Transformation of 3,4-Bis(isopropylidene)-2,5-dichloro-1,2,5-thiadiborolane into *nido*-2,4,5-Thiadicarbahexaborane(5) Derivatives − Formation and Computational Elucidation of a Thiadicarbanonaborane(8) with a *ni*-9<IV+IV> Configuration[☆]

Volker Beez[a], Peter Greiwe[a], Hans Pritzkow[a], Matthias Hofmann[b], Paul v. R. Schleyer*[b,c], and Walter Siebert*[a]

Anorganisch-Chemisches Institut der Universität Heidelberg[a],
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Computer-Chemie-Centrum, Institut für Organische Chemie[b],
der Universität Erlangen-Nürnberg,
Nägelsbachstraße 25, D-91054 Erlangen, Germany

Center for Computational Quantum Chemistry, University of Georgia[c],
Cedar Street 1004, Athens, GA 306052−2525, USA

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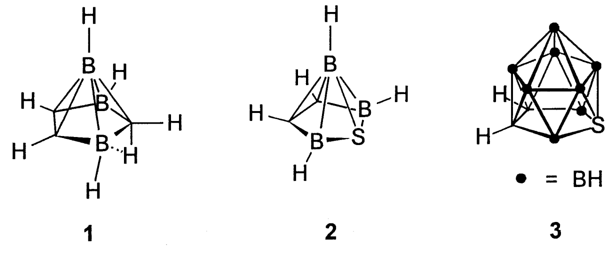
The 3,4-bis(isopropylidene)-2,5-dichloro-1,2,5-thiadiborolane (**5b**), obtained from 3,4-bis(dichloroboryl)-2,5-dimethyl-2,4-hexadiene (**4**) and $(Me_3Si)_2S$, reacts with $Li[RBH_3]$ (R = H, C_6H_5, C_6Me_4H) to yield the corresponding derivatives of the *nido*-4,5-diisopropyl-2,4,5-thiadicarbahexaboranes **2**. Replacements of the chlorine atoms in **5b** with two hydrido, or with one hydrido and one aryl (phenyl or duryl) group, followed by the hydroboration of the isopropylidene substituents with RBH_2 (R = H, C_6H_5, C_6Me_4H) lead to four *nido*-2,4,5-thiadicarbahexaboranes (**2a–d**) in low yields. Their composition follows from MS and NMR data; not refined X-ray structural data of **2d** support the proposed skeletal structure. In addition to **2a**, larger thiacarboranes were detected by GC/MS and ^{11}B NMR. The structure of the nine-vertex cluster **6a** could be identified by applying the ab initio/IGLO/NMR method. Geometry optimizations at the MP2(fc)/6–31G* level rule out the C_s *nido*-$SC_2B_6H_8$ isomer **7**. The C_{2v} structure of **6** consists of a nine-vertex cluster with two elongated B–B distances. As this 22e cluster **6** represents an exception to the Wade rules, the nature of the bonding of nine-vertex clusters with different electron counts is discussed.

The thiacarboranes and thiadicarboranes with nine to eleven skeletal atoms, *arachno*-SCB_7H_{11}[1][2], *arachno*-SCB_8H_{12}[2], *nido*-SCB_9H_{11}[2], *arachno*-$SC_2B_6H_{10}$[3], *nido*-$SC_2B_8H_{10}$,[4][5][6] have been obtained from the reactions of neutral carboranes or their anions with sulfur or sulfur compounds. Among the smaller but still unknown thiacarboranes, the *nido*-$SC_2B_3H_5$ cluster (**2**) is of particular interest to us, since it could be isoelectronic with 2,3,5-tricarbahexaborane(7) (**1**)[7]. Formal replacement of the CH_2 group in **1** by sulfur leads to **2**. The axial hydrogen in **1** bends and is involved to some extent in a 3c,2e CHB bonding.[7][8] The reaction of the $C_2B_{10}H_{13}^-$ anion with $KHSO_3$ in acid degrades the carborane and incorporates a sulfur atom to yield *arachno*-8,6-$SCH_2B_7H_9$[5]. The analogous reaction of **1** or its anion $C_3B_3H_6^-$ with $KHSO_3$ does not seem feasible, because no BH groups should be eliminated. Such BH units are needed to abstract the oxygen atoms of $KHSO_3$ (as is the case with $C_2B_{10}H_{13}^-$). The structurally and electronically related *nido*-$SC_2B_8H_{10}$ (**3**) is obtained in aqueous solution from the reaction of $K_2S_2O_5$ with $K[7,8\text{-}C_2B_9H_{12}]$. One BH group and a hydrogen atom are replaced by a sulfur atom to give **3**. The cluster **3** differs from **2** by the $(BH)_5$ belt.

We now present our results on the designed synthesis of derivatives of **2**, obtained from the hydroboration substitution reactions of the unsaturated 1,2,5-thiadiborolane derivative **5b**. Other products are formed as well. Of these, the thiadicarbanonaborane **6a** could be identified by GC-MS, ^{11}B-NMR spectra, and by applying the ab initio/IGLO/NMR method.

Scheme 1



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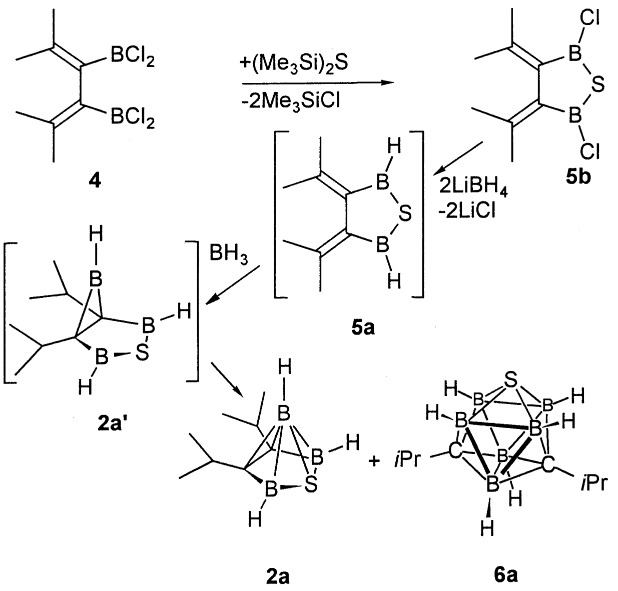
Results and Discussion

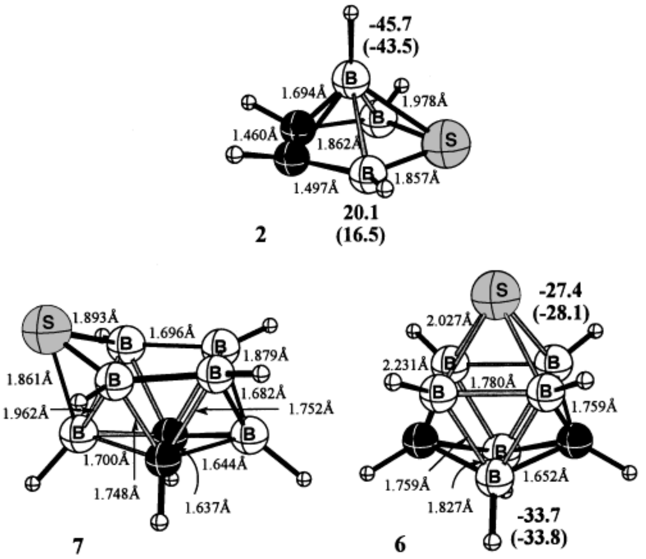
The reaction of 3,4-bis(dichloroboryl)-2,5-dimethyl-2,4-hexadiene (**4**)[9] with hexamethyldisilathiane leads to elimination of chlorotrimethylsilane to give 3,4-bis(isopropylidene)-2,5-dichloro-1,2,5-thiadiborolane (**5b**) in 86% yield (Scheme 1). Compound **5b** is isolated as a slightly yellow liquid[10] by distillation in vacuum. It is extremely air- and moisture-sensitive due to the high reactivity conferred by the B−Cl and B−S bonds. The composition of **5b** follows from NMR and MS data, whereas the assignment of the ^{1}H- and ^{13}C-NMR signals for the *exo*- and *endo*-methyl substituents of the isopropylidene groups was not possible.



The reactions of **5b** with lithium borates, Li[RBH$_3$] (R = H, C$_6$H$_5$, C$_6$Me$_4$H), yield several products. We presume that the first step involves substitution of the chlorine atoms in **5b** by hydrogen from LiBH$_4$ to give **5a**, but it was not isolated. In the next step, BH$_3$, formed in situ, hydroborates the double bonds of **5b**. The bicyclic organothiaborane **2a′** is an isomer of the product **2** whose existence as an intermediate may be supposed, but was not proven.With the formation of the *nido*-thiacarborane **2a** the coordination numbers increase from three to six for the apex boron atom and from three to four for the basal boron atoms. In addition to **2a**, other products are formed which could not be separated completely by distillation. The ^{11}B-NMR spectrum shows low-field signals for organoboranes and organothiaboranes as well as high-field signals. Unexpectedly, the GC-MS spectrum of the reaction mixture exhibits the molar peak for the thiadicarbanonaborane(8) derivative **6a** at $m/z = 213$ with the correct isotopic pattern for six boron atoms. In the $\{^1H\}^{11}B$-NMR spectrum three sets of signals at $\delta = 1.3/2.2$ (intensity ratio ca. 2:1), $-20.1/-20.7$ (ca. 1:2) and at $-28.2/-33.8$ (ca. 1:2) are observed, the latter signals are assigned to **6a**.

If S were to contribute four bonding electrons, the product S(CR)$_2$(BH)$_6$ would have a 22 skeletal electron count[11]; this suggests a nine-vertex *nido* cluster. Structure **7** is a *ni*-9<V> cluster with a pentagonal open face. The MP2(fc)/6−31G* optimized structure of **7** is shown in Figure 1 together with the computed IGLO ^{11}B-NMR chemical shifts for **2** and **6**. The experimental 2:1 ^{11}B intensity pattern would be in line with structure **7** only if the S atom fluctuated from one BBB capping position to the other. However, the averaged theoretical shifts (4.3, −6.4) which might result from such fluctuation are in gross disagreement with the experimental values (−28.2, −33.8). Hence, structure **7** can be discarded from consideration. While the sulfur atom is at the vertex of lowest connectivity ($k = 3$), the carbon atoms in **7** are placed at $k = 5$ and not at the more favorable $k = 4x$ positions. For alternatives with carbons in the open face (at $k = 4$ positions), more than the observed two signals in the ^{11}B NMR spectrum are expected.

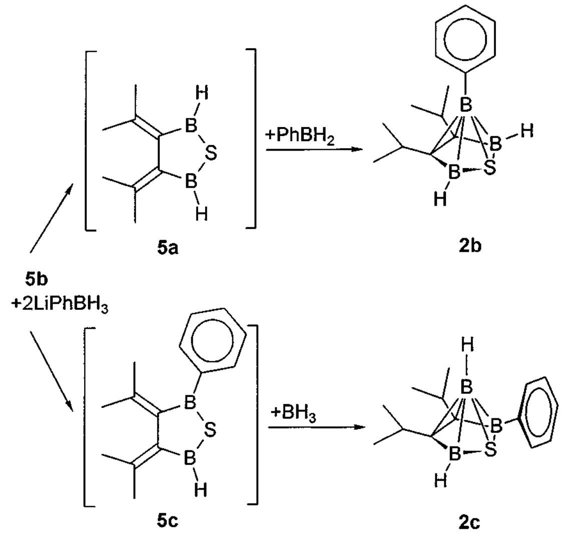
Figure 1. Computed geometries and ^{11}B chemical shifts of SC$_2$B$_3$H$_5$(**2**), C_s isomer SC$_2$B$_6$H$_8$ (**7**), and C_{2v} isomer SC$_2$B$_6$H$_8$ (**6**)



A C_{2v} starting geometry, where the S resides above a BBBB rectangular face, would be optimized to structure **6**; it is 66.3 kcal mol^{-1} lower in energy than **7**. Since the chemical shifts computed for **6** are very close to the values measured for **6a**, both have the same basic structure. The framework of **6** can be regarded as a triply capped trigonal prism and all hetero atoms are at the capping $k = 4$ positions. There are two large BB separations (2.23 Å) which suggest that the cluster should be considered as a *ni*-9<IV+IV> cluster with two tetragonal faces[12]. Such a cluster would be consistent with the *nido* electron count provided the S atom contributes four to a total of 22 skeletal electrons. For clarification we applied the NBO localization scheme.[13] Only one lone pair orbital on sulfur with an occupancy close to 2 (1.966) was found. This implies that the remaining four valence electrons are involved in cluster bonding which results in a *nido* electron count for SC$_2$B$_6$H$_8$, **6** (22 skeletal electrons).

The parent nine-vertex cluster anion *closo*-[B$_9$H$_9$]$^{2-}$is unusual in having non-degenerate frontier orbitals: HOMO-1, HOMO, and LUMO (A_1', A_2', and A_2'', respectively). This implies that addition of two or removal of two or even four skeletal electrons need not cause symmetry reduction and disruption of the basic D_{3h} cluster structure. However, reduction or oxidation of $[B_9H_9]^{2-}$ changes the cluster B−B separations depending on the bonding and antibonding character of the occupied MOs. Both addition and removal of two electrons from $[B_9H_9]^{2-}$ elongate the B1-B1′ and shorten the B1−B1 distance (for numbering the atoms compare Table 2). The same effects are observed if all three capping HB vertices in $[B_9H_9]^{2-}$ are replaced by isolobal HC^+ groups to give the isoelectronic $[C_3B_6H_9]$ species: "hypo-*closo*", "*closo*", or "*nido*" (Table 2). With capping sulfur atoms (S^{2+} is isolobal to HC^+), adding two electrons to *closo*-$[S_3B_6H_6]^{4+}$ also results in shortening of B1−B1 and elongation of B1−B1′. However, the B1−B1′ bonds are larger in $[S_3B_6H_6]^{4+}$ and $[S_3B_6H_6]^{2+}$ than in the other cases. Hence, the large B1−B1′ separation (2.231 Å) involving the S cap in **6** turns out to be normal for a *nido* electron count in the nine-vertex cluster. This is in agreement with structural data of the unusual silicid compound $Rb_{12}Si_{17}$, which contains four crystallographically different Si_9^{4-} clusters besides Si_4^{4-} tetrahedra. Three of them (**B**, **C**, and **D**) are described as tricapped trigonal prisms elongated along the threefold axes. The cluster **B** has two long edges (3.09) and one short edge (2.63 Å).[14] In the Zintl phase K_4Pb_9 two different clusters, a monocapped square antiprism and an elongated tricapped trigonal prism with two long edges (3.90) and one short edge (3.45 Å) are present.[15]

Scheme 2



The analogous reaction of **5b** with lithium phenylborate yields the isomers **2b** and **2c** which could not be separated. According to the NMR data, the isomers are formed in a 5:1 molar ratio, the isomer with the phenyl group in the apex position being favored. This finding indicates that the chlorine atoms in **5b** are predominantly substituted by hydrogen atoms (leading to **2b**) rather than by the phenyl group (**2c**).

In order to study the steric influence of the aryl group on the formation of isomers, **5b** was reacted with lithium durylborate. Surprisingly this reaction leads to derivative **2d** with the duryl group in a basal position (Figure 2). This result may be interpreted in terms of the different reactivities of the lithium borates.

Spectra and Structural Characterization

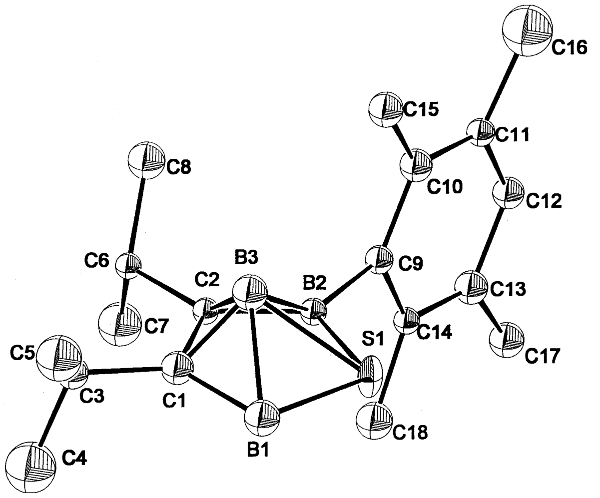
The ^{11}B-NMR data support the assigned structures of the compounds **2a−d**. Their substitution patterns follow from the ^{1}H- coupled ^{11}B-NMR spectra, which clearly show doublets for **2a**, **c**, **d** at high field ($\delta = -39$ to -41). The absence of this signal for **2b** indicates that the phenyl group is in the apex position. Both **2a** and **2b** have C_s symmetry, whereas **2c** and **2d** have C_1 symmetry and show three different ^{11}B-NMR signals in a 1:1:1 ratio. The ^{1}H-NMR spectra of **2c** and **2d** exhibit two sets of signals for the isopropyl group, in agreement with C_1 symmetry. The ^{13}C-NMR data also support the proposed constitutions. Since a mixture of compounds was present, it was not possible to assign the ^{1}H- and ^{13}C-NMR signals to **6a**.

Despite numerous crystallisation attempts, only **2d** yielded single crystals. A structure analysis was carried out on a crystal belonging to the orthorhombic space group $Pn2_1a$ with $a = 7.518$ (5), $b = 20.12$ (2), $c = 12.86$ (1) Å, $V = 1946$ Å^3, $Z = 4$. The bad quality of the crystals yielded only a very limited data set, which allowed the solution of the structure but not a reliable refinement. However, the analysis supports the proposed connectivity of the atoms in a *nido* arrangement. Due to the large uncertainty in bond distances and angles these details are not discussed here. The computed geometry parameters of **2** (see Figure 1) should be reliable and closely resemble the geometric features of **2a** as suggested by the close agreement between experimental ^{11}B-NMR chemical shifts for **2a** and values computed for **2**. The open five-membered face is essentially planar (the angle between the BCCB and the BSB plane is 176.1°) and the bond lengths S−B = 1.857, B−C = 1.497, C−C = 1.460 Å are shorter than in the analogous *nido*-thiadicarbaundecaborane(10) **3** (S−B = 1.915, B−C = 1.597, C−C = 1.542 Å).[16]

Computational Details

Geometries of **2**, **6**, and **7** have been optimized at HF/6−31G* and MP2(fc)/6−31G* levels of theory using the Gaussian 94 program.[17] The structures correspond to local minima on the SCF potential energy surface as shown by analytical frequency calculations (absence of imaginary frequencies). Chemical shifts have been computed with the IGLO program[18] applying Huzinaga's basis set[19] of DZ or II′ quality in the recommended contraction scheme[18c]. A gas phase chemical shift of 16.6 ppm[20] for B_2H_6 and shielding constants of 115.6 (DZ) and 103.0 (II′) have been used as reference to the experimental standard, $BF_3 \cdot OEt_2$.

Figure 2. Molecular structure of compound **2d**



Model compounds listed in Table 2 have been optimized by the B3LYP DFT (density functional theory) method using the three parameter exchange parameter by Becke (B3)[21] and the correlation functional by Lee, Yang, and Parr (LYP),[22] including both local and non-local terms, as implemented in Gaussian 94.[17]

Table 1. Computed chemical shifts[a] for **2**, **6**, and **7** in comparison to experimental values

2, C_s	DZ	−45.7 (B1)	+20.1 (B2,5)
Exp. **2a**		*−43.5 (1 B)*	*+16.5 (2 B)*
7, C_s	DZ	31.0 (B1), −22.5 (B8)	−6.0 (B2,5), −6.8 (B6,8)
7, C_s av.	DZ	+4.3 (B1,8)	−6.4 (B2,5,6,8)
6, C_{2v}	DZ	−32.5 (B1,3)	−25.6 (B5,6,7,8)
6, C_{2v}	II′	−33.7 (B1,3)	−27.4 (B5,6,7,8)
Exp. **6a**		*−33.8 (2 B)*	*−28.1 (4 B)*

[a] δ^{11}B.

Table 2. Computed distances[a] in nine-vertex clusters having tricapped trigonal prism structures (D_{3h}- or D_{3h}-like) and different numbers of skeletal electrons

$[B_9H_9]^q$	B1−B1[b]	B1−B1′[c]	B1−B2[d]
$q = 2+$	1.947	2.133	1.772
$q = 0$	1.795	2.022	1.751 “hypo-closo”
$q = 2-$	1.987	1.792	1.712 “closo”
$q = 4-$	1.803	2.157	1.791 “nido”
$[B_6H_6(CH)_3]^q$	B1−B1	B1−B1′	B1−C
$q = 3+$	1.904	2.148	1.704 “hypo-closo”
$q = 1+$	2.021	1.796	1.611 “closo”
$q = 1-$	1.761	2.036	1.651 “nido”
$[B_6H_6(S)_3]^q$	B1−B1	B1−B1′	B1−S
$q = 4+$	2.122	2.091	1.978 “closo ”
$q = 2+$	1.782	2.345	1.999 “nido ”
$[B_6H_6(CH)_2S]$	B1−B1	B1−B1′	B1−X
at CH cap:	1.759	1.827	1.652 “nido”[c]
at S cap:	1.780	2.231	2.027

[a] //B3LYP/6−31G* geometries. − [b] Distance in the $(B1)_3$ deltahedral base. − [c] Distance between the deltahedral bases $(B1)_3$ and $(B1')_3$. − [d] Distance between B1 and the capping atom B2, CH, or S. − [e] //RMP2(fc)/6−31G*.

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Experimental Section

All reactions and manipulations were performed in dry glassware under argon by using standard Schlenk techniques. Solvents were distilled from appropriate drying agents under argon before use. − $Et_2O \cdot BF_3$ was used as the external standard for ^{11}B NMR. As internal standards for ^{1}H-and ^{13}C-NMR spectra the signals of the deutero solvents were used and calculated for TMS. NMR: $CDCl_3$ solutions, Bruker AC 200. − MS: Varian MAT CH7 and GCMS HP 5971. − The following starting materials were prepared by methods described in literature: 3,4-bis(dichloroboryl)-2,5-dimethyl-2,4-hexadiene (**4**)[9], lithium phenylborate[9], lithium durylborate[23]. Hexamethyldisilathiane and lithium borate were commercially obtained.

2,5-Dichloro-3,4-bis(isopropylidene)-1,2,5-thiadiborolane (**5b**): 6.84 g (38.4 mmol) of hexamethyldisilathiane were added dropwise to a solution of 10.44 g (38.4 mmol) of **4** in 150 ml of n-hexane at 0° C. After 4 h heating to reflux, the solvent was removed under vacuum. Distillation yielded 7.68 g (33.0 mmol, 86%) of slightly yellow **5b**, b.p. 61° C/ $8 \cdot 10^{-3}$ Torr. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.74, 2.21 (2 s, 2×6 H, $CCH_{3\,\mathrm{exo}}$ or *endo*). − ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 62. − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 23.1, 26.6 (2 s, $C\mathit{C}H_{3\,\mathrm{endo}}$ or *exo*), 142 [s, br, $B\mathit{C}C(CH_3)_2$], 149.7 [s, $\mathit{C}(CH_3)_2$]. − MS(EI), *m/z* (%) = 232 [M^+] (42.0), 217 [$M^+ - CH_3$] (39.4), 190 [$M^+ - C_3H_6$] (17.8), 41 ($C_3H_5^+$, 78.7).

nido-4,5-Diisopropyl-2,4,5-thiadicarbahexaborane(5) (**2a**): 215 mg (9.87 mmol) of lithium borate were suspended in 20 ml of hexane and 880 mg (3.78 mmol) of **5b** in 5 ml of hexane were added at −78° C. After 1 h at this temp. the mixture was stirred 12 h at room temp.. The suspension was filtered and the solvent was removed under vacuum. Distillation yielded 70 mg (0.39 mmol, 10%) of colorless impure **2a**, b.p. 70° C/1.5 Torr, which could not be separated from **6a** and other by-products. − ^{1}H-NMR data of **2a** ($CDCl_3$, 200 MHz): δ = 1.17, 1.27 [2 d, 2×6 H, $HC(C\mathit{H}_3)_2$, $^3J_{H,H}$ = 6,8 Hz *endo* or *exo*], 2.45 [sept, 2 H, $\mathit{H}C(CH_3)_2$, $^3J_{H,H}$ = 6.8 Hz], (HB not detected). − ^{11}B-NMR data of **2a** ($CDCl_3$, 64 MHz): δ = −43.5 (d, 1 B, $^1J_{B,H}$ = 208 Hz), 16.5 (d, 2 B, $^1J_{B,H}$ = 167 Hz). MS(EI) data of **2a** : *m/z* (%) = 178 [M^+] (40.9), 163 [$M^+ - CH_3$] (17.5), 135 [$M^+ - C_3H_7$] (19.1), 41 [$C_3H_5^+$] (100). − ^{11}B-NMR data of **6a** ($CDCl_3$, 64 MHz): δ = −28.1 (d, 2 B, $^1J_{B,H}$ = 179 Hz), −33.8 (d, 1 B, $^1J_{B,H}$ = 173 Hz). − MS(EI) data of **6a**: *m/z* (%) = 213 [M^+] (100), 198 [$M^+ - CH_3$] (33.0), 170 [$M^+ - C_3H_7$] (29.6), 41 [$C_3H_5^+$] (15.5).

Mixture of nido-4,5-Diisopropyl-1-phenyl-2,4,5-thiadicarbahexaborane(5) (**2b**) *and nido-4,5-Diisopropyl-3-phenyl-2,4,5-thiadicarbahexaborane(5)* (**2c**): 780 mg (8.0 mmol) of lithium phenylborate were suspended in 50 ml of hexane and 930 mg (4.0 mmol) of **5b** solved in 20 ml of hexane were added under reflux conditions. After 2 h at this temp. the mixture was stirred 12 h at room temp.. The suspension was filtered and the solvent was removed under vacuum. Distillation yielded 180 mg (0.7 mmol, 18%) of colorless **2b**, **c**, b.p. 60−75° C/ $5 \cdot 10^{-2}$ Torr. − NMR data of **2b**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.27, 1.32 [2d, 2x6 H, $HC(C\mathit{H}_3)_{2\,\mathrm{endo}}$ or *exo*, $^3J_{H,H\,=\,6}$,8 Hz], 2.75 [sept, 2 H, $\mathit{H}C(CH_3)_2$, $^3J_{H,H}$ = 6,8 Hz], 7.12−7.67 (m, 5 H, C_6H_5). − ^{11}B NMR ($CDCl_3$, 64 MHz): δ = −31.8 (s, 1 B), 20.0 (d, 2 B, $^1J_{B,H}$ = 155 Hz). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 24.4, 25.6 (2 s, $C\mathit{C}H_{3\,\mathrm{endo}}$ or *exo*), 27.8 [s, $H\mathit{C}(CH_3)_2$], 127.4, 127.6 (2 s, *ortho*- or *meta*-C), 138.6 (s, *para*-C), (CB not detected). NMR data of **2c**: ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.00, 1.13, 1.25, 1.34$ [4d, 4×3 H, $HC(CH_3)_2$, $^3J_{H,H} = 6.8$ Hz], 2.53 [sept, 2 H, $HC(CH_3)_2$, $^3J_{H,H}$ = 6,8 Hz], 7.12−7.67 (m, 5 H, C_6H_5). − ^{11}B NMR ($CDCl_3$, 64 MHz): $\delta = -41.4$ (d, 1 B, $^1J_{B,H}$ = 206 Hz), 15.3 (d, 1 B, $^1J_{B,H}$ = 172 Hz), 27.5 (s, 1B). − ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 23.6, 23.9, 24.0, 24.9$ [4 s, $HC(CH_3)_2$], 27.1, 28.8 [2 s, $HC\ (CH_3)_2$], 131.2, 133.9 (2 s, *ortho*- or *meta*-C), 138.6 (s, *para*-C), (CB not detected). − MS(EI): *m/z* (%) = 254 [M^+] (100), 239 [$M^+ - CH_3$] (13.1), 211 [$M^+ - C_3H_7$] (24.2), 41 [$C_3H_5^+$] (93.8).

nido-4,5-Diisopropyl-3-duryl-2,4,5-thiadicarbahexaborane(5) (**2d**): 1.6 g (10.0 mmol) of lithium durylborate were suspended in 100 ml of hexane and 1.16 mg (5.0 mmol) of **5b** solved in 100 ml of hexane were added under reflux conditions. After 2 h at this temp. the mixture was stirred 12h at room temp., then filtered, and the solvent was removed under vacuum. Sublimation yielded 480 mg (1.5 mmol, 31%) of colorless **2d**, s.p. 105° C/ $5\cdot10^{-2}$ Torr. − ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.01, 1.12, 1.26, 1.34$ [4d, 4×3 H, $HC(CH_3)_2$, $^3J_{H,H}$ = 6,8 Hz], 2.15, 2.24, 2.26, 2.32 (4 s, 4×3 H, *ortho*- or *meta*-CH_3), 2.50, 2.56 [2 sept, 2×1 H, $HC(CH_3)_2$, $^3J_{H,H}$ = 6,8 Hz], 7.00 (s, 1 H, *para*-CH). − ^{11}B NMR ($CDCl_3$, 64 MHz): $\delta = -39.5$ (d, 1 B, $^1J_{B,H}$ = 203 Hz), 16.0 (d, 1 B, $^1J_{B,H}$ = 145 Hz), 28.4 (s, 1 B). − ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 19.9, 20.4, 20.5, 20.6$ (4 s, *ortho*- or *meta*- CCH_3), 22.9, 23.0, 24.9, 25.7 [4 s, $HC(CH_3)_2$], 27.7, 27.8 [2 s, $HC(CH_3)_2$], 109, 121 (2 s, br, CB), 131.7, 133.2, 133.3, 135.0 (4 s, *ortho*- or *meta*-CCH_3), 138.0 (s, *para*-CH). − MS(EI): *m/z* (%) = 310 [M^+] (100), 295 [$M^+ - CH_3$] (5.0), 267 [$M^+ - C_3H_7$] (62.2), 41 [$C_3H_5^+$] (49.8).

☆ Dedicated to Professor *Peter Jutzi* on the occasion of his 60th birthday.

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