 2H, H4/5 or H7/11), 1.71(s, 2H, H8/10), 1.76 (mult, thf), 2.05 (s, 2H, H3/6), 2.36 (s, 1H, CC*H*), 3.61 (mult, thf), 4.07 (mult, 16H, 12-K-4). ^{11}B NMR (thf-d_8, 160 MHz, $Et_2O\cdot BF_3$, J (Hz)): −8.6 (d, $^1J = 134$, B3/6), −11.9 (d, $^1J = 134$, B8/10), −15.6 (d, $^1J = 122$, B4/5 or 7/11), −17.6 (d, B4/5 or 7/11), −18.9 (d, B9 a. B12). $^{13}C\{^1H\}$ NMR (thf-d_8, 125 MHz): −9.9 (CH_3Si1), 1.2 (CH_3Si2), 25.1 (thf), 66.9 (12-K-4), 67.2 (thf), 70.3 (Si1C*C*H), 82.3 (Si1*C*CH). ^{29}Si NMR (thf-d_8, 100 MHz): −52.2 (Si2), −112.3 (Si1). C, H ([%], calcd in parenth): C 34,78 (34,50), H 7,96 (7,96).

Preparation of 1-Methyl-2-phenyl-1,2-disila-*closo*-dodecaborane(12) (5). To a solution of 1.1469 g (3.49 mmol) of 1,2-diphenyl-1,2-disila-*closo*-dodecaborane(12) in 35 mL of thf was added 1.25 mL of a solution of methylmagnesium bromide in Et_2O (3 M, 1.07 equiv). The solution yellowed slightly. After 1 h a freshly prepared suspension of 1.3260 g (4.02 mmol, 1.15 equiv) of Ph_3CBF_4 (4.02 mmol, 1.15 equiv) in thf was added. The trityl salt dissolved instantly, while the solution turned deep yellow. After 35 min the solvent was removed under reduced pressure, and the oily residue was sublimated overnight at 160 °C/10^{-3} mbar. The product was dissolved in very little diethyl ether and cooled to −30 °C. Beautiful colorless needles resulted that were suitable for X-ray structure analysis. Yield: 0.330 g (35%, M = 266.50 g mol^{-1}). $^1H\{^{11}B\}$ NMR (acetone-d_6, 500 MHz, TMS, J (Hz)): 1.47 (s, 3H, $SiCH_3$), 1.93 (s, 2H, H8/10), 2.04 (s, 2H, H4/5/7/11), 2.11(s, 2H, H9/12), 2.19 (s, 2H, H3/6)**,** 7.66 (mult, 2H, m-Ph), 7.81 (mult, 1H, *p*-Ph), 7.98 (mult, 2H, *o*-Ph). ^{11}B NMR (acetone-d_6, 160 MHz, $Et_2O\cdot BF_3$, J (Hz)): −11.5 (d, B8/10), −12.9 (d, B9/12), −14.1 (d, B3/6), −14.8 (d, B4/5/7/11). $^{13}C\{^1H\}$ NMR (acetone-d_6, 125 MHz): −10.9 (CH_3MeSi), 130.6 (*o*- or *m*-Ph), 135.0 (*p*-Ph), 137.7 (*o*- or *m*-Ph), *i*-Ph was not observed. ^{29}Si NMR (acetone-d_6, 100 MHz): −35.1 (MeSi), −42.9 (PhSi). HRMS for $^{12}C_7{}^1H_{18}{}^{11}B_{10}{}^{28}Si_2$: 268.188032 (calcd 268.187762).

X-ray Structure Determination of 3c and 5. Geometry and intensity data were collected on Enraf-Nonius CAD4 diffractometers equipped with graphite monochromators. A summary of crystal data, data collection parameters, and convergence results is compiled in Table 2. In the case of **5** an empirical absorption correction based on azimuthal scans[19] was applied before averaging over symmetry equivalent reflections. The structures were solved by direct methods[20] and refined on structure factors with the SDP program suite.[21] The quality of the structure determination of **3c** suffers from disorder in the crown ether moiety and highly anisotropic displacement parameters in the cocrystallized thf molecule. In the refinement of **3c** the oxygen and carbon atoms of the crown ether group were refined isotropically, remaining non-hydrogen atoms were assigned anisotropic displacement parameters, and hydrogen atoms were included as riding in calculated positions with B−H = 1.1 Å, C−H = 0.98 Å, a common refined displacement parameter for the hydrogen atoms bonded to boron, and $U_{iso}(H) = 1.3U_{eq}(C)$ for the H atoms bonded to carbon. In **5** all non-hydrogen atoms were refined with anisotropic displacement parameters, and the positional parameters and a common isotropic displacement parameter were refined for the hydrogen atoms bonded to boron; carbon-bonded H atoms were treated as riding with C−H = 0.98 Å, $U_{iso}(H) = 1.3U_{eq}(C)$. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbh, 76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CCDC-133530 (**3c**) and CSD-133529 (for **5**).

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Supporting Information Available: Listings of all fractional atomic coordinates and equivalent isotropic displacement parameters, interatomic distances and angles, and anisotropic displacement parameters. Listings of the Cartesian coordinates of the calculated geometry for the anion of **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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