

Cyclic Alkyl(aryl)boranes for 1,1-Carboboration of Monoalkynyltin Compounds

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

Two cyclic alkyl(aryl)boranes, a 1-bora-indane derivative **1**, and a tricyclic derivative **4**, containing the boron atom in a six-membered ring, were structurally characterized by NMR techniques in solution. The solid-state structure of the 1-bora-indane **1** was determined by X-ray crystallography. The reactivity of these cyclic alkyl(aryl)boranes towards monoalkynyltin compounds, $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{Me}$ and $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{Fc}$ (Fc = ferrocenyl), was studied using multinuclear magnetic resonance methods (^1H , ^{11}B , ^{13}C , ^{119}Sn NMR). Novel alkenylboranes were formed by 1,1-carboboration reactions. This process involves an expansion of both five- and six-membered rings. Insertion into the respective B–C(aryl) bond was preferred with high selectivity. In the case of the six-membered ring in **4**, the ring expansion to seven-membered rings proved to be readily reversible, and the thermodynamically stable reaction products were formed by ring contraction and concomitant transfer of the exocyclic B- ^nPr group.

Key words: Triorganoboranes, 1,1-Carboboration, Alkynyltin Compounds, NMR Spectroscopy, X-Ray Analysis

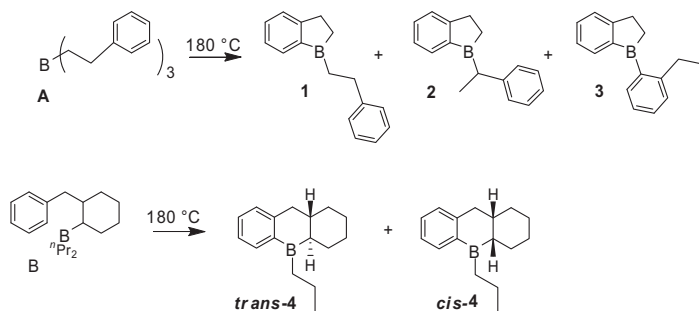
Introduction

Arylboron compounds have found widespread applications in various fields of chemistry and related sciences. Most prominent are arylboronic acids, *e. g.* in Suzuki coupling reactions [1], triarylboranes bearing electronegative substituents as co-catalysts in olefin polymerization [2, 3] and as catalysts in hydrosilylation reactions [4–6], triphenylborane amine adducts as additives in antifouling agents [7–10], or various arylboranes as composites of OLEDs because of their photophysical properties [11]. Triarylboranes can be readily prepared by standard procedures [12–14] and have attracted much attention, whereas alkyl(aryl)boranes have not been studied in great detail, owing to the limited stability of non-cyclic dialkyl(aryl)- or alkyl(diaryl)boranes towards disproportionation. However, cyclic alkyl(aryl)boranes are known to be fairly stable in this respect, and can be prepared by various routes [12–14]. Köster *et al.* have reported pioneering work in this field, opening a facile

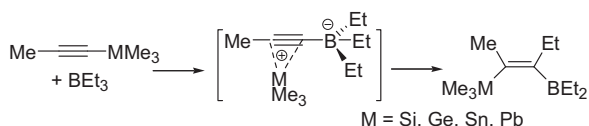
route to such compounds *via* pyrolysis of triorganoboranes (Scheme 1) [15–17], as shown for **A** and **B**.

In the case of **A**, the structures **1** and **3** had been proposed for the products [15–17]. This was confirmed in the present work by analysis of the original mixtures, and in addition, compound **2** was detected. In any case, **2** and **3** were found to be minor side products, and we have set out to isolate pure samples of **1** for structural characterization. In the case of **B**, the formation of **4** was proposed as a mixture of isomers without structural assignment [15–17]. Here, we confirm this proposal by ^1H and ^{13}C NMR spectroscopy and assign the major isomer as *trans*-**4**.

Both **1** and **4** are attractive examples for studying 1,1-carboboration reactions [18–20], since they possess three different B–C bonds [21]. The principles of 1,1-carboboration are shown in Scheme 2 for triethylborane. In the cases of **1** and **4**, it is of interest to find out which of the B–C bonds is preferred to form a new C–C bond. We have selected alkynyl(trimethyl)tin compounds for this study, be-



Scheme 1. Examples of cyclic alkyl(aryl)boranes produced by pyrolysis of triorganoboranes.



Scheme 2. Principles of 1,1-carboboration reactions.

cause they are easy to handle and react much more readily when compared with the corresponding silanes. Thus, we have used $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{Me}$ (**5**) and $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{Fc}$ (**6**; Fc = ferrocenyl) under mild reaction conditions, hoping to distinguish eventually between kinetically and thermodynamically controlled products.

Results and Discussion

Cyclic alkyl(aryl)boranes

The pure crystalline 1-bora-indane derivative **1**, which is extremely sensitive towards traces of oxygen and moisture, was slowly deposited from one of several mixtures containing variable amounts of **1**, **2**, and **3** (Scheme 1). ^{13}C NMR spectra (Fig. 1, Table 1) have

provided conclusive evidence for the proposed structures of these boranes. The increased line widths of the ^{13}C NMR signals for carbon atoms linked to boron can be traced to partially relaxed one-bond $^{13}\text{C}-^{11}\text{B}$ spin-spin coupling [22]. From this broadening and the ^{11}B nuclear spin relaxation time (**1**: $T^Q(^{11}\text{B}) = 0.8$ ms), the coupling constants $^1J(^{13}\text{C}, ^{11}\text{B})$ can be evaluated [23]: $^1J(^{13}\text{C}, ^{11}\text{B}) = 63 \pm 1.5$ (^{13}C -7a), 60 ± 2 (^{13}C -2), 55 ± 2 Hz (^{13}C -8). These data agree well with calculated data [24–27] 62.2, 59.3, 54.2 Hz, using the optimized gas-phase geometry of **1**, as has also been shown previously for other organoboranes [28].

The molecular structure of **1** (Fig. 2) shows essentially planar 1-bora-indane rings. All bond lengths are in the expected ranges. Variations in the C–C bond lengths for the aromatic carbon atoms of the 1-bora-indane do not indicate $\text{BC}(pp)\pi$ interactions, although these are suggested by the ^{11}B and ^{13}C chemical shifts. similar to other phenylboranes [29]. The endocyclic angle $\text{C1}-\text{B9}-\text{C9}$ ($105.4(2)^\circ$) is small, considering the trigonal planar surroundings of the boron atom and points towards ring strain and increased reactivity of the B–C bonds. There appear to be weak intermolecu-

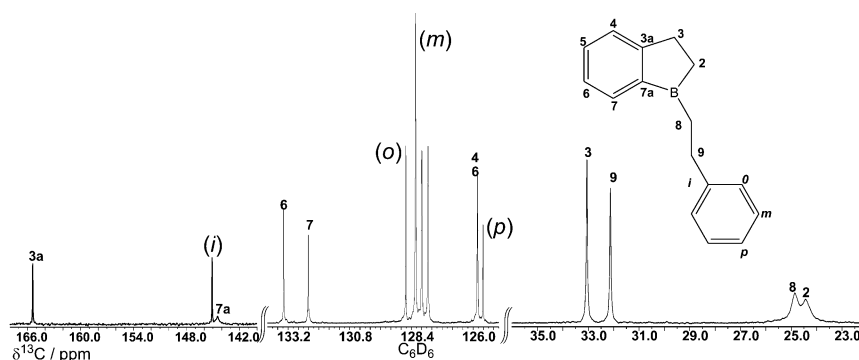
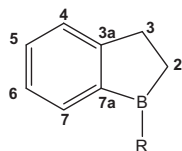


Fig. 1. 100.5 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the 1-bora-indane derivative **1** showing expansions for relevant regions. Note the broadening of ^{13}C NMR signals for C(7a), C(2) and C(8), which is due to partially relaxed $^{13}\text{C}-^{11}\text{B}$ spin-spin coupling [22].

Table 1. ^{11}B and ^{13}C NMR data^a of the 1-bora-indanes **1–3**.

$\delta^{13}\text{C}$	1	2	3
2	24.5 (br)	23.7 (br)	27.0 (br)
3	33.1	32.7	33.6
3a	165.6	166.6	166.4
4	125.8	125.6	128.4
5	133.4	133.4	133.6
6	125.8	125.9	125.9
7	132.5	133.2	134.3
7a	144.5 (br)	143.5 (br)	144.8 (br)
B-R	24.9 (br) CH_2 , 32.2 CH_2 , 145.1 (<i>i</i>), 127.6 (<i>o</i>), 128.3 (<i>m</i>), 125.6 (<i>p</i>)	35.0 (br) CH , 17.5 (Me), 146.1 (<i>i</i>), 128.4 (<i>o</i>), 128.8 (<i>m</i>), 125.3 (<i>p</i>)	141.2 (br), 148.0, 125.4, 133.6, 129.9, 133.3, 30.1, 17.6, CH_2CH_3
$\delta^{11}\text{B}$	81.7	80.0	77.8

^a In C_6D_6 (10%) at 296 K; (br) denotes the broadened ^{13}C NMR signal of carbon atoms linked to boron [22].

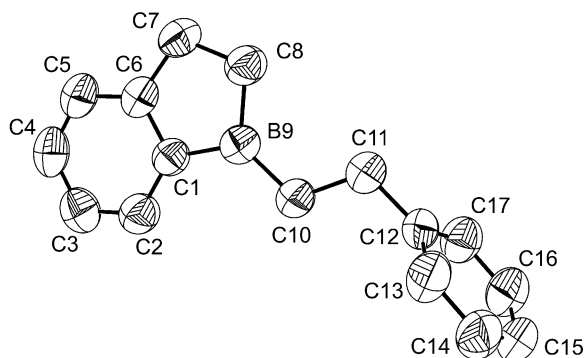


Fig. 2. Molecular structure of the 1-bora-indane **1** (ORTEP; 50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths (pm), angles and dihedral angles (deg): C1–B9 154.7(3), C8–B9 157.1(3), C10–B9 155.7(3), C10–C11 152.5(3), C11–C12 150.1(3); C1–B9–C8 105.4(17), C8–B9–C10 126.96(18), C10–B9–C1 127.64(18), B9–C10–C11 117.57(17), C10–C11–C12 114.06(16); C1–B9–C10–C11 177.63(19), C8–B9–C10–C11 1.1(3), B9–C10–C11–C12 175.74(18), C10–C1–C12–C13 79.7(3), C10–C11–C12–C17 97.2(2).

lar interactions (π stacking; smallest distance between layers: 374.2 pm) between the 1-bora-indane rings. Although the particular orientation (almost perpendicular to the 1-bora-indane rings) of the phenyl group in the PhCH_2CH_2 substituent may be enforced by crystal packing, this structure was also found as an energy minimum for the gas phase after optimizing the geom-

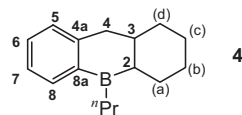
etry of **1** at the B3LYP/6-311+g(d,p) [30–32] level of theory. The alternative structure, with all rings in one plane was not confirmed as a minimum in energy.

Although the ^1H NMR spectrum of the borane **4**, an air-sensitive yellowish waxy solid, is expectedly fairly complex, some of its signals are useful for assignment purposes, *e. g.* the ^1H NMR signal for H-2 and both signals for H-4, which are at low and high frequency,

Table 2. ^{11}B and ^{13}C NMR data^a of the isomers *trans*-**4** and *cis*-**4**.

$\delta^{13}\text{C}$	<i>trans</i> - 4	<i>cis</i> - 4
2	39.9 (br)	37.7 (br)
3	39.5	41.1
4	46.9	42.2
4a	150.6	149.4
5	128.3	129.3
6	133.2	133.4
7	125.8	125.7
8	135.6	135.3
8a	137.1 (br)	136.6 (br)
B-R	23.4 (br), 19.4, 18.5	24.5 (br), 19.5, 18.3
a,b,c,d	27.6, 25.3, 24.8, 35.6	27.8, 26.9, 28.8, 31.4
$\delta^{11}\text{B}$	75.3	75.3

^a In C_6D_6 (10%) at 296 K; (br) denotes the broadened ^{13}C NMR signal of carbon atoms linked to boron [22].



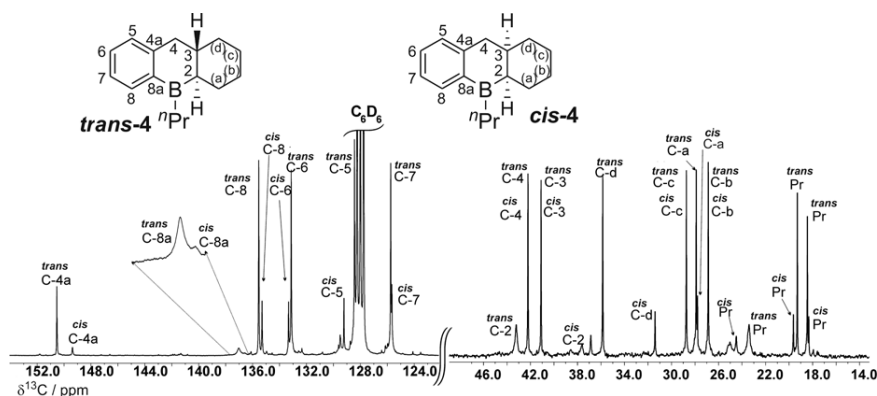
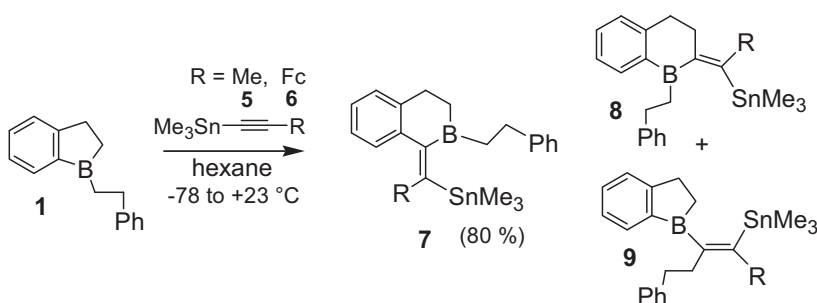


Fig. 3. 100.5 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** showing expansions for relevant regions. Note the broadening ^{13}C NMR signals for C(8a), C(2) and BCH_2 , which is due to partially relaxed ^{13}C - ^{11}B spin-spin coupling [22].



Scheme 3. 1,1-Carboboration reactions of **1** with monoalkynyltin compounds.

respectively, of unresolved multiplets. The splitting of the H-2 and H-4 signals by ^1H - ^1H coupling is well resolved, and the signals can be readily assigned to the major isomer. The ^{13}C NMR spectrum is much more straightforward (Fig. 3, Table 2). Together with 2D $^1\text{H}/^{13}\text{C}$ shift correlations (HSQC [33], HMBC [34]), and selective gradient enhanced 1D $^1\text{H}/^1\text{H}$ NOE difference spectra [35], all ^{13}C NMR signals can be assigned. Especially the NOE experiment (irradiating at the ^1H -2 resonance) proves unambiguously that the major isomer is *trans*-**4** (ca. 80%). Calculated $\delta^1\text{H}$ and $\delta^{13}\text{C}$ values [36] follow the trend of the experimental data, corroborating the assignments. The calculated energies for the optimized geometries of *trans*-**4** and *cis*-**4** are almost the same, *trans*-**4** being 0.5 kcal mol^{-1} more stable.

Reactions of the cyclic alkyl(aryl)boranes **1** and **4** with alkynyl(trimethyl)tin compounds

In both boranes **1** and **4**, the reaction with alkynyltin compounds may lead to insertion into one of the endocyclic B–C bonds or to transfer of the exocyclic or-

ganyl group, as shown for **1** in Scheme 3. It was hoped that ^{119}Sn chemical shifts [37–39] would be sufficiently sensitive to mirror small changes in the surroundings of the tin atom. Indeed, three ^{119}Sn NMR signals for **7**(Me), **8**(Me) and **9**(Me) (Fig. 4) reflect this situation when **5** was used, whereas for **6** mainly **7**(Fc) and a small amount of **8**(Fc) were the products. Expansion of the five-membered ring in **1** appears to be the major driving force, and for 1,1-carboboration the B–C(7a) bond is preferred over the B–C(2) bond. The structure assignment of **7** follows from the ^{13}C NMR spectra which show the typical broad signals for boron-bonded carbon [22], and the required set for aryl carbon atoms, now in markedly different places (Table 3) when compared with **1**. For **8**, the broad $^{13}\text{C}(2)$ NMR signal is missing, being replaced by the $^{13}\text{C}(\text{CH}_2)$ NMR signal for the methylene unit linked to a C=C bond. Moreover, ^{119}Sn - ^{13}C spin-spin coupling constants ($^{117}/^{119}\text{Sn}$ satellites), in particular those across three bonds to the aromatic carbon atom in **7**, and to the CH_2 unit in **8**, found in the typical range, are conclusive. The *cis* position of the Me_3Sn group relative to boron is assumed by comparison with pre-

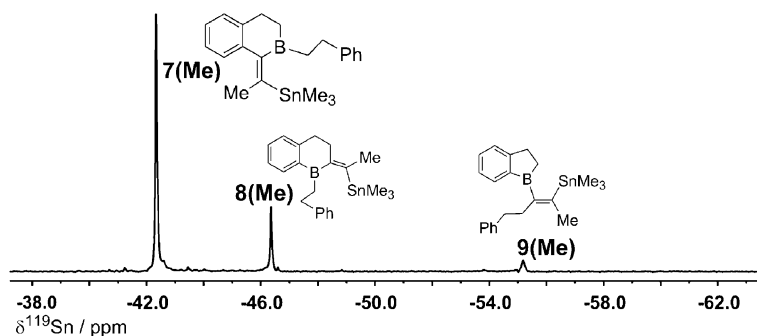


Fig. 4. 149.1 MHz $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of the reaction mixture starting from **1** and **5**, measured immediately after the sample had reached r.t., using the refocused INEPT pulse sequence [42, 43]. At ambient temperature, the ratio of the components present in the mixture remains constant.

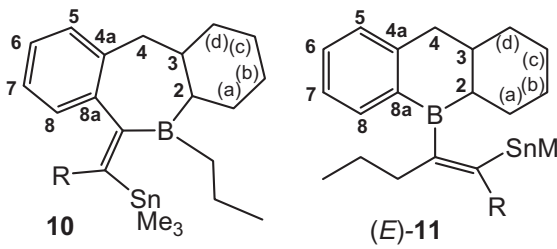
Table 3. Selected NMR parameters^a of products from the reaction of **1** with **5** and **6** (Scheme 3).

	$\delta^{13}\text{C}$								$\delta^{119}\text{Sn}$	$\delta^{11}\text{B}$
	Me_3Sn	$\text{Sn}-\text{C}=\text{C}$	$\text{C}=\text{B}$	$\text{R}-\text{C}=\text{C}$	C-2, C-3	C-3a, C-7a	C-4,5,6,7	B- $\text{CH}_2\text{CH}_2\text{-Ph}$		
7(Me) ^b (C_6D_6)	-6.5 [331.3]	147.9 [496.1]	159.8 (br)	23.2 [59.6]	30.6 (br), 31.5	128.9 [7.0], 138.5 [85.0]	125.7, 134.2, 127.4, 127.4	25.8 (br), 29.2, 144.4, 127.8, 128.3, 125.4	-42.2	82.2 (710)
7(Fe) ^c (CDCl_3)	-2.8 [329.1]	143.1 [520.0]	160.0 (br) [67.5]	69.4 (Cp), 89.0 [53.2], 69.0, ^d 67.3	30.5 (br), 31.4	129.1 [8.1], 140.5 [89.8],	126.1, 133.4, 126.0, 133.0	26.6 (br), 29.5, 144.4, 127.8, 128.3, 125.4	-54.7 (4.8)	81.5 (1320)
8(Me) ^b (C_6D_6)	-6.2 [331.0]	n.a.	159.6 (br)	22.5 [64.5]	41.0 [69.8], 36.4 [7.8]	n. a. n. a.	n. a.	26.5 (br), n. a.	-46.4	n. o.
8(Fe) ^c (CDCl_3)	-5.0 [328.0]	141.4 [521.0]	161.0 (br)	68.3 (Cp), 90.5 [62.3], n. a.	40.4 [67.0], 36.4 [8.0]	n. a. n. a.	n. a.	26.0 (br), n. a.	-50.9	n. o.
9(Me) ^b (C_6D_6)	-7.6 [321.0]	n.a.	158.0 (br)	25.9 [65.4]	27.0 (br) n. a.	n. o., 166.0 (br)	n. a.	n. a.	-55.2	n. o.

^a Measured at 296 K; coupling constants $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ in Hz are given in brackets; (br) denotes the broad ^{13}C NMR signal of carbon atoms linked to boron; n. a. means not assigned because signals are weak, and there is partial overlap with other strong signals; n. o. means not observed, because the signal is weak and broad; ^b mixture of **7(Me)** with small amounts of **8(Me)** and **9(Me)**, see Fig. 1; ^c mixture of **7(Fe)** with a small amount of **8(Fe)**; ^d broad because of slow rotation of the ferrocenyl group about the $\text{Fc}-\text{C}=\text{C}$ bond.

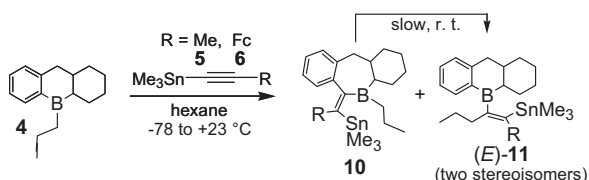
vious results [18–20, 40], in agreement with fairly narrow ^{119}Sn NMR signals [40]. The chemical shifts $\delta^{11}\text{B}$ show small changes, indicating that a reaction had taken place and that three-coordinate boron atoms are still present [41]. Since the ^{11}B NMR signals of

the products are rather broad, up to 2000 Hz, different products with similar structures cannot be distinguished by ^{11}B NMR spectroscopy. The formation of side products **8** and **9** is conceivable, considering either insertion into the $\text{B}-\text{C}(2)$ bond to give again

Table 4. Selected NMR parameters^a of the products^b from the reaction of *trans*-**4** with **5** and **6**.


	$\delta^{13}\text{C}$								$\delta^{119}\text{Sn}$	$\delta^{11}\text{B}$
	Me_3Sn	$\text{Sn}-\text{C}=\text{C}$	$=\text{C}-\text{B}$	$\text{R}-\text{C}=\text{C}$	$\text{C}-2,3,4$	$\text{C}-4\text{a}, \text{C}-8\text{a}$	$\text{C}-5,6,7,8$	$\text{CH}_2\text{CH}_2\text{CH}_3$		
10(Me) ^c (C_6D_6)	−9.1 [321.6]	132.5 [514.8]	165.8 (br)	21.1 [63.7]	49.2 (br), 48.0, 44.5	141.8 [4.0], 137.8 [91.5]	127.1, 129.7, 129.7, 126.9	24.5 (br), 19.8, 17.8	−42.4	80.7
10(Fc) ^d (CDCl_3)	−5.7 [321.1]	133.7 [535.3]	165.6 (br) [71.6]	69.4 (Cp), 89.5 [60.7] 70.4, 68.3	44.2 (br), 50.9, 44.0	141.5 [4.7], 139.5 [96.3]	127.7, 129.7, 129.6, 127.5	24.6 (br), 19.1, 17.8	−46.5	80.2
11(Me) ^e (C_6D_6)	−8.1 [319.0]	136.8 [536.2]	158.3 (br) [67.4]	20.2 [68.8]	45.0 br, 41.0, 42.0	150.7, 137.2 (br)	128.5, 133.7, 125.8, 138.2	34.2 [80.2], 23.2 [9.9], 15.0	−48.4	74.4
11(Fc) ^f (CDCl_3)	−4.9 [320.8]	137.4 [536.1]	161.4 (br) [65.0]	69.6 (Cp), 90.6 [72.3], 70.4, 67.9	44.1 (br), 40.5, 42.0	150.1, 137.3 (br)	128.7, 133.7, 125.9, 137.7	37.4 [83.3], 24.1 [8.5], 15.2	−54.3	74.8

^a Measured at 296 K in C_6D_6 ; coupling constants $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ in Hz are given in brackets; (br) denotes the broad ^{13}C NMR signal of carbon atoms linked to boron; ^b all signals for **10** and **11** are accompanied by weak signals representing the products formed by the reaction of *cis*-**4** with **5** and **6**; in the case of **11**, only the NMR data of the major isomer are given, since those of the minor isomer are very similar; ^c other ^{13}C NMR data: 28.8 (a), 29.6 (b), 27.7 (c), 38.4 (d); ^d other ^{13}C NMR data: 26.7 (a), 27.5 (b), 27.7 (c), 38.4 (d); ^e other ^{13}C NMR data: 28.7 (a), 27.0 (b), 29.0 (c), 36.0 (d); ^f other ^{13}C NMR data: 28.7 (a), 27.0 (b), 29.1 (c), 35.9 (d).

Scheme 4. 1,1-Carbaboration reactions of **4** with monoalkynyltin compounds.

a six-membered ring **8**, or transfer of the exocyclic $\text{CH}_2\text{CH}_2\text{Ph}$ group, leaving the 1-bora-indane system unaffected, as in **9**.

In the case of **4**, 1,1-carbaboration (Scheme 4) can proceed in a similar way as for **1**. However, the expansion of the six-membered ring may take place less

readily and the additional condensed six-membered ring in both isomers of **4** may be a further obstacle as far as the reactivity of endo- and exocyclic B–C bonds is concerned. In the beginning, the reaction of **4** with **5** affords a mixture containing mainly **10(Me)** (ca. 60%) and two compounds assumed to be stereoisomers of (*E*)-**11(Me)** (without assignment; together ca. 40%). After two weeks at r.t., only the stereoisomers of (*E*)-**11(Me)** ($\approx 2 : 1$ ratio) are left, together with some impurities. These final products arise because of a transfer of the exocyclic propyl group. In Fig. 5, the comparable situation is illustrated by ^{119}Sn NMR spectroscopy for the analogous reaction of **4** with **6**. The first product formed is **10(Fc)**, already accompanied by small amounts of the isomers (*E*)-

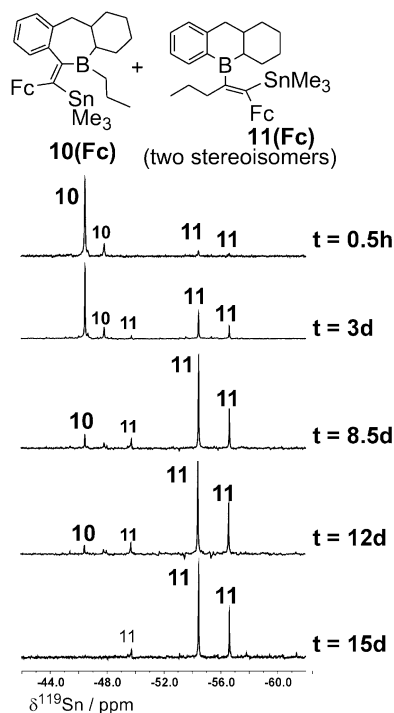


Fig. 5. 149.1 MHz $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra of the reaction mixture starting from **4** and **6**, measured at times after the sample had reached r.t., using the refocused INEPT pulse sequence [42, 43]. The smaller numbers refer to the respective isomer arising from the reaction of *cis*-**4**. No assignment was made for the (*E*) isomers **11**. In the case of one of the isomers of **11**, the signal for the minor isomer starting from *cis*-**4** was not detected with certainty.

11(Fc), which are formed *via* transfer of the exocyclic propyl group. Apparently, the insertion into the B–C(aryl) bond leads to the kinetically controlled products **10(Me)** or **10(Fc)** containing a seven-membered ring. The ring expansion is clearly evident from ^{13}C NMR spectra (Table 4), in particular from the $^{13}\text{C}(8a)$ NMR signal which, in contrast to **4** and (*E*)-**11**, is sharp and accompanied by $^{117}/^{119}\text{Sn}$ satellites, typical of $^3J(^{119}\text{Sn}, ^{13}\text{C})$. Thermodynamically, the six-membered ring is probably more favorable, giving rise to transfer of the exocyclic propyl group. In addition to the isomers of *trans*-**4** and *cis*-**4**, there are two stereoisomers of (*E*)-**11** for each of the starting isomers **4**. In the course of the rearrangement of **10** into **11**, the preferred stereochemistry, leading to the respective (*E*)-isomers, is retained. This can be concluded considering the $\delta^{13}\text{C}$ data and almost identical coupling constants, in particular $^3J(^{119}\text{Sn}, ^{13}\text{C}_{\text{CH}_2})$, which are sensitive to

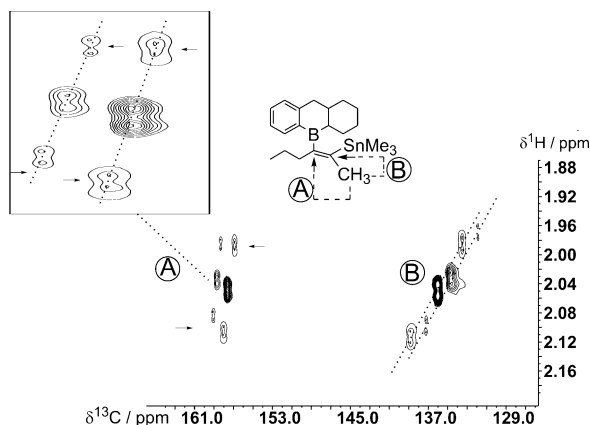


Fig. 6. 400 MHz $^1\text{H}/^{13}\text{C}$ HMBC shift correlation [34], taking advantage of the two-bond and three-bond ^{13}C – ^1H spin-spin coupling of the $^{13}\text{C}(\text{Sn}=\text{C})$ and $^{13}\text{C}(\text{B}=\text{C})$ nuclei to $^1\text{H}(\text{C}=\text{CH}_3)$ as indicated by encircled B and A, respectively. The positive tilt (dashed lines) of $^{119}/^{117}\text{Sn}$ satellite cross peaks (arrows) indicates [44] alike signs of $^3J(^{119}\text{Sn}, ^1\text{H}=\text{C}-\text{CH}_3)$, $^2J(^{119}\text{Sn}, ^{13}\text{C}_{\text{B}=\text{C}})$, and $^1J(^{119}\text{Sn}, ^{13}\text{C}_{\text{Sn}=\text{C}})$, all < 0 .

trans- and *cis*-coupling pathways. Sterical congestion around the C=C bond in **11** is evident by exchange-broadened $^{13}\text{C}(\text{SnMe}_3)$ NMR signals, and the presence of stereoisomers is in agreement with hindered rotation about the B–C= bond. Mainly the two stereoisomers of (*E*)-**11(Me)** and (*E*)-**11(Fc)** are the final products ($\approx 90\%$ after three weeks at r.t.) in an approximate 2 : 1 ratio. The results shown in Scheme 4 and in Fig. 5 indicate the reversibility of the 1,1-carboboration reactions.

For the detection of the fairly weak and partially broadened olefinic ^{13}C NMR signals of the two isomers of (*E*)-**11(Me)** HMBC experiments [34] proved to be particularly convenient (Fig. 6), since they also allow to determine the signs of $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ ($n = 1, 2$) ($^2J(^{119}\text{Sn}, ^1\text{H}=\text{C}-\text{CH}_3) < 0$ is known [37–39]). This is of importance for $n = 2$, because such coupling constants in vinyl- or alkenyltin compounds are generally small and may be of either sign [37–39]; for instance, in $\text{Sn}(\text{CH}=\text{CH}_2)_4$, $^2J(^{119}\text{Sn}, ^{13}\text{C}) < 1$ Hz. In the case of (*E*)-**11**, the magnitude of $^2J(^{119}\text{Sn}, ^{13}\text{C}_{\text{C}=\text{C}})$ is larger, and its sign is < 0 (Fig. 6).

Conclusions

Following the structural characterization of two cyclic alkyl(aryl)boranes, their reactivity towards

monoalkynyl(trimethyl)tin compounds was studied using multinuclear magnetic resonance methods. 1,1-Carboboration took place readily, affording novel alkenylboranes. Ring expansion of both five- and six-membered rings was preferred, at least in the first steps. This involved insertion into the respective B–C(aryl) bond with high selectivity. In the case of the six-membered ring, the ring expansion to seven-membered rings proved to be reversible, and the thermodynamically stable reaction products were formed by transfer of the exocyclic B-ⁿPr group.

Experimental

General and starting materials

All preparative work as well as handling of the samples was carried out observing precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. Crude samples containing **1** were available from Köster's work [15–17], from which pure crystalline **1** (m. p. 49–50 °C) could be separated and used for synthesis, NMR measurements, and X-ray crystal structural analysis. The original mixture containing the isomers *trans*-**4** and *cis*-**4** (ca. 80 : 20) was also available from Köster's work [15–17] as a yellowish waxy solid, and was used without further purification. Trimethyl(propynyl)tin **5** [45] and ferrocenylethynyl(trimethyl)tin **6** [46–48] were prepared as described.

NMR measurements in CDCl₃ or C₆D₆ (concentration ca. 5%–10%) with samples in 5 mm tubes at 23 ± 1 °C: Varian Inova 400 MHz spectrometer for ¹H, ¹¹B, ¹³C, and ¹¹⁹Sn NMR; chemical shifts are given relative to Me₄Si [$\delta^1\text{H}$ (CHCl₃) = 7.24; $\delta^{13}\text{C}$ (CDCl₃) = 77.0; $\delta^1\text{H}$ (C₆HD₅) = 7.15; $\delta^{13}\text{C}$ (C₆D₆) = 128.0; external Me₄Sn [$\delta^{119}\text{Sn}$ = 0 for $\Xi(^{119}\text{Sn})$ = 37.290665 MHz]; external BF₃·OEt₂ [$\delta^{11}\text{B}$ = 0 for $\Xi(^{11}\text{B})$ = 32.083971 MHz]. Chemical shifts are given to ±0.1 ppm for ¹³C and ¹¹⁹Sn, and ±0.4 ppm for ¹¹B; coupling constants are given ±0.4 Hz for $J(^{119}\text{Sn}, ^{13}\text{C})$. ¹¹⁹Sn NMR spectra were measured directly by single pulse methods or by using the refocused INEPT pulse sequence [42, 43] based on $^2J(^{119}\text{Sn}, ^1\text{H})$ (55 Hz) after optimizing the delay times in the pulse sequence. Melting points (uncorrected) were determined using a Büchi 510 melting point apparatus. All quantum chemical calculations were carried out using the GAUSSIAN 09 program package [49].

¹H NMR data of 1-(2-phenyl-ethyl)-1-bora-indane **1** in C₆D₆: $\delta^1\text{H}$ = 1.32 (2H, t, 5.2 Hz, H-2), 2.79 (2H, t, 5.2 Hz, H-3), 7.36 (1H, m, H-4), 7.23 (1H, m, H-5), 7.26 (1H, m, H-6), 7.69 (1H, d, 7.2 Hz, H-7), 1.85 (2H, t, 8.1 Hz, BCH₂), 2.83 (2H, t, 8.1 Hz, Ph-CH₂), 7.02–7.11 (5H, m) Ph).

Table 5. Crystallographic data of the 1-bora-indane **1**.

	1
Formula	C ₁₆ H ₁₇ B
Crystal	colorless cube
Dimensions, mm ³	0.24 × 0.18 × 0.16
Temperature, K	293
Crystal system	monoclinic
Space group	P2 ₁ /c
Lattice parameters	
<i>a</i> , pm	935.36(19)
<i>b</i> , pm	1302.7(3)
<i>c</i> , pm	1079.8(2)
β , deg	100.793(3)
<i>Z</i>	4
Absorption coefficient μ , mm ^{−1}	0.1
Measuring range in ϑ , deg	2.22–26.01
Refl. collected / unique / <i>R</i> _{int}	8818 / 2485 / 0.085
Refined parameters	154
<i>R</i> 1 / <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.046 / 0.101
<i>R</i> 1 / <i>wR</i> 2 (all data)	0.1055 / 0.1200
Max. / min. residual electron density, e pm ^{−3} × 10 ^{−6}	0.115 / −0.092

¹H NMR data of 9-propyl-10H-1,2,3,4,4a,10a-hexahydro-9-boraanthracene *trans*-**4** (see Fig. 3 or Table 2 for numbering) in C₆D₆: $\delta^1\text{H}$ = 0.59 (1H, “t”, $^3J(^1\text{H}, ^1\text{H})$ = 11.9 Hz, H-2), 1.38 (1H, m, H-3), 2.46, 2.53 (2H, dd, $^2J(^1\text{H}, ^1\text{H})$ = 15.5 Hz), $^2J(^1\text{H}, ^1\text{H})$ = 3.5 Hz, H-4), 7.02 (1H, m, H-5), 7.20 (1H, m, H-6), 7.10 (1H, , m, H-7), 7.83 (1H, m, H-8), 1.13, 2.29 (2H, m, H-a), 1.70 (2H, m, H-b), 1.76 (2H, m, H-c), 1.01, 1.63 (2H, m, H-d), 1.56, 1.37, 0.97 (7H, m, m, t, B-ⁿPr).

1,1-Carboboration reactions (general procedure)

A stirred solution of the respective cyclic alkyl(aryl)borane (2 mmol) in hexane (20 mL) was cooled to −78 °C, and an equimolar amount of the alkynyltin compound (**5** or **6**) dissolved in hexane (20 mL) was slowly added. After the mixture had reached r.t., all volatile materials were removed in a vacuum, leaving yellow oily residues. These were completely soluble in C₆D₆ or CDCl₃, and were studied by NMR spectroscopy for a period of several weeks.

7(Me): ¹H NMR (CDCl₃): $\delta^1\text{H}$ [$^nJ(^{119}\text{Sn}, ^1\text{H})$] = 0.33 [52.3] (9H, s, SnMe₃), 2.26 [53.3] (3H, s, Me–C≡), 1.70 (2H, t, 5.7 Hz, H-2), 2.80 (2H, t, 5.7 Hz, H-3), 1.85 (2H, t, 8.1 Hz, B-CH₂), 2.84 (2H, t, 7.4 Hz, Ph-CH₂), 7.06–7.43 (9H, m, aryl, Ph).

7(Fc): ¹H NMR (CDCl₃): $\delta^1\text{H}$ [$^nJ(^{119}\text{Sn}, ^1\text{H})$] = 0.57 [50.6] (9H, s, SnMe₃), 2.26 [53.3] (3H, s, Me–C≡), 1.78 (2H, t, 4.4 Hz, H-2), 2.78 (2H, t, 4.4 Hz, H-3), 1.90 (2H,

t, 7.4 Hz, B-CH₂) 2.84 (2H, t, 7.4 Hz, Ph-CH₂), 3.95 (2H, m), 4.13 (5H, s, Cp), 4.20, 4.28 (2H, 2H, m, m, C₅H₄), 7.13–7.48 (9H, m, aryl, Ph).

10(Me): ¹H NMR (CDCl₃): δ¹H [ⁿJ(¹¹⁹Sn, ¹H)] = 0.1 [51.8] (8H, s, SnMe₃), 1.85 [51.7] (3H, s, =C-Me), 6.97–7.04 (4H, m, aryl), 2.80–0.80 (12H, m, CH, CH₂).

10(Fc): ¹H NMR (CDCl₃): δ¹H [ⁿJ(¹¹⁹Sn, ¹H)] = 0.28 [50.5] (9H, s, SnMe₃), 3.96 (5H, s, Cp), 3.82, 3.95 (2H, 2H, m, m, C₅H₄), 6.96–7.07 (4H, m, aryl), 2.93–0.82 (12H, m, CH, CH₂).

11(Me): ¹H NMR (C₆D₆): δ¹H [ⁿJ(¹¹⁹Sn, ¹H)] = –0.07 [51.7] (9H, s, SnMe₃), 2.07 [52.1] (3H, s, =C-Me), 6.98–7.86 (4H, m, aryl), 2.55–0.86 (12H, m, CH, CH₂).

11(Fc): ¹H NMR (CDCl₃): δ¹H [ⁿJ(¹¹⁹Sn, ¹H)] = 0.05 [51.5] (9H, s, SnMe₃), 4.07 (5H, s, Cp), 4.05, 4.23 (2H, 2H, m, m, C₄H₄), 6.99–7.99 (4H, m, aryl), 3.28–1.43 (12H, m, CH, CH₂).

Crystal structure determination of the 1-bora-indane **1**

Details pertinent to the crystal structure determination are listed in Table 5 [50]. Crystals of appropriate size were selected and sealed in Lindemann capillaries. The data collections were carried out at 293 K using a Stoe IPDS I system (MoK_α, λ = 71.073 pm, graphite monochromator). Absorption corrections did not improve the data set. Structure solution and refinement were accomplished using SHELXS/L-97 [51, 52].

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