

2,5-Dihydro-1,2,5-azoniasilaboratole Derivatives – Useful Starting Materials in Heterocyclic Synthesis

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1-Alkynyl(diethylamino)dimethylsilanes [C≡CR: R = Me (**1a**), *n*Bu (**1b**), SiMe₃ (**1c**)] react with triethylborane stereoselectively by 1,1-ethyloboration to give the alkenes with the boryl and silyl group in *cis*-positions at the C=C bond. Owing to the strongly intramolecular coordinative N–B bond, these products are 2,5-dihydro-1,2,5-azoniasilaboratoles (**2a–c**). Protic reagents such as azoles (indole, pyrazole, imidazole, triazole, indazole, benzotriazole) react with **2** to give diethylamine and the respective *N*-azolyl derivatives

3–8 which contain tetracoordinate boron in the case of **4–8**. Compound **7**, derived from indazole, was characterized by an X-ray analysis. With ethanol, the corresponding 2,5-dihydro-1,2,5-oxoniasilaboratole **9** are obtained. Treatment of **2** with water affords 1,2,5-oxasilaborolanes **11**, presumably via an intermediate **10** with the structure of a 2,5-dihydro-1,2,5-oxoniasilaboratole. All products were characterized by their ¹H-, ¹¹B-, ¹³C-, ¹⁵N-, and ²⁹Si-NMR data.

Heterocycles containing reactive silicon- and boron-element bonds are of considerable interest for further synthetic use. In organotin chemistry, 1,1-organoboration of 1-alkynyltin compounds proved to be extremely useful in heterocyclic syntheses^[1], whereas similar strategies in organosilicon chemistry have so far been demonstrated only for four types of heterocyclic systems, namely 1,2-dihydro-1,2,5-disilaborepines^[2], siloles^[3–5], 1,1'-spirobisiloles^[6], and recently for the synthesis of heterobicyclic boron compounds^[7].

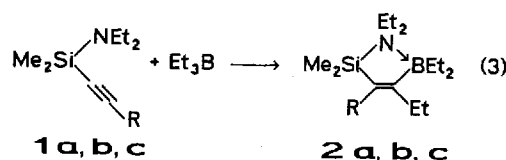
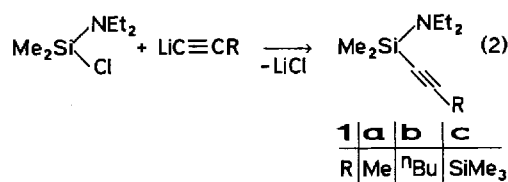
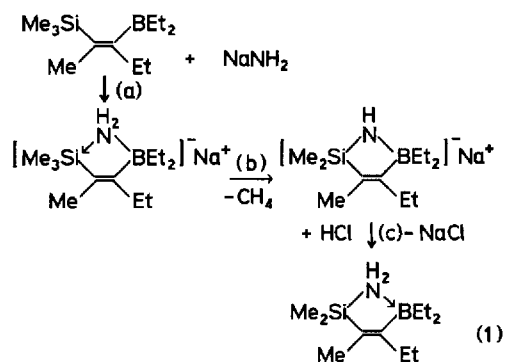
The synthesis of 2,5-dihydro-1,2,5-azoniasilaboratole of the type **2** was described previously by the route shown in eq. (1)^[3]. In this paper we report on a more direct way [eq. (3)], using 1,1-organoboration, by starting from 1-alkynyl-(diethylamino)dimethylsilanes **1** and triethylborane, Et₃B. The compounds **1** were prepared in high yield according to eq. (2), whereas in the literature differing routes such as the aminolysis of 1-alkynylchlorodimethylsilanes^[8] or 1-alkynyl(trifluorosulfonato)dimethylsilane^[9] are described.

The synthetic potential of the heterocycles **2** was tested in reactions with some protic reagents such as various azoles, ethanol, and water.

Results and Discussion

Preparative Results

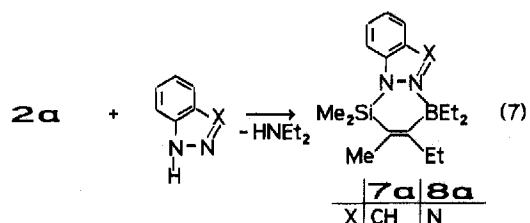
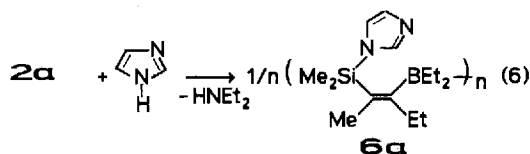
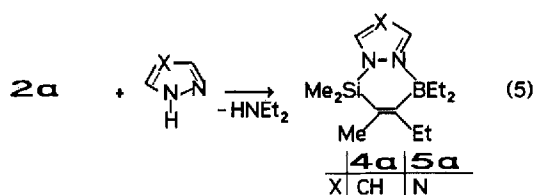
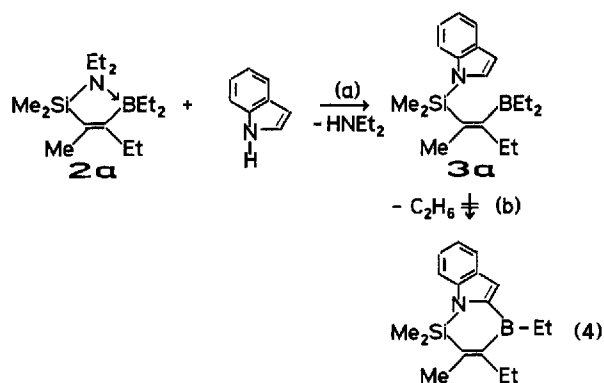
The 1-alkynyl(diethylamino)dimethylsilanes **1** are colorless liquids, easy to purify by distillation, but sensitive to moisture. In contrast to the corresponding tin compounds^[10,11], they are not in equilibrium with the symmetrically substituted silanes, even at a temperature of 100–120 °C. The reaction of **1** with Et₃B proceeds slowly (several days) at 100 °C, either in pure Et₃B or in toluene, and gives the compounds **2** in high yield [eq. (3)].



The 2,5-dihydro-1,2,5-azoniasilaboratole **2** are colorless liquids and can be distilled at reduced pressure. They are sensitive to traces of moisture, but can be stored for several

months without showing any sign of decomposition. The coordinative N–B bond is evident from all NMR data. Although it is well-known that *N*-silylamines are rather weak bases, this does not prevent an intramolecular ring closure by the coordinative N–B bond. In the following, the reactions are described mainly for **2a**, but the same type of reactions can also be carried out with **2b** or **2c** as was found by experiments on a small scale for NMR measurements.

The reaction of **2a** with indole [eq. (4)] proceeds smoothly and essentially quantitative to give **3a**, indicating that even weak protic reagents react with **2**. In compound **3**, all NMR data (Table 4) point to the presence of a tricoordinate boron atom, as expected because of the poor basic properties of the indole nitrogen atom. The yield of **3a** after distillation was only 57%, owing to thermal decomposition. Originally, it was hoped to induce elimination of ethane to obtain a new heterocycle [eq. (4b)], but there was no convincing evidence for the formation of this product.

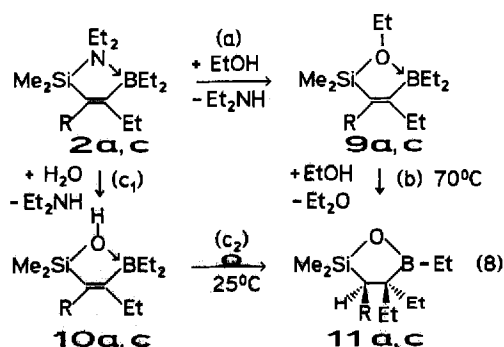


Pyrazole and 1,2,4-triazole react with **2a** to give the heterocycles **4a** and **5a** [eq. (5)] in very high yield (up to 90% after distillation). In the case of **4a**, the corresponding tin^[12] and lead derivatives^[13] are also known, and therefore a

complete NMR data set is available now for comparison (vide infra). Imidazole reacts with **2a** [eq. (6)] in the same way as the other azoles. However, the product **6a** is a polymer because of coordinative N–B bonds between the imidazole nitrogen atom in 3-position and the boryl group. Its general properties have not been studied as yet.

The general validity of this route to new heterocyclic systems is further illustrated by the smooth reactions of **2** with indazole and benzotriazole [eq. (7)] to give the tricyclic compounds **7a** and **8a**, respectively. After recrystallization from CH_2Cl_2 , the product **7a**, derived from indazole, gave crystalline material suitable for a single-crystal X-ray analysis (vide infra).

Treatment of **2a** or **2c** with an excess of ethanol leads to an almost quantitative conversion with formation of the 2,5-dihydro-1,2,5-oxoniasilaboratoles **9a** and **9c** [eq. (8a)]. Such compounds were prepared^[14] in a way analogous to that shown in eq. (1), except that potassium hydroxide instead of NaNH_2 was used in the first step [eq. (1a)]. The reaction of the resulting potassium salts, after elimination of methane, with various electrophiles, similar to the reaction eq. (1c), affords different *O*-substituted derivatives corresponding to **9**. This study^[14] has shown that the first logical product of the hydrolysis of **2** should be **10**, with hydrogen linked to oxygen [eq. (8c₁)]. Apparently, compounds of type **10** are fairly instable and rearrange to 1,2,5-oxasilaborolanes **11**^[14]. In contrast to the procedure reported previously^[14], the reaction according to eq. (8c_{1,c2}) proceeds without formation of side products, and the compounds **11** were obtained in $\geq 70\%$ yield after distillation. The compound **2c** was included here, since it seemed important to find out whether $\text{R} = \text{SiMe}_3$ hinders the rearrangement of **10c** to **11c**. However, the reaction proceeds in the same way as for $\text{R} = \text{Me}$. Interestingly, treatment of **2** with an excess of EtOH at 70°C for several hours also leads to **11** [eq. 8b] together with the formation of diethyl ether.

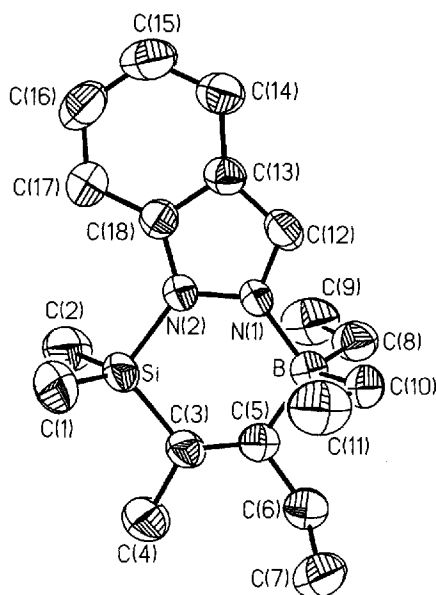


X-Ray Analysis of the Tricyclic Compound **7a**

Experimental data relevant to the X-ray analysis of **7a** are listed in the experimental part^[15]. The molecular structure of **7a** is shown in Figure 1. All bond lengths are found in the expected range. The tricyclic system is almost planar: The planes of the indazole and of the atoms Si–C(3)–C(5)–B form an angle of 6.5°. The surroundings of the silicon atom corresponds to a slightly distorted tetra-

hedron because of the endocyclic bond angle $N(2)-Si-C(3) = 105.8(1)^\circ$. In the case of the boron atom, the deviation from tetrahedral angles is smaller. As observed for several other molecular structures with the Et_2B group in a similar environment^[16,17], both *B*-ethyl groups are oriented towards the six-membered ring.

Figure 1. Molecular structure of **7a**. Selected bond lengths [pm] and angles [°]: $B-N(1)$ 163.2(4), $B-C(5)$ 162.1(4), $Si-N(2)$ 179.1(2), $Si-C(3)$ 182.8(3), $C(3)-C(5)$ 134.3(4), $N(1)-N(2)$ 136.9(3); $C(5)-B-N(1)$ 111.9(2), $N(2)-Si-C(3)$ 105.8(1), $B-N(1)-N(2)$ 127.5(2), $Si-N(2)-N(1)$ 122.4(2), $B-C(5)-C(3)$ 128.2(3), $Si-C(3)-C(5)$ 122.8(3)



NMR-Spectroscopic Results

^{13}C -, ^{15}N -, and ^{29}Si -NMR data of the 1-alkynyl(diethylamino)dimethylsilanes **1** are listed in Table 1. Tables 2 and 3 contain ^{11}B -, ^{13}C -, ^{15}N -, and ^{29}Si -NMR data of the 2,5-dihydro-1,2,5-azoniasilaboratoles **2** and of the products **3a–8a** obtained by the reaction of **2a** with the azoles. In Table 4, ^{11}B -, ^{13}C -, and ^{29}Si -NMR data of the 2,5-dihydro-1,2,5-oxoniasilaboratoles **9** and 1,2,5-oxasilaborolanes **11** are given. In Tables 2, 3, and 4 NMR data of corresponding tin and lead compounds were included for comparison.

Table 1. ^{13}C -, ^{15}N -, and ^{29}Si -NMR data^[a] of 1-alkynyl(diethylamino)dimethylsilanes **1a–c**

No.	1a	1b	1c
R ¹	Me	ⁿ Bu	SiMe ₃
$\delta^{13}C(SiC\equiv)$	83.9 [93.5]	84.6 [93.5]	112.2 [77.8,13.8]
$\delta^{13}C(C\equiv R)$	101.2 [18.7]	106.2 [17.7]	114.2 [12.8,82.7]
$\delta^{13}C(SiMe_2)$	0.7 [64.0]	0.8 [64.0]	0.4 [64.9]
$\delta^{13}C(R)$	4.5	22.2,31.1,19.8,13.7	0.0 [57.1]
$\delta^{13}C(NEt_2)$	40.7, 16.1	40.6, 15.9	40.5, 15.8
$\delta^{15}N$	-348.4 [23.2]	-348.3 [23.2]	-348.1 [23.2]
$\delta^{29}Si$	-18.6	-17.5	-18.5, -19.3 (SiMe ₃)

^[a] In C_6D_6 (ca. 15–25% v/v) at $25 \pm 1^\circ C$; coupling constants $^nJ(^{29}Si, ^{13}C)$ and $^1J(^{29}Si, ^{15}N)$ [Hz] are given in square brackets.

Table 2. ^{11}B -, ^{13}C -, ^{15}N -, and ^{29}Si -NMR data^[a] of the 2,5-dihydro-1,2,5-azoniasilaboratoles **2a–c** and of **2a(Sn)** and **2a(Pb,NH₂)** for comparison

No.	2a	2a(Sn)	2a(Pb,NH₂)	2b	2c
R	Me	Me	Me	ⁿ Bu	SiMe ₃
$\delta^{13}C(SiC\equiv)$	124.7 [82.7]	128.9 [653.9]	144.0 [741.1]	130.9 [81.7]	129.3 [61.0, 63.0]
$\delta^{13}C(B-C)$	182.5 (br)	182.0 (br)	178.1 (br)	182.4 (br)	212.2 (br)
$\delta^{13}C(SiMe_2)$	0.6 [52.2]	-2.1 [276.0]	12.4 [+10.4]	2.0 [52.2]	3.2 [51.2]
$\delta^{13}C(C\equiv R)$	12.4 [9.8]	18.8 [135.7]	23.0 [289.9]	33.7,28.3,23.3,14.4	2.5 [49.2]
$\delta^{13}C(C\equiv Et)$	25.8, 14.3	25.4, 14.8 (115.0) [5.6]	26.5, 14.5 (252.4) [28.3]	26.0, 15.2	32.9, 16.4
$\delta^{13}C(BEt_2)$	13.9 (br), 11.8	14.6 (br), 12.0	18.4 (br), 10.8	13.9 (br), 11.8	13.9 (br), 11.8
$\delta^{13}C(NEt_2)$	45.8, 13.2	45.5, 14.7	--	46.0, 13.2	46.4, 13.4
$\delta^{11}B$	6.0	1.6	-2.1	5.0	4.0
$\delta^{15}N$ [b]	-332.2 [6.5]	-330 ($\delta^{14}N$)	-364.5 (n.m.)	-338.3 [6.5]	-337.6 [5.3]
$\delta^{29}Si$	25.5	+124.1 ($\delta^{119}Sn$)	427.6 ($\delta^{207}Pb$)	25.5	30.4, -14.9 (SiMe ₃) [16.3] [16.3]

^[a] In C_6D_6 (ca. 15–25% v/v) at $25 \pm 1^\circ C$; coupling constants [Hz] $^nJ(^{29}Si, ^{13}C)$, $^1J(^{29}Si, ^{15}N)$, and $^2J(^{29}Si, ^{29}Si)$ are given in square brackets, $^nJ(^{119}Sn, ^{13}C)$ [**2a(Sn)**] and $^nJ(^{207}Pb, ^{13}C)$ [**2a(Pb,NH₂)**] in curved brackets; (br) denotes a broadened ^{13}C (B)-NMR signal; n.m. = not measured. - ^[b] $\delta^{15}N$ data for comparison: **2a(NH₂)**: -354.4^[3], **2a(NHMe)**: -356.8^[31], **2a(NMe₂)**: -358.0^[31].

All NMR data support the proposed structures. The $\delta^{13}C$, $\delta^{15}N$, and $\delta^{29}Si$ data as well as the coupling constants $^1J(^{29}Si, ^{13}C)$ and $^1J(^{29}Si, ^{15}N)$ of the compounds **1** are typical of both alkynylsilanes^[18] and aminosilanes^[19].

The $^1H(BCH_2)$ -NMR signals of the compounds **2** show the expected pattern for diastereotopic protons proving the coordinative N–B bond. In contrast, the coordinative B–O bond in **9** appears to be weaker [compare also the $\delta^{11}B$ data for **9a** and **9a(Sn,OMe)**, **9a(Pb,OMe)**], since the splitting of the $^1H(BCH_2)$ -NMR signals is not resolved. The diastereotopic nature of these protons is lost if the coordinative B–O bond is opened and rotation of the Et_2B group about the B–C= bond is fast with respect to the NMR time scale. In principle, one expects the pattern for diastereotopic protons also for the $^1H(NCH_2)$ signals of **2** which, however, is only observed in the case of **2c**. Therefore, it is possible that the N–B bond is opened and closed at a rate which does not allow rotation of the Et_2B group but rotation of the Et_2N group about the longer Si–N bond, at least in **2a**, **b**. Low-temperature 1H - and ^{13}C -NMR spectra of **2a**, **2c** and of the corresponding tin derivative **2a(Sn)** indicate that these rings are non-planar, since different signals of the SiMe groups are clearly resolved at low temperature (-70 to $-80^\circ C$). The presence of the Me₃Si group in **2c** causes an increase in the barrier to ring inversion. The ΔG_c^\ddagger values^[20] of **2a** and **2a(Sn)** are of similar magnitude: 39.0 ± 0.5 and 38.1 ± 0.5 kJ/mol; that of **2c** is larger: $\Delta G_c^\ddagger = 47.2 \pm 0.5$ kJ/mol.

There are only few examples of geminal coupling constants $^2J(^{29}Si, ^{13}C)$ across an olefinic carbon atom. Such data were readily observed in the compounds studied here. Their sign is negative [$^2K(^{29}Si, ^{13}C) > 0$; K is the reduced coupling constant: $K(A,X) = 4\pi^2 \cdot J(A,X) \cdot (\gamma_A \gamma_X \hbar)^{-1}$], as determined by using Ψ -BIRD modified 1H -detected (HMQC^[21]) $^1H/^{29}Si$ shift correlations^[22], and also 2D z -filtered $^{13}C/^1H$ heteronuclear shift correlations^[23]. The abso-

Table 3. ^{11}B -, ^{13}C -, ^{15}N -, and ^{29}Si -NMR data of the indole derivative **3a** and the heterobi- and -tricyclic compounds **4a–8a**

No	3a	4a	4a(Sn)	4a(Pb)	5a	6a	7a	8a
derived from	indole	pyrazole	pyrazole	pyrazole	triazole	imidazole	indazole	benzotriazole
$\delta^{13}\text{C}(\text{SiC}=\text{C})$	126.6 [80.7]	117.7 [85.6]	125.7 [672.8]	146.6 [670.8]	116.7 [86.6]	121.8 [82.6]	118.5 [85.2]	117.1 [86.6]
$\delta^{13}\text{C}(\text{BC}=\text{C})$	167.4 (br)	176.4 (br)	175.8 (br)	172.6 (br)	176.2 (br)	185.7 (br)	174.6 (br)	175.9 (br)
$\delta^{13}\text{C}(\text{SiMe}_2)$	-1.3 [57.1]	-0.3 [56.1]	-3.8 [312.0]	15.3 [+38.4]	-0.6 [56.1]	1.4 [46.0]	-0.9 [55.6]	-1.1 [56.1]
$\delta^{13}\text{C}(=\text{CMe})$	14.8	14.1 [9.5]	20.4 [133.0]	23.4 [288.8]	12.8	18.6	14.0	13.1
$\delta^{13}\text{C}(=\text{CEt})$	22.4, 12.1	25.0, 13.3 [7.0]	25.8, 14.7 [116.6] [16.3]	27.1, 15.2 [247.0] [29.4]	24.5, 13.6	27.8, 13.7	25.1, 13.4	25.2, 13.7
$\delta^{13}\text{C}(\text{BEt}_2)$	20.5 (br), 9.0	19.0 (br), 10.3	19.2 (br), 10.9	17.7 (br), 11.1	18.2 (br), 9.8	16.3 (br), 10.0	19.7 (br), 10.2	18.6 (br), 10.5
$\delta^{13}\text{C}(\text{azole})$	130.2 (2) 104.7 (3) 131.6 (3a) [c]	138.1 (3) 107.6 (4) 134.1 (5)	137.8 (3) 106.3 (4) 136.4 (5)	135.4 [14.7] [b] 105.7 (9.0) 137.2 [22.6] [b]	148.2 [b] 149.6 [b]	138.9 (2) 125.6 (4) 121.1 (5)	134.0 122.7 143.6 [d]	143.7 136.7 111.8 [e]
$\delta^{11}\text{B}$	87.2	-0.7	-0.6	-1.2	-0.5	-3.2	0.5	3.6
$\delta^{15}\text{N}$	-240.4 [12.6]	-165.8 [7.4] -123.8	-155.2 [104.5] -119.0 (8.5)	-154.2 [358.4] -126.9	-158.7 [4.8] -127.6 -125.4	n.m. n.m.	-191.0 -112.9	n.m. n.m.
$\delta^{29}\text{Si}$	1.4	-0.1	9.1 ($\delta^{119}\text{Sn}$)	+180.5 ($\delta^{207}\text{Pb}$)	2.0	3.9	-1.9	4.6

[a] In C_6D_6 (ca. 15–25% v/v) at $25 \pm 1^\circ\text{C}$; coupling constants [Hz] $^1J(^{29}\text{Si},^{13}\text{C})$, $^nJ(^{29}\text{Si},^{15}\text{N})$ are given in square brackets, $^nJ(^{119}\text{Sn},^{13}\text{C})$, $^nJ(^{119}\text{Sn},^{15}\text{N})$ [**4a(Sn)**], $^nJ(^{207}\text{Pb},^{13}\text{C})$ and $^1J(^{207}\text{Pb},^{15}\text{N})$ [**4a(Pb)**] in curved brackets; (br) denotes a broadened $^{13}\text{C}(\text{B})$ -NMR signal; n.m. = not measured. – [b] No assignment given. – [c] Further $\delta^{13}\text{C}$ values of the indole group: 119.8 (4), 120.5 (5), 121.1 (6), 113.1 (7), 140.2 (7a). – [d] Further $\delta^{13}\text{C}$ values of the indazole group: 112.0, 128.6, 122.6, 121.9. – [e] Further $\delta^{13}\text{C}$ values of the benzotriazole group: 129.5, 126.0, 120.4.

Table 4. ^{11}B -, ^{13}C -, ^{15}N -, and ^{29}Si -NMR data[a] of 2,5-dihydro-1,2,5-oxoniasilaboratolanes **9a**, **9c**, of the compounds **9a(Sn,OMe)** and **9a(Pb,OMe)**[c] for comparison, and of the 1,2,5-oxasilaborolanes **11a** and **11c**

No.	9a	9a(Sn,OMe)	9a(Pb,OMe)	9c	No.	11a	11c
R	Me	Me	Me	SiMe_3	R	Me	SiMe_3
$\delta^{13}\text{C}(\text{SiC}=\text{C})$	124.2 [87.5]	128.7 [697.5]	150.1 [652.9]	130.9 [66.9,61.0]	$\delta^{13}\text{C}(\text{SiC}-3)$	22.7 [60.1]	21.3 [48.2, 49.2]
$\delta^{13}\text{C}(\text{BC}=\text{C})$	173.9 (br)	176.3 (br)	174.8 (br)	201.6 (br)	$\delta^{13}\text{C}(\text{BC}-4)$	40.7 (br)	44.8 (br)
$\delta^{13}\text{C}(\text{SiMe}_2)$	-0.6 [54.1]	-1.6 [288.3]	20.9 [-38.7]	1.7 [55.1]	$\delta^{13}\text{C}(\text{SiMe}_2)$	-1.9 [55.1], 0.6 [57.1]	1.7 [53.2], 2.8 [59.0]
$\delta^{13}\text{C}(=\text{CR})$	11.9 [11.8]	18.7 [146.0]	23.3 [279.0]	2.2 [51.2]	$\delta^{13}\text{C}(\text{C}-3-\text{R})$	11.7	2.2 [50.2]
$\delta^{13}\text{C}(=\text{CEt})$	23.3, 13.2 [8.9]	24.5, 13.8 [116.6] [16.9]	26.6, 14.0 [247.4] [27.2]	31.1, 14.7	$\delta^{13}\text{C}(\text{C}-4-\text{Et})$	26.5, 28.8, 7.3, 7.7	31.8, 33.4, 11.9, 12.6
$\delta^{13}\text{C}(\text{BEt}_2)$	14.3 (br), 10.5	13.4 (br), 10.5	14.1 (br), 10.7	14.6 (br), 10.4	$\delta^{13}\text{C}(\text{BEt})$	12.4 (br), 9.9	11.0 (br), 7.9
$\delta^{13}\text{C}(\text{OEt})$	60.1, 60.3	49.0 {4.4} (Me)	49.3 {6.5} (Me)	60.3, 16.4			
$\delta^{11}\text{B}$	23.0	10.7	8.2	19.9	$\delta^{11}\text{B}$	58.7	59.2
$\delta^{29}\text{Si}$	26.5	174.6 ($\delta^{119}\text{Sn}$)	656.0 ($\delta^{207}\text{Pb}$)	33.8, -15.0 (SiMe_3) [17.0] [17.0]	$\delta^{29}\text{Si}$	38.9	38.8, -2.5 (SiMe_3) [c] [c]

[a] In C_6D_6 (ca. 15–25% v/v) at $25 \pm 1^\circ\text{C}$; coupling constants [Hz] $^nJ(^{29}\text{Si},^{13}\text{C})$, and $^2J(^{29}\text{Si},^{29}\text{Si})$ are given in square brackets and $^nJ(^{119}\text{Sn},^{13}\text{C})$, $^nJ(^{207}\text{Pb},^{13}\text{C})$ in curved brackets; (br) denotes a broadened $^{13}\text{C}(\text{B})$ -NMR signal. – [b] Ref. [32]. – [c] Ref. [13,25b].

lute magnitude of these coupling constants is somewhat larger than in most alkenes bearing the Me_3Si and the Et_2B group in *cis* positions. This finding is in agreement with the same trend for $^2J(^{119}\text{Sn},^{13}\text{C})$ and $^2J(^{207}\text{Pb},^{13}\text{C})$ in the corresponding tin and lead compounds (see Tables 2–4). This was also observed for $^2J(^{29}\text{Si},^{29}\text{Si}) \approx 16$ to 17 Hz, e.g. in **2c** and in **9c** when compared with $^2J(^{29}\text{Si},^{29}\text{Si}) = 8.6$ Hz in 2-(diethylboryl)-1,1-bis(trimethylsilyl)-1-butene^[24], sug-

gesting that the sign of this coupling constant is also positive [$^2K(^{29}\text{Si},^{29}\text{Si}) > 0$].

The data set of the compounds **4a**, **4a(Sn)**, and **4a(Pb)** (Table 3) shows that most NMR data of **4a** and **4a(Sn)** are similar, as in the case of **2a** and **2a(Sn)** (Table 2) and **9a** and **9a(Sn,OMe)** (Table 4). However, in the case of **4a(Pb)** some marked changes can be noted, revealing the influence of a strained ring structure with extremely polar bonds.

This is also obvious from the comparison of the data for **2a**, **2a**(Sn), and **2a**(Pb,NH₂), **9a**, **9a**(Sn,OMe), and **9a**(Pb,OMe), although one tin compound and the lead compounds are not strictly analogous since they do not contain NEt₂ or OEt groups. The coupling constant $^1J(^{207}\text{Pb},^{13}\text{C}_{\text{Me}})$ in both **2a**(Pb,NH₂) and in **4a**(Pb) is small, although still positive as in Me₄Pb, as proved by 2D $^{13}\text{C}/^1\text{H}$ heteronuclear shift correlations^[25]. The sign of $^1J(^{207}\text{Pb},^{13}\text{C}_{\text{Me}})$ in **9a**(Pb,OMe) is negative, one of the few examples where an inversion of this coupling sign was observed^[25b]. Furthermore, there is a marked shift of ≈ 29 ppm to low field for the ^{13}C (Pb–C=) resonance signal in **4a**(Pb) as compared to that of ^{13}C (Si–C=) in **4a**. The changes in the bonding situation seems to concern mainly the “soft” part of the molecule with Pb–C bonds since $\delta^{15}\text{N}$ values are much less affected. However, one notes that the coupling constants $|^1J(^{29}\text{Si},^{13}\text{C}_{\text{C=}})|$, $|^1J(^{119}\text{Sn},^{13}\text{C}_{\text{C=}})|$, and $|^1J(^{207}\text{Pb},^{13}\text{C})|$ are rather large (all reduced coupling constants $^1K(\text{M}^{13}\text{C}_{\text{C=}})$ were found to be positive for the compounds studied). In contrast, the coupling constants $^1J(^{29}\text{Si},^{15}\text{N})$ are fairly small, but most probably still positive^[19] [$^1K(^{29}\text{Si},^{15}\text{N}) > 0$], in **2a** (6.5 Hz), **4a** (7.4 Hz), and **5a** (4.8 Hz) when compared with **3a** (12.6 Hz). This implies negative contributions to the reduced coupling constants $^1K(^{29}\text{Si},^{15}\text{N})$ (assuming the dominance of the Fermi contact term as coupling mechanism^[26]) which arise most probably from the strongly polarized Si–N bond in **2a** and in the heterobicyclic molecules. The polarization of the Sn–N and Pb–N bond in the analogous tin and lead compounds will be even greater, and negative contributions to $^1K(^{119}\text{Sn},^{15}\text{N})$ and $^1K(^{207}\text{Pb},^{15}\text{N})$ are expected to increase. Therefore, the reduced coupling constants $^1K(^{119}\text{Sn},^{15}\text{N})$ and $^1K(^{207}\text{Pb},^{15}\text{N})$ will be large and negative. In the case of most triorganotin amides, the coupling constants $^1J(^{119}\text{Sn},^{15}\text{N})$ are small and negative^[19] [$^1K(^{119}\text{Sn},^{15}\text{N}) < 0$]. So far, $^1J(^{207}\text{Pb},^{15}\text{N})$ values for all organolead(IV) amides were found to be large and positive^[19,27] [$^1K(^{207}\text{Pb},^{15}\text{N}) < 0$]. It should be noted that the value $^1J(^{207}\text{Pb},^{15}\text{N}) = 358.4$ Hz for **4a**(Pb) exceeds all values for organolead(IV) amides measured as yet.

The NMR data of the 2,5-dihydro-1,2,5-oxoniasilaboratoles (Table 4) are conclusive and agree with literature data^[14]. The same is true for the 1,2,5-oxoniasilaborolanes where already the ^{11}B -NMR spectra^[28] of crude reaction solutions show the presence of tricoordinate boron atoms.

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Experimental

All compounds were handled under Ar or N₂ by using carefully dried solvents and glassware. Deuterated solvents were stored over molecular sieves and saturated with Ar. (Diethylamino)chlorodimethylsilane was prepared according to the published procedure^[29]. – $^1\text{H}/^{13}\text{C}$ NMR: Jeol JNM-EX270E, Bruker ARX 250, Bruker AC 300, Bruker AM 500 (270.67 MHz/67.94 MHz, 250.13 MHz/62.8 MHz, 300.13 MHz/75.5 MHz, 500.13 MHz/125.8 MHz, respec-

tively). – ^{11}B NMR: Jeol FX90Q (28.7 MHz), Et₂O · BF₃ as external standard. – ^{15}N NMR (refocused INEPT pulse sequence^[30] with ^1H decoupling): Bruker AC 300 and AM 500 (30.4 and 50.7 MHz), neat MeNO₂ as external standard. – ^{29}Si NMR (refocused INEPT pulse sequence^[30] with ^1H decoupling): Bruker ARX 250 and AC 300 (49.7 and 59.6 MHz), with SiMe₄ as external standard ($\delta^{119}\text{Sn}$ and $\delta^{207}\text{Pb}$ data are given with respect to external Me₄Sn and Me₄Pb). – MS: EI-MS (70 eV), Varian MAT CH 7. – IR (in hexane): Perkin Elmer 983 G. – Elemental Analyses: Pascher, Remagen, and Dornis & Kolbe, Mülheim.

1-Alkynyl(diethylamino)dimethylsilanes (1a–c): To a suspension of 180 mmol of the respective lithiated alkyne in 250 ml of hexane 30 g (180 mmol) of (diethylamino)chlorodimethylsilane was added at room temp. within 30 min. After heating of the reaction mixture at reflux for 5 h, insoluble material was filtered off. The solvent was removed in vacuo and the fractional distillation of the residue gave the compounds **1a** (79%), **1b** (78%), and **1c** (55%) as colorless, moisture-sensitive liquids.

1a: B.p. 40°C/15 Torr. – IR: $\nu(\text{C}\equiv\text{C}) = 2190$ cm⁻¹. – ^1H NMR (C₆D₆): $\delta = 0.04$ (s, 6H, Me₂Si); 2.82, 0.88 (q, 4H, t, 6H, Et₂N); 1.57 (s, 3H, MeC≡). – C₉H₁₉NSi (169.3): calcd. C 63.6, H 11.3, N 8.3; found C 63.4, H 11.2, N 8.5.

1b: B.p. 120°C/15 Torr. – IR: $\nu(\text{C}\equiv\text{C}) = 2181$ cm⁻¹. – ^1H NMR (C₆D₆): $\delta = 0.16$ (s, 6H, Me₂Si); 2.82, 0.96 (q, 4H, t, 6H, Et₂N); 2.02, 1.32, 1.31, 0.76 (t, 2H, m, 2H, m, 2H, t, 3H, *n*BuC≡).

1c: B.p. 90°C/15 Torr. – IR: $\nu(\text{C}\equiv\text{C}) = 2110$ cm⁻¹. – ^1H NMR (C₆D₆): $\delta = 0.08$ (s, 9H, Me₃Si); 0.15 (s, 6H, Me₂Si); 2.78, 0.95 (q, 4H, t, 6H, Et₂N). – C₁₁H₂₅NSi₂ (227.5): calcd. C 58.1, H 11.1, N 6.2; found C 57.9, H 11.2, N 6.2.

1,1,4,5,5-Pentaethyl-2,5-dihydro-2,2-dimethyl-3-R-1,2,5-azoniasilaboratoles (2a–c): A mixture of the respective 1-alkynyl(diethylamino)dimethylsilane **1a–c** (25 mmol) and an excess of triethylborane (135 mmol) were heated at 100°C (reflux) for 3 d. Excess triethylborane was removed in vacuo and collected for the next reactions. Fractional distillation of the yellowish, oily residue gave the pure compounds **2a** (81%), **2b** (87%), and **2c** (92%) as colorless, moisture-sensitive, oily liquids.

2a: B.p. 115°C/0.005 Torr. – ^1H NMR (C₆D₆): $\delta = 0.14$ (s, 6H, Me₂Si); 2.61, 0.85 (q, 4H, t, 6H, Et₂N); 0.66, 0.77, 1.08 (m, 2H, m, 2H, t, 6H, Et₂B); 1.65 (s, 3H, MeC=); 2.36, 1.02 (q, 2H, t, 3H, EtC=). – MS, *m/z* (%): 267 (2) [M⁺], 252 (8), 267 (100), 130 (20), 41 (10). – C₁₅H₃₄BNSi (267.3): calcd. C 67.4, H 12.8, N 5.2; found C 67.2, H 12.7, N 5.0.

2b: B.p. 150°C/0.005 Torr. – ^1H NMR (C₆D₆): $\delta = 0.22$ (s, 6H, Me₂Si); 2.63, 0.88 (q, 4H, t, 6H, Et₂N); 0.64, 0.76, 1.04 (m, 2H, m, 2H, t, 6H, Et₂B); 2.17, 1.31, 0.92 (t, 2H, m, 4H, t, 3H, *n*BuC=); 2.32, 1.01 (q, 2H, t, 3H, EtC=). – MS, *m/z* (%): 309 (1) [M⁺], 294 (2) [M⁺ – Me], 280 (100), 130 (15), 49 (8), 41 (5).

2c: B.p. 137°C/0.005 Torr. – ^1H NMR (C₆D₆): $\delta = 0.16$ (s, 9H, Me₃Si); 0.27 (s, 6H, Me₂Si); 2.62, 2.60, 0.88 (m, 2H, m, 2H, t, 6H, Et₂N); 0.54, 0.71, 1.01 (m, 2H, m, 2H, t, 6H, Et₂B); 2.47, 1.04 (q, 2H, t, 3H, EtC=). – MS, *m/z* (%): 310 (1) [M⁺ – Me], 296 (100), 252 (5), 130 (12), 73 (10), 59 (5). – C₁₇H₄₀BNSi₂ (325.5): calcd. C 62.7, H 12.4, N 4.3; found C 62.6, H 12.4, N 4.1.

(E)-3-(Diethylboryl)-2-(1-indolyldimethylsilyl)-2-pentene (3a): Indole (1.2 g, 10 mmol) was added in one portion to a solution of 2.7 g (10 mmol) of **2a** in 50 ml of hexane. The mixture was heated at reflux for 1 h. After the solvent and diethylamine had been removed in vacuo, fractional distillation of the residue at 115°C/0.005 Torr gave 1.8 g (57%) of **3a** as a colorless liquid. – ^1H NMR (C₆D₆): $\delta = 0.66$ (s, 6H, Me₂Si); 1.42, 1.17 (q, 4H, t, 6H, Et₂B); 1.95 (s, 3H, MeC=), 2.31, 1.22 (q, 2H, t, 3H, EtC=); 6.82 (d, 1H,

3'-H); 7.35 (m, 1H, 4'-H), 7.36 (d, 1H, 2'-H); 7.37 (m, 1H, 6'-H); 7.75 (m, 1H, 7'-H); 7.86 (m, 1H, 5'-H). – MS, *m/z* (%): 311 (14) [M^+], 282 (85), 254 (100), 174 (30), 117 (20), 97 (15), 87 (10), 73 (10), 59 (15), 43 (5). – $C_{19}H_{31}BNSi$ (311.4): calcd. C 73.3, H 8.7, N 4.5; found C 73.2, H 8.7, N 4.6.

4,5,5-Triethyl-2,2,3-trimethyl-1-aza-6-azonia-2-sila-5-boratabicyclo[4.3.0]nona-3,6,8-triene (4a): To a solution of **2a** (2.7 g, 10 mmol) in 50 ml of diethyl ether 0.68 g of pyrazole was added in one portion at room temp. Then the mixture was stirred for 15 h. Solvent and diethylamine were removed in vacuo, and fractional distillation of the residue gave 2.44 g of **2a** (b.p. 110°C/0.005 Torr) which solidified as a colorless solid (m.p. 40°C). – 1H NMR (C_6D_6): δ = 0.41 (s, 6H, Me_2Si); 0.76, 0.66, 0.39 (m, 2H, m, 2H, t, 6H, Et_2B); 1.84 (s, 3H, $MeC=$); 2.24, 0.99 (q, 2H, t, 3H, $EtC=$); 7.84 (d, 1H, 7-H); 6.53 (dd, 1H, 8-H); 7.60 (d, 1H, 9-H). – MS, *m/z* (%): 233 (100) [$M^+ - Et$], 205 (90), 189 (30), 175 (25), 137 (20), 125 (30), 111 (30), 97 (85), 83 (50), 81 (40), 69 (35), 67 (25), 59 (45), 43 (30). – $C_{14}H_{27}BN_2Si$ (262.3): calcd. C 64.1, H 10.4, N 10.7; found C 63.9, H 10.3, N 10.6.

The compounds **5a** and **8a** were prepared in the same way. In the case of **6a**, hexane was used as solvent, whereas CH_2Cl_2 was employed as solvent for the preparation of **7a**.

5a: Yield 87%, b.p. 130°C/0.005 Torr, m.p. 45°C. – 1H NMR (C_6D_6): δ = 0.40 (s, 6H, Me_2Si); 0.79, 0.67, 0.26 (m, 2H, m, 2H, t, 6H, Et_2B); 1.72 (s, 3H, $MeC=$); 2.11, 0.86 (q, 2H, t, 3H, $EtC=$); 8.22, 8.23 (s, 1H, s, 1H, 7,9-H). – $C_{13}H_{26}BN_3Si$ (263.3): calcd. C 59.3, H 9.9, N 16.0; found C 59.2, H 9.9, N 15.8.

6a: Yield 100%. – 1H NMR (C_6D_6): δ = 0.37 (s, 6H, Me_2Si); 1.10, 0.62 (m, 4H, t, 6H, Et_2B); 2.03 (s, 3H, $MeC=$); 2.57, 1.18 (q, 2H, t, 3H, $EtC=$); 6.98, 7.14, 7.30 (1H broad, 1H broad, imidazole).

7a: Yield 72%, b.p. 135°C/0.005 Torr, m.p. 90°C. – 1H NMR (C_6D_6): δ = 0.45 (s, 6H, Me_2Si); 0.35, 0.71, 0.27 (m, 2H, m, 2H, t, 6H, Et_2B); 1.92 (s, 3H, $MeC=$); 2.18, 0.93 (q, 2H, t, 3H, $EtC=$); 7.18 (ddd, 1H), 7.41 (ddd, 1H), 7.53 (dd, 1H), 7.72 (ddd, 1H), 8.30 (d, 1H) indazole. – $C_{18}H_{30}BN_2Si$ (312.3): calcd. C 69.2, H 9.7, N 9.0; found C 69.0, H 9.8, N 9.1. – X-ray analysis^[15]: Colorless platelet, crystal size [mm] 0.60 × 0.40 × 0.08, crystal system triclinic, space group $P\bar{1}$; unit cell dimensions [pm]: $a = 752.5(2)$, $b = 922.7(2)$, $c = 1512.7(3)$, $\alpha = 83.23(2)$, $\beta = 76.27(2)$, $\gamma = 71.42(2)^\circ$, volume 966.1(4) Å³, $Z = 2$, $\rho(\text{calcd.}) = 1.074$ Mg/m³, absorption coefficient 0.120 mm⁻¹, $F(000) = 340$, diffractometer Siemens P4, temperature 296 K; radiation [pm] Mo- K_{α} , $\lambda = 71.073$, graphite monochromator, 2θ range 3.0 to 50.0°, scan type ω ; reflections collected 4198, independent/observed reflections 3361 ($R_{\text{int}} = 0.115$)/3361 [$F > 0.0\sigma(F)$], number of refined parameters 200; solution: direct methods (SHELXTL PLUS), weighting scheme $w^{-1} = \sigma^2(F) + 0.0000 F^2$, final R indices (obs. data): $R = 9.09$, $wR = 3.95\%$; max./min. residual electron density [eÅ⁻³] 0.28/–0.28.

8a: Yield 97%, b.p. 130°C/0.005 Torr, m.p. 80°C. – 1H NMR (C_6D_6): δ = 0.62 (s, 6H, Me_2Si); 0.87, 0.35 (m, 4H, t, 6H, Et_2B); 1.92 (s, 3H, $MeC=$); 2.33, 1.05 (q, 2H, t, 3H, $EtC=$); 7.49 (ddd, 1H), 7.62 (ddd, 1H), 7.73 (dd, 1H), 8.18 (dd, 1H) benzotriazole. – $C_{17}H_{29}BN_3Si$ (313.3): calcd. C 65.2, H 9.4, N 13.5; found C 65.0, H 9.3, N 13.7.

1,4,5,5-Tetraethyl-2,5-dihydro-2,2-dimethyl-3-R-1,2,5-oxoniasilaboratolanes (9a, 9c): A solution of **2a** (1.6 g, 6 mmol) in 15 ml of ethanol was stirred for 20 h at room temp. Then ethanol and diethylamine were removed in vacuo, and 1.33 g (92%) of **9a** (R = Me) was obtained by fractional distillation (35°C/0.005 Torr) as a colorless liquid. – 1H NMR (C_6D_6): δ = 0.13 (s, 6H, Me_2Si); 0.53, 0.70 (m, 4H, m, 6H, Et_2B); 1.63 (s, 3H, $MeC=$); 2.07, 0.96 (q, 2H,

t, 3H, $EtC=$); 3.58, 1.00 (q, 2H, t, 3H, EtO). – $C_{13}H_{29}BOSi$ (240.3): calcd. C 65.0, H 12.2; found C 64.8, H 12.1.

Compound **9c** (R = $SiMe_3$) was prepared in the same way as described for **9a**. Yield 96%, b.p. 55°C/0.005 Torr. – 1H NMR (C_6D_6): δ = 0.21 (s, 9H, Me_3Si); 0.16 (s, 6H, Me_2Si); 0.55, 0.68 (m, 4H, m, 6H, Et_2B); 2.27, 0.98 (q, 2H, t, 3H, $EtC=$); 3.55, 1.06 (q, 2H, t, 3H, EtO). – MS, *m/z* (%): 297 (8) [$M^+ - H$], 284 (10), 269 (100), 241 (65), 183 (15), 169 (20), 73 (35), 59 (10).

4,4,5-Triethyl-2,2-dimethyl-3-R-1,2,5-oxasilaborolanes (11a, 11c): A solution of 2.7 g (10 mmol) of **2a** in 10 ml of THF was added to 50 ml of water, and the mixture was stirred for 15 h at 60°C. After several extractions with hexane, the combined organic layers were dried with Na_2SO_4 , and then the solvents were removed in vacuo. Fractional distillation of the residue gave 1.38 g (65%) of **11a** (R = Me) as a colorless liquid with b.p. 30°C/0.005 Torr. – 1H NMR (C_6D_6): δ = 0.27, 0.31 (s, 3H, s, 3H, Me_2Si); 0.43 (q, 1H, 3-H); 1.43 (d, 3H, 3-Me); 0.83, 1.11 (m, 2H, t, 3H, EtB); 1.37, 1.44, 1.51, 1.69, 0.72, 0.80 (m, 1H, m, 1H, m, 1H, m, 1H, t, 3H, t, 3H, Et_2C-4). – $C_{11}H_{25}BOSi$ (212.2): calcd. C 63.3, H 11.9; found C 63.1, H 11.8.

Compound **11c** (R = $SiMe_3$) was prepared in the same way as described for **11a**. Yield 78%, b.p. 45°C/0.005 Torr. – 1H NMR (C_6D_6): δ = 0.06 (s, 9H, Me_3Si); 0.23, 0.29 (s, 3H, s, 3H, Me_2Si); 0.85, 1.10 (m, 2H, t, 3H, EtB); 0.41 (s, 1H, 3-H); 1.34, 1.48, 1.52, 1.72, 0.74, 0.81 (m, 1H, m, 1H, m, 1H, m, 1H, t, 3H, t, 3H, Et_2C-4). – $C_{13}H_{31}BOSi_2$ (242.3): calcd. C 64.4, H 12.9; found C 64.3, H 13.0.

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