Stannacyclohexanes and spiro-tin compounds with a stannole or a stannolene group

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Abstract

1,1-Diethynyl-1-stannacyclohexane (5) was prepared, and its reaction with triethylborane or 9-isobutyl-9-borabicyclo[3.3.1]nonane gave the corresponding spiro-tin compounds 6 and 7 with a stannole fragment. The molecular structure of the derivative 7 was determined by X-ray analysis (triclinic, space group $P\bar{1}$; $a = 835.2(7)$, $b = 1117.5(2)$, $c = 1165.6(2)$ pm; $\alpha = 72.05(3)$, $\beta = 74.32(3)$, $\gamma = 50.61(3)°$). Treatment of 6 with trimethyltin ethoxide gave at first quantitatively the spiro-tin compound 8 with a 2-stannolene unit which rearranges upon heating into the spiro-tin compound 9 with a 3-stannolene unit. The reaction of 7 with trimethyltin butoxide gave quantitatively another tetracyclic compound 10, analogous to 8. All compounds were characterised by ^{1}H, ^{11}B, ^{13}C and ^{119}Sn NMR data. Numerous coupling signs $^nJ(^{119}Sn^1H)$ and $^nJ(^{119}Sn^{13}C)$ and $^2J(^{119}Sn^{117}Sn)$ were determined by 2D $^{13}C/^1H$ and $^{119}Sn/^1H$ heteronuclear shift correlations. Compound 7 was studied by solid-state ^{13}C and ^{119}Sn CPMAS NMR. This revealed the presence of a second crystalline phase in the bulk of the solid material, as confirmed by powder X-ray diffraction data. ^{119}Sn CPMAS NMR spectra of 7 show resolved scalar $^{119}Sn-^{11}B$ coupling ($^3J(^{119}Sn^{11}B) = 68 \pm 5$ and 65 ± 5 Hz).

Keywords: Tin; Boron; X-ray; NMR; Stannole; Stannolene; Stannacyclohexane

1. Introduction

Cyclic organotin compounds are attractive reagents in organometallic chemistry [1,2]. Their reactive Sn–C bonds are readily cleaved by electrophilic attack, and frequently it is possible to substitute the organotin moiety by other elements or organoelement groups, in particular if element or organoelement halides are used as electrophiles. In this context spiro-tin compounds may also find applications, as has been shown recently for the synthesis of tetraalkyl-1,6-dibromo-2,3,4,5-tetra-carba-*nido*-hexaboranes(6) [3]. Stannacyclohexane derivatives such as 1 [4] or 3 [5], or the spiro-tin compound 2 [5] (Scheme 1) can serve as starting points for new spiro-tin compounds. The diethynyl tin derivative 5 (Scheme 1) must be considered as a particularly promising candidate for this purpose. In addition to their synthetic potential, structural properties of spiro-tin compounds are of interest as well as their NMR data. Chemical shifts $\delta^{13}C$ and $\delta^{119}Sn$ and coupling constants involving the ^{119}Sn nucleus can be compared with

data for corresponding monocyclic tin compounds. We have shown that diethynyltin compounds react with trialkylboranes via two consecutive 1,1-organoboration reactions to give exclusively stannoles [6,7]. Recently,
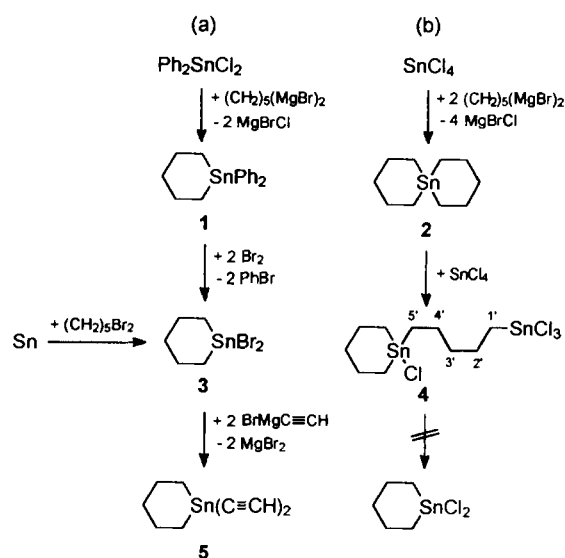

Scheme 1.

we have found that such stannoles react with trimeth-yltin alkoxides to 2-stannolenes which rearrange to 3-stannolenes upon heating [8]. In this work we report on the synthesis of **5** and its reactivity towards triethyl-borane, Et_3B, and 9-isobutyl-9-borabicyclo[3.3.1]non-ane, ^iBu-9-BBN. The product of the latter reaction, a spiro-tin compound with a stannole ring, was charac-terised by a single-crystal X-ray diffraction analysis. Particular emphasis is given to the NMR data, including the determination of coupling signs of $^nJ(^{119}Sn^1H)$ and $^nJ(^{119}Sn^{13}C)$, and the solid-state ^{13}C and ^{119}Sn CPMAS NMR spectra.

## 2. Results and discussion

2.1. Synthesis

As shown in Scheme 1(a), there is a straightforward route to the diethynyltin compound **5**, starting from the diphenyl derivative **1** via the tin dibromide **3**. The tin dibromide **3** can also be prepared directly from 1,5-di-bromopentane and tin [9]. In principle, it should also be possible to start from the spiro-tin compound **2**, and convert **2** by treatment with tin tetrachloride to the ring cleavage product **4** (Scheme 1(b)). Although the reac-tion between **2** and $SnCl_4$ affords selectively the com-pound **4** and is complete at room temperature, heating of **4** does not give the tin dichloride corresponding to **3**, but rather a polymeric material. In any case, the di-ethynyltin derivative **5** is readily accessible via the reaction between **3** and two equivalents of ethynylmag-nesium bromide, and its reactivity towards trialkylbo-ranes can be studied.

The reaction of **5** with a slight excess of Et_3B is complete when the reaction mixture is warmed from −78°C to room temperature. The stannole **6** is formed selectively (Eq. (1)). Similarly, compound **5** reacts with one equivalent of ^iBu-9-BBN to give the tetracyclic stannole derivative **7**, in which the original 9-borabi-cyclo[3.3.1]nonane system is enlarged by two carbon atoms; the ^iBu group remains unaffected (Eq. (2)). These results correspond to previous findings for the reaction of dialkyldiethynyltin compounds with Et_3B [7] or 9-alkyl-9-borabicyclo[3.3.1]nonanes [10]. The en-largement of the bicyclic ring system is the result of a kinetically controlled reaction [11]. Crystals of com-pound **7**, suitable for X-ray analysis, are obtained from hexane solution (vide infra).

(2)
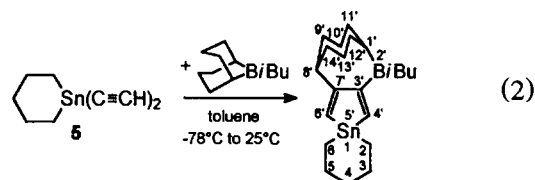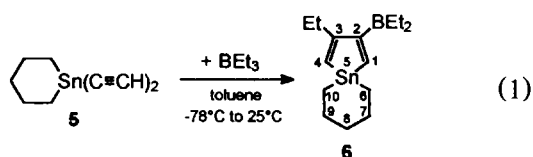
The reaction of the stannole **6** with trimethyltin ethoxide proceeds in the same way as described for stannoles which are not part of a spiro-structure [8]. Trimethyltin ethoxide is a typical ambiphilic reagent. Its nucleophilic site, the OEt group, seeks for an interaction with the boryl group while its electrophilic site, the Me_3Sn group, is then ready for further reactions. Al-though there are numerous possibilities for electrophilic attack, addition to the C=C bond takes place together with the 1,2-shift of an ethyl group from boron to carbon, leading selectively to the spiro compound **8** with a 1-stannolene unit (Eq. (3(a))). Such stannolenes are known to undergo an irreversible allylic rearrange-ment of the boryl group upon heating [8]. Exactly the same behaviour is observed in the case of compound **8** when the spiro-tin compound **9** is formed with a 2-stan-nolene unit (Eq. (3(b))).

(3)
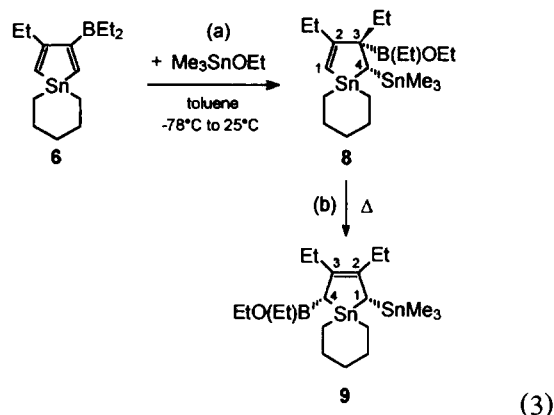
The reaction of the tetracyclic compound **7** with trimethyltin butoxide proceeds in a way similar to that shown in Eq. (3(a)). In the case of **7**, the exocyclic ^iBu group is transferred exclusively to give the tetracyclic compound **10** (Eq. (4)).
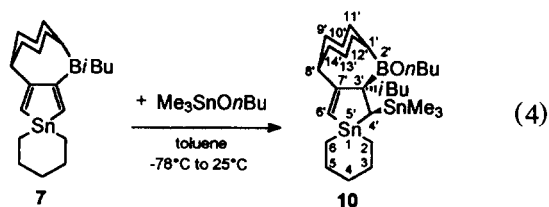

(1)

(4)

Table 1

Experimental data related to the single-crystal X-ray analysis of the tetracyclic compound 7 [12]

Formula (molecular mass)	$C_{21}H_{32}BSn$ (413.98)
Crystal; size (mm^3)	Colourless, irregularly; $0.45 \times 0.40 \times 0.16$
Crystal system; space group; Z	Triclinic; $P\bar{1}$; 2
Unit cell dimensions (pm); (°)	$a = 835.2(2)$, $b = 1117.5(2)$, $c = 1165.6(2)$; $\alpha = 72.05(3)$, $\beta = 74.32(3)$, $\gamma = 50.61(3)$
Volume (pm^3) $\times 10^6$; ρ (Mg m^{-3})	992.7(3); 1.355
Absorption coefficient (mm^{-1})	1.285
Diffractometer; temperature (K)	Siemens P4; 173
Radiation (pm)	Mo Kα 71.073 (graphite monochromator)
2θ range; scan type; range (ω)	$3.0°$ to $55.0°$; ω; $1.30°$
Measured reflections	5437
Independent/observed reflections	4501 ($R_{int} = 0.77\%$)/4501 ($F > 0.0\sigma(F)$)
Solution	Direct methods (SHELXTL PLUS)
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000F^2$
R value/ωR value (observed data)	2.64%/2.55%
Max./min. residual electron density (e pm^{-3}) $\times 10^{-6}$	0.82/ − 0.48

Upon heating **10** rearranges to two other compounds (δ^{119}Sn[$^2J(^{119}$Sn^{119}Sn)] 47.1, 19.0 [12.2] and −3.2, −86.9 [218.2]), which have not been characterised as yet.

2.2. X-ray analysis of the tetracyclic compound 7

Colourless crystals of irregular shape were obtained from hexane at 5°C. Experimental data relevant to the single crystal X-ray analysis are given in Table 1 [12], and the molecular structure of **7** is depicted in Fig. 1 together with selected bond lengths and angles. This is the first molecular structure of a stannole bearing hydrogen atoms at the carbon atoms adjacent to the tin atom, and it gives the first structural data for a molecule

containing the stannacyclohexane ring. The environment of the tin atom corresponds to a strongly distorted tetrahedron with small endocyclic bond angles, the smaller one [Cl–Sn–C4 = 82.2(1)°] belonging to the stannole system. The stannole ring is almost planar, the stannacyclohexane ring adopts a chair conformation, and the bicyclic system containing the boron atom shows a twisted arrangement of the carbon atoms C10 to C17 with respect to the four atoms B–C2–C3–C14 which are almost in one plane (torsion angle 3.1°). The plane formed by C2–C10–C18, including the exactly trigonal planar coordinated boron atom, is twisted against the best plane of the stannole ring by 47.3°, which means that there are only weak BC(pp)π interactions in the solid state. The bond angles at C1 [Sn–Cl–
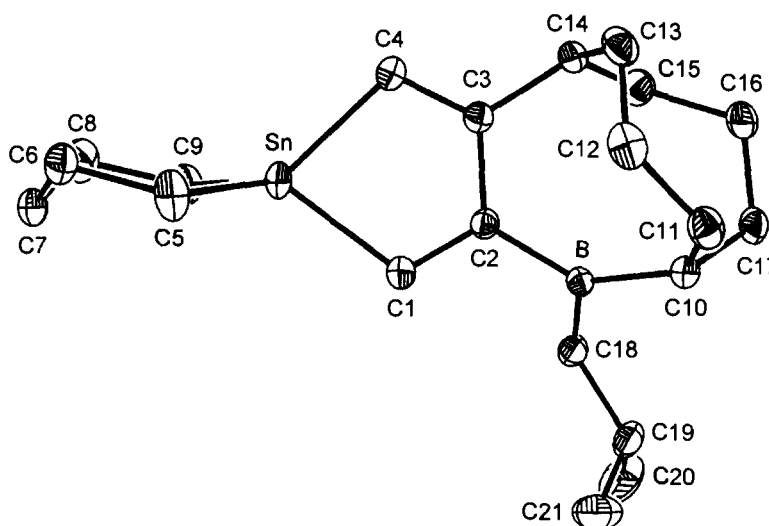

Fig. 1. Molecular structure of the tetracyclic stannole **7**. Selected bond lengths (pm), bond and torsion angles (°): Sn–Cl 213.3(2), Sn–C4 212.7(2), Sn–C5 215.0(2), Sn–C9 214.8(2), Cl–C2 135.5(3), C2–C3 150.6(3), C3–C4 134.7(3), B–C2 157.4(3), B–C10 159.2(3), B–C18 159.0(3), C5–Sn–C9 102.1(1), Cl–Sn–C4 82.2(1), Sn–Cl–C2 110.7(2), Cl–C2–C3 117.4(2), C2–C3–C4 119.8(2), Sn–C4–C3 109.8(2), B–C2–Cl 117.0(2), B–C2–C3 125.6(2), C2–B–C10 127.5(2), C2–B–C18 115.5(2), C10–B–C18 116.9(2), C18–B–C2–Cl 49.0(0.3), C18–B–C2–C3 −132.5(0.2).
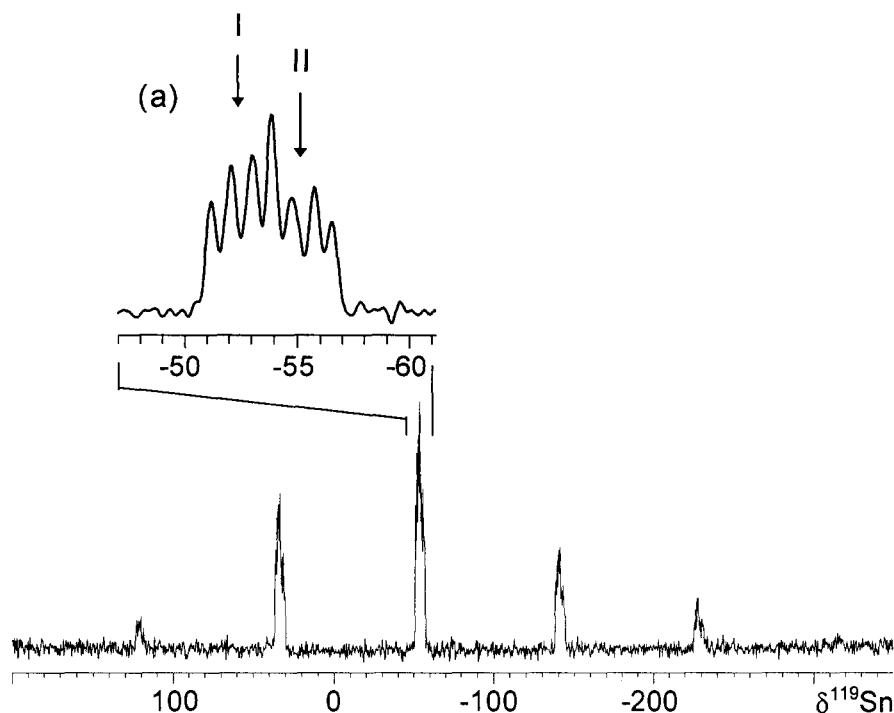
Fig. 2. 74.6 MHz ^{119}Sn solid-state CPMAS NMR spectrum of the tetracyclic stannole **7** (rotation frequency 6500 Hz). The expansion plot (a) shows the isotropic region. The isotropic chemical shifts of the two species are marked with arrows. The $^3J(^{119}Sn^{11}B)$ coupling constants are 68 ± 5 Hz (I) and 65 ± 5 Hz (II) according to simulation.

C2 = 110.7(2)°] and C4 [Sn–C4–C3 = 109.8(2)°] are similar to those observed for a 1,1′-spirobistannole bearing four Me$_3$Si groups [13].

2.3. Solid-state ^{13}C and ^{119}Sn CPMAS NMR spectra of 7

Both solid-state ^{13}C and ^{119}Sn CPMAS NMR spectra of **7** indicate the presence of two species in a ratio of 4:3 in the bulk of the solid material, in contrast with the result of the single-crystal X-ray analysis. The small shift differences point towards conformational isomers, most likely due to small conformational differences in

the $C_{10}H_{14}B$ system. Since the X-ray analysis does not suggest any disorder in the molecular structure of **7**, the single crystal used represent only one of the isomers. The powder X-ray diffraction data of the bulk solid material indicates the presence of a second crystalline species when compared with data calculated from the single-crystal X-ray diffraction study. The difference ($\Delta\delta^{119}Sn = -14.0, -16.7$) between isotropic $\delta^{119}Sn$ values in solution and in solid state is rather large and indicates that the mean conformation of the flexible rings in solution is different from that in the solid state. This is also evident from $\delta^{13}C(4')$ with $\Delta\delta^{13}C = 5.5$.

Table 2
^{13}C and ^{119}Sn NMR data ^{a} of stannacyclohexane derivatives 1–5

Com-pound	$\delta^{119}Sn$	$\delta^{13}C$			Other
		Sn–CH$_2$	–CH$_2$	–CH$_2$	
1	−108.7	10.4	27.9	31.9	139.5 [460.8] (i), 136.6 [35.4] (o), 128.2
		[339.3]	[31.4]	[51.8]	[47.6] (m), 128.6 [11.6] (p)
2	−82.8	9.0	28.5	32.4	
		[−297.8]	[+30.4]	[−46.9]	
3	81.1	27.1	25.2	35.0	
		[392.4]	[32.7]	[78.5]	
4	130.4 ^{b}	19.1	27.3	31.3	17.7 [358.3] (5), 25.3 [24.4] [5.6] (4),
		[308.8]	[36.6]	[60.4]	36.3 [113.1] [66.4] (3), 24.6 [60.4] (2),
					33.6 [656.7] (1)
5 ^{c}	−203.3	13.8	27.3	31.0	84.2 [565.2] (C≡), 98.5 [114.7] (≡CH)
		[452.3]	[35.4]	[72.0]	

^{a} 50% in CDCl$_3$; 298 K; $^nJ(^{119}Sn^{13}C)$ in Hertz are given in square brackets
^{b} $\delta^{119}Sn(SnCl_3) = 3.0$.
^{c} 50% in toluene-d_8.
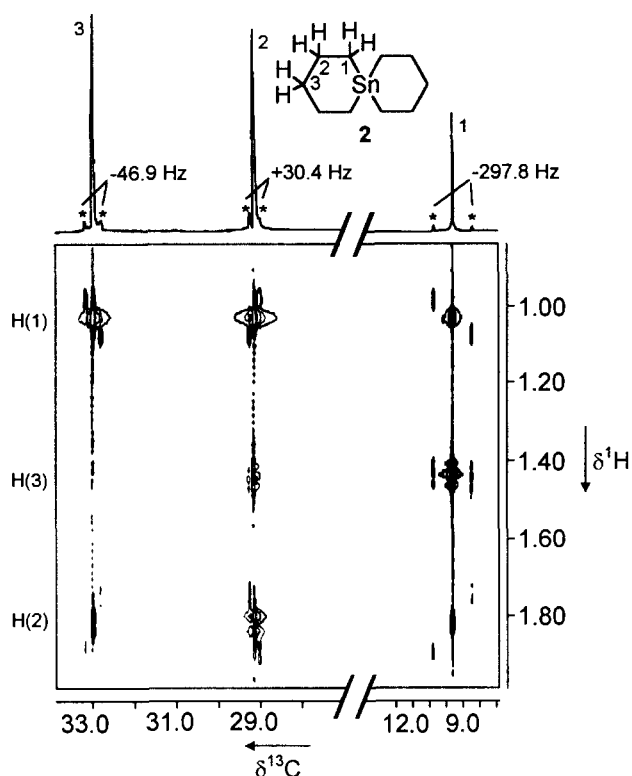
Fig. 3. 2D ^{13}C/^{1}H HETCOR (based on $^{2,3}J(^{13}$C^{1}H); residual signals are also present arising from $^1J(^{13}$C^{1}H)) of 6-stannaspiroundecane (2).

The ^{119}Sn CPMAS NMR spectrum of **7** (Fig. 2) shows resolved ^{119}Sn–^{11}B spin–spin coupling with $^3J(^{119}$Sn^{11}B) = 68 ± 5 and 65 ± 5 Hz. This is the second example [14] for the detection of $^3J(^{119}$Sn^{11}B) in solid-state ^{119}Sn CPMAS NMR spectra, whereas this coupling is not resolved in solution.

2.4. NMR spectroscopy in solutio..

NMR data of the starting materials are collected in Table 2. Some data have been reported in the literature [15], but signs of coupling constants involving ^{119}Sn

were not determined. We have determined the signs of $^nJ(^{119}$Sn^{13}C) (n = 1, 2, 3) for compound **2**, with respect to the known signs of $^2J(^{119}$Sn^{1}H) (> 0) and $^3J(^{119}$Sn^{1}H) (< 0) [16], using 2D ^{13}C/^{1}H HETCOR experiments based on $^1J(^{13}$C^{1}H) and $^nJ(^{13}$C^{1}H) (n = 2, 3). The tilt of the cross-peaks for $^{117/119}$Sn satellites allows for comparison of the signs of the respective coupling constants $J(^{119}$Sn^{13}C) and $J(^{119}$Sn^{1}H) (Fig. 3), a positive tilt being indicative of alike signs whereas a negative tilt indicates opposite signs [17]. Since the absolute magnitudes of the $^nJ(^{119}$Sn^{13}C) values for the stannacyclohexane systems in the other compounds are found within a narrow range, a change of the coupling signs is unlikely. The signs of $^nJ(^{119}$Sn^{13}C) (see Table 2) are in agreement with those determined for other alkyltin compounds [16].

The stannoles **6** and **7** are characterised by the NMR data in Table 3. The ^{13}C NMR signals for the olefinic carbon atoms are typical [7] of the stannole system. There are two sharp signals with $^{117/119}$Sn satellites corresponding to $^1J(Sn^{13}$C), another sharp signal with satellites for a smaller coupling constant $|^{2,3}J(Sn^{13}$C)|, and a broad ^{13}C NMR signal, typical of a boron-bonded carbon atom [18]. A 2D ^{13}C/^{1}H HETCOR experiment shows that the coupling constants $^2J(Sn^1$H) (known to be less than 0 [16]) and $^{2,3}J(Sn^{13}$C) have the same sign (Fig. 4). The magnitude and sign of these coupling constants can be explained by assuming a dominant contribution from the coupling pathway across three bonds.

The deshielding of ^{13}C(1) in **7** relative to **6** can be traced to the rigid tricyclic structure in **7**, where a greater degree of coplanarity between the unoccupied boron p_z orbital and the π orbitals of the C(1)=C(2) bond is enforced [18]. There is little difference in the ^{13}C NMR data for the stannole **6** and the analogous diethyltin derivative [7]. The increased ^{119}Sn nuclear shielding in **6** (by around 40 ppm) with respect to its diethyltin analogue is due to the integration of the tin atom in the six-membered ring and is also observed for

Table 3
^{13}C and ^{119}Sn NMR data [a] of stannoles (6, 7)

Compound	δ^{119}Sn	δ^{13}C						
		Sn–CH$_2$	–CH$_2$	–CH$_2$	Stannole [b]			
					C(1)	C(2)	C(3)	C(4)
6 [c,d]	−21.7	11.3	28.5	32.4	126.6	175.0	162.4	119.5
		[311.5]	[32.3]	[53.9]	[382.7]	(br)	[84.4]	[456.0]
7 [e,f]	−38.6	11.0	28.6	32.0	140.1	172.0	169.9	121.3
		[312.5]	[31.7]	[56.1]	[373.5]	(br)	[70.8]	[443.1]

[a] 50% in toluene-d_8; 298 K; $^nJ(^{119}$Sn^{13}C) in Hertz are given in square brackets.
[b] For simplicity the stannole ring carbon atoms of **7** are numbered analogously to **6**.
[c] δ^{11}B = 86.7.
[d] Other δ^{13}C values: 30.9 [61.9], 13.0 (Et^3), 21.2, 9.0 (BEt$_2$).
[e] δ^{11}B = 83.7.
[f] Other δ^{13}C values: 43.5 [65.9] (8′), 31.4 (9′, 14′), 22.3 (10′, 13′), 33.8 (11′, 12′), 33.1 (br) (1′), 43.4 (br), 26.5, 26.0 (^{1}Bu) (for numbering see Eq. (2)).
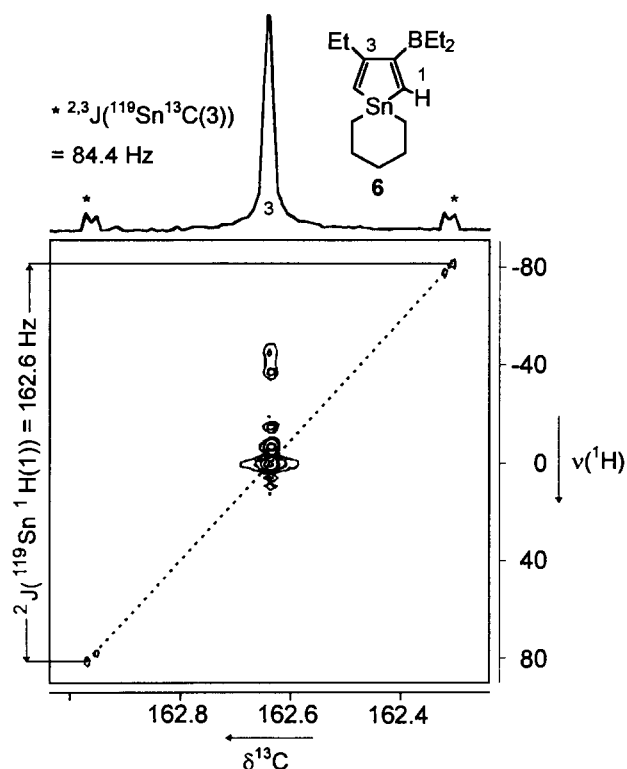
Fig. 4. 2D ^{13}C/^{1}H HETCOR (based on $^3J(^{13}C^1H)$) of 2-diethyl-boryl-3-ethyl-5-stannaspiro[4,5]deca-1,3-diene (6).

other pairs of compounds, e.g. for 5 (δ^{119}Sn -203.3) and Et$_2$Sn(C≡CH)$_2$ (δ^{119}Sn -141.3).

Most NMR data of the spiro-tin compounds 8 and 9 with stannolene units (Table 4) are rather similar to those reported for analogous dimethyltin compounds [8], in support of the proposed structures. The ^{119}Sn nuclear shielding in 8 and 9 is increased again by ca. 40–50 ppm as a result of the influence of the six-membered ring. The $|^2J(SnSn)|$ value for 8 (21.1 Hz) is slightly smaller than for its dimethyltin analogue (33.2 Hz), whereas the $|^2J(SnSn)|$ value for 9 (63.8 Hz) is markedly larger than that for the dimethyltin compound (31.5 Hz). There is also a larger difference in the δ^{119}Sn values for 8 ($\delta + 45.8$) and 9 ($\delta + 34.8$) than for their dimethyltin analogues ($\delta + 83.9$ and $+82.4$).

The $|^2J(^{119}Sn^{119}Sn)|$ value of 158.6 Hz of 10 is noticeably greater than in other 2-stannolenes (13–33 Hz) [8]. The sign of $^2J(^{119}Sn^{117}Sn)$ in 10 was determined as negative, with respect to the known sign of $^2J(^{117}Sn^1H)$ (> 0) [16], using a 2D ^{119}Sn/^{1}H HETCOR experiment based on $^2J(^{119}Sn^1H)$ (Fig. 5). The magnitude and sign of $^2J(SnSn)$ depend on various factors: the intervening atom, the nature of the substituents both on tin and the intervening atom, and the stereochemistry of the whole molecule, in particular the Sn–X–Sn bond angle [16]. In this case, the main factor

Table 4
^{13}C and ^{119}Sn NMR data [a] of stannolenes (8, 9, 10)

Compound	δ^{119}Sn	δ^{13}C						
		Sn–CH$_2$	–CH$_2$	–CH$_2$	Stannolene			
					C(Sn,Sn)	C(R,B)/C(R)	C(R)	C(Sn)
8	45.8 [b]	14.0	29.1	32.5	12.4 [c]	55.1 [d]	170.8 [e]	122.3
	[21.1]	[311.1]	[30.1]	[53.2]	[346.1]	(br)	[77.4]	[414.3]
		13.8			[224.4]		[62.2]	[20.5]
		[287.3]						
9	34.8 [f]	13.9	28.8	32.3	17.7 [g]	139.2 [h]	136.4 [i]	33.8 [j]
	[63.8]	[261.3]	[29.2]	[51.7]	[305.8]	[43.8]	[52.4]	(br)
		[22.6]			[230.2]	[15.9]	[9.3]	
		12.4	28.8					
		[397.2]	[30.5]					
10	18.1 [k]	16.2	29.1	32.3	14.2 [l]	37.5 [m]	175.1 [n]	128.0
	[158.6]	[280.1]	[31.6]	[50.2]	[n.m.]	(br)	[55.6]	[406.5]
		[19.6]			[n.m.]		[16.9]	
		13.1	29.0					
		[306.3]	[31.6]					

[a] 50% in toluene-d_8 298 K; $^nJ(^{119}Sn^{13}C)$ in Hertz are given in square brackets.
[b] δ^{119}Sn (SnMe$_3$) = 15.1 [21.1], δ^{11}B = 51.5.
[c] δ^{13}C (Me$_3$Sn) = -6.9 [311.0] [9.4].
[d] δ^{13}C (Et) = 28.1 [47.9], 12.9 [4.8] [3.3]; δ^{13}C (BEt) = 8.9 (br), 8.6; δ^{13}C (OEt) = 61.4, 17.3.
[e] δ^{13}C (Et) = 28.8 [77.4], 7.9.
[f] δ^{119}Sn (SnMe$_3$) = 12.1 [63.8], δ^{11}B = 51.0.
[g] δ^{13}C (Me$_3$Sn) = -7.0 [307.2] [9.3].
[h] δ^{13}C (Et) = 28.6 [69.0] [15.9], 13.9.
[i] δ^{13}C (Et) = 29.2 [54.4] [10.6], 14.1.
[j] δ^{13}C (BEt) = 11.7, 9.1; δ^{13}C (OEt) = 60.4, 17.8.
[k] δ^{119}Sn (SnMe$_3$) = 2.8 [158.6], δ^{11}B = 51.5.
[l] δ^{13}C (Me$_3$Sn) = -5.3 [306.3] [8.7].
[m] δ^{13}C (^{t}Bu) = 56.5 [57.8] [17.4], 26.2, 25.7, 24.8, δ^{13}C (BCH) = 27.5 (br); δ^{13}C (O^{n}B) = 64.4, 33.6, 19.4, 14.1.
[n] δ^{13}C (CH) = 44.5 [66.5], other δ^{13}C values for 9'–14' are not assigned.
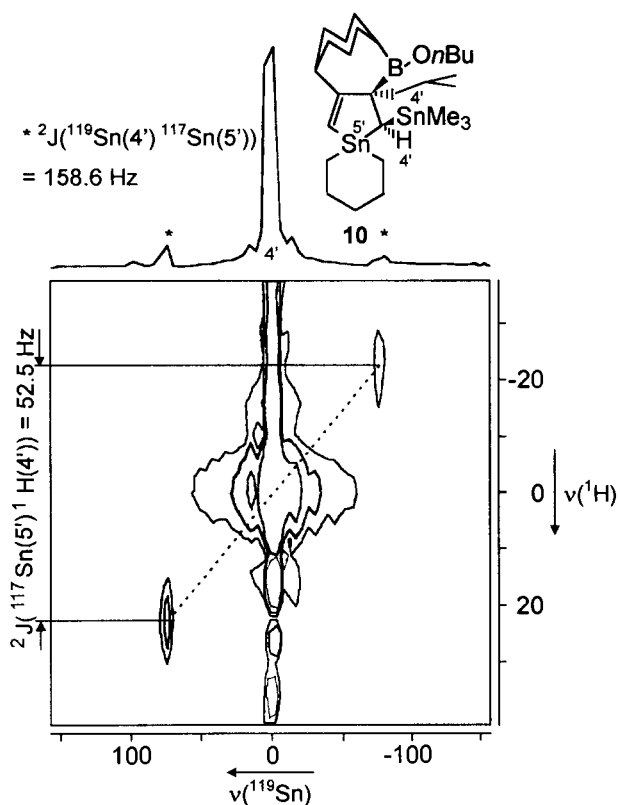
Fig. 5. 2D ^{119}Sn/^{1}H HETCOR (based on $^2J(^{119}$Sn^{1}H)) of 2'-bora-3'-isobutyl-2'-n-butoxy-4'-trimethylstannyl-1-stannaspiro[hexane-1,5'-tricyclo[6.3.3.0$^{3',7'}$]tetradec-6'-ene] (10).

is the Sn–C–Sn bond angle. The Sn–C–Sn bond angle of **10** is supposed to be smaller than in other 2-stannolenes, leading to an increase of $|\,^2J(^{119}$Sn^{119}Sn)$|$ caused by the steric requirement of the bicyclic system attached to the stannolene unit. To corroborate this assumption, the structure of **10** was calculated by the MM$^+$ method [19]. The reliability of this method was checked by calculating the structures of **7** and of 4-((2'-(S)-Butoxy)ethylboryl)-3,4-diethyl-1,1-dimethyl-5-trimethylstannyl-2-stannolene [8]. The latter compound shows a typical $^2J(^{119}$Sn^{119}Sn) value of -12.9 Hz with an Sn–C–Sn bond angle of 114.7(2)° (calc.: 113.6°). The calculation for **10** gives an Sn–C–Sn bond angle of 105.9°. The sign of $^2J(^{119}$Sn^{119}Sn) is in general negative, if the bond angle Sn–X–Sn is between 90° and 120°, and it becomes positive if the angle exceeds 120° [16]. Thus the $^2J(^{119}$Sn^{119}Sn) value of -158.6 Hz in **10** can be explained by the change in bond angle Sn–C–Sn.

3. Experimental details

All preparations and the handling of compounds were carried out under Ar, using carefully dried glassware and solvents. The stannacycles **1–3** [4,5] were prepared following literature methods. Deuterated solvents were stored over molecular sieve and saturated with Ar. ^{1}H/^{13}C NMR: Bruker ARX 250, Bruker AC

300, Bruker AM 500 (250.13/62.90 MHz, 300.13/75.5 MHz and 500.13/125.8 MHz respectively). ^{11}B NMR: Jeol FX90Q (28.7 MHz), Et$_2$O · BF$_3$ as external standard. ^{119}Sn NMR: Bruker ARX 250, Bruker AC 300 (93.3 MHz and 111.9 MHz), SnMe$_4$ as external standard. All ^{13}C and ^{119}Sn CPMAS experiments were carried out using a Bruker MSL 200 NMR spectrometer, equipped with the necessary CPMAS double bearing probes and a Bruker B-VT 1000 temperature control unit. A completely filled ZrO$_2$ rotor (4 mm outside diameter) was used. The matching conditions for Hartmann–Hahn cross-polarisation (^{1}H 90° pulse length 5 μs) were set on adamantane (^{13}C) and (C$_6$H$_{11}$)$_4$Sn (^{119}Sn) respectively. The ^{119}Sn CPMAS experiment (see also Fig. 2) was carried out at 298 K with a recycle delay of 5 s and a contact time of 1 ms, 240 transients were recorded at a rotation frequency of 6500 Hz. The ^{13}C CPMAS experiments were carried out in the temperature range 243–298 K, recycle delay 10 s, contact time 1 ms, rotation frequency 3501 Hz, 240 transients were recorded at 298 K and 64 transients at lower temperatures. Isotropic chemical shifts are given with respect to the same external references as for the solution-state spectra. The powder X-ray diffraction data were measured using a Siemens D5000 diffractometer.

3.1. 5-(1'-Chloro-1'-stannacyclohexyl)-1-trichlorostannylpentane (4)

SnCl$_4$ (11.78 g, 45.2 mmol) was slowly added to a solution of 11.43 g (45.2 mmol) of **2** in 30 ml of hexane at ambient temperature. After stirring for 1 h the solvent was removed in vacuo, leaving the colourless oily product **4** (22.96 g, 44.7 mmol, 99.0%). The attempt to distill **4** did not lead to 1,1-dichloro-1-stannacyclohexane, but afforded a polymer at 215°C/10^{-3} Torr. Further heating led to extensive decomposition.

4. ^{1}H NMR (CDCl$_3$): δ [$^nJ(^{119}$Sn^{1}H)] = 1.42 [41.7] m, 4H, SnCH$_2$; 2.01 [90.3] m, 4H, CH$_2$; 1.53 m, 2H, CH$_2$; 1.43 [54.2] t, 2H, C^{5}H$_2$; 1.56 m, 2H, C^{3}H$_2$; 1.76 m, 2H, C^{4}H$_2$; 1.99 m, 2H, C^{2}H$_2$; 2.42 [86.8] t, 2H, C^{1}H$_2$.

3.2. 1,1-Diethynyl-1-stannacyclohexane (5)

Ethynylmagnesium bromide in THF (0.105 mol in 125 ml THF), prepared as described in Ref. [20], was cooled to -78°C for 1 h, before 17.4 g (0.05 mol) of **3** was added. Mechanical stirring was continued while the mixture warmed up to ambient temperature over night. All volatile material was removed in vacuo and condensed in a trap at -78°C. The residue was heated to 190°C in vacuo to collect as much of the product as possible. The solvent was evaporated at 20 Torr and fractional distillation of the residue through a 15 cm Vigreux column gave 4.74 g pure **5** (19.8 mmol, 39.8%) as a colourless moisture-sensitive liquid (b.p. 80°C/10^{-2} Torr).

5. ^{1}H NMR (toluene-d_8): δ [$^nJ(^{119}$Sn^{1}H)] = 1.14 [68.3] dd, 4H, SnCH$_2$; 1.68 [105.0] m, 4H, CH$_2$; 1.23 m, 2H, CH$_2$; 2.09 [37.2] s, 2H, ≡CH.

3.3. 2-Diethylboryl-3-ethyl-5-stannaspiro[4,5]deca-1,3-diene (6) and 2'-bora-2'-isobutyl-1-stannaspiro[hexane-1,5'-tricyclo[6.3.3.0$^{3',7'}$]tetradeca-3',6'-diene] (7) (NMR-scale experiments)

A solution of 1.0 mmol of **5** in 0.3 ml of toluene-d_8 (NMR-tube) was cooled to −78°C. After adding 1 mmol of the respective borane (BEt$_3$ or 9-^{i}Bu-9-BBN) the mixture was warmed slowly to ambient temperature.

6. ^{1}H NMR (toluene-d_8): δ [$^nJ(^{119}$Sn^{1}H)] = 1.09 [52.6] dd, 4H, SnCH$_2$; 1.74 [82.3] m, 4H, CH$_2$; 1.31 m, 2H, CH$_2$; 6.04 [164.7] t, 1H, =C^{4}H; 6.02 [162.6] s, 1H, =C^{1}H; 2.14 [9.0] dq, 2H, Et^3; 0.94 t, 3H, Et^3; 1.18 q, 4H, BEt$_2$; 0.86 t, 6H, BEt$_2$.

7. ^{1}H NMR (toluene-d_8): δ [$^nJ(^{119}$Sn^{1}H)] = 1.22 dd, 4H, SnCH$_2$; 1.85 m, 4H, CH$_2$; 1.32 m, 2H, CH$_2$; 6.96 [161.4] s, 1H, =C^{4}H; 6.00 [162.8] s, 1H, =C^{6}H; 3.21 m, 1H, C^{8}H; 2.03 m, 1H, C^{1}H, 1.95, 1.12 m, 4H, C$^{9'}/^{14'}$H$_2$; 1.93, 1.55 m, 4H, C$^{11'}/^{12'}$H$_2$; 1.55 m, 4H, C$^{10'}/^{13'}$H$_2$; 2.05 m, 1H, B^{i}Bu; 1.42 d, 2H, B^{i}Bu; 0.94 d, 6H, B^{i}Bu.

3.4. 2,3-Diethyl-3-(ethoxyethylboryl)-4-trimethylstannyl-5-stannaspiro[4,5]dec-1-ene (8), 2,3-diethyl-4-(ethoxyethylboryl)-1-trimethylstannyl-5-stannaspiro[4,5] dec-2-ene (9) and 2'-bora-3'-isobutyl-2'-n-butoxy-4'-trimethylstannyl-1-stannaspiro[hexane-1,5'-tricyclo[6.3.3.0$^{3',7'}$]-tetradec-6'-ene] (10) (NMR-scale experiments)

A solution of 1.0 mmol of **6/7** in 0.3 ml of toluene-d_8 (NMR-tube) was cooled to −78°C. After adding 1 mmol of trimethyltin(IV)ethoxid/trimethyltin(IV)-n-butoxide the mixture was warmed slowly to ambient temperature. To obtain **9**, the NMR-tube, containing compound **8**, was heated to 80°C for about 1 h.

8. ^{1}H NMR (toluene-d_8): δ [$^nJ(^{119}$Sn^{1}H)] = 1.05 dd, 4H, SnCH$_2$; 1.89 m, 4H, CH$_2$; 1.44 m, 2H, CH$_2$; 6.46 [133.5] s, 1H, =C^{1}H; 2.08, 1.77 m, 2H, Et^2; 0.79 t, 3H, Et^2; 2.07, 1.51 m, 2H, Et^3; 1.14 t, 3H, Et^3; 3.62 q, 2H, OEt; 1.10 t, 3H, OEt; 1.04 q, 2H, BEt; 0.81 t, 3H, BEt; 0.78 s, 1H, C^{4}H; 0.19 [52.8] s, 9H, SnMe$_3$.

9. ^{1}H NMR (toluene-d_8): δ [$^nJ(^{119}$Sn^{1}H)] = 1.20, 1.22 m, 4H, SnCH$_2$; 1.82 m, 4H, CH$_2$; 1.39 m, 2H, CH$_2$; 2.42 [24.8] s, 1H, C^{4}H; 1.88 [79.8] s, 1H, C^{1}H; 2.49, 1.89 m, 2H, Et^2; 1.04 t, 3H, Et^2; 2.28, 2.09 m, 2H, Et^3; 1.02 t, 3H, Et^3; 3.75 m, 2H, OEt; 1.15 t, 3H, OEt; 1.13 t, 3H, BEt; 0.85 m, 2H, BEt; 0.19 [51.0] s, 9H, SnMe$_3$.

10. ^{1}H NMR (toluene-d_8): δ [$^nJ(^{119}$Sn^{1}H)] = 1.05, 1.15 m, 4H, SnCH$_2$; 1.68, 1.87 m, 4H, CH$_2$; 1.26 m, 2H, CH$_2$; 6.14 [128.0] s, 1H, =C^{6}H; 1.75, 1.44 m, 2H, ^{i}Bu^3; 1.73 m, 1H, ^{i}Bu^3; 0.78, 0.74 m, 6H, ^{i}Bu^3; 3.63 t, 2H, O^{n}Bu; 1.43 m, 2H, O^{n}Bu; 1.25 m, 2H, O^{n}Bu; 0.77

t, 3H, O^{n}Bu; 0.77 [54.9] s, 1H, C^{4}H; −0.06 [49.5] s, 9H, SnMe$_3$; other δ^1H values for C$^{1'}/^{8'}$H, C$^{9'-14'}$H$_2$ are not assigned.

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