

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230517419>

Stabilization of Triorganotin Cations — Competition between Intramolecular Coordinative O, S or NSn Bonds and Side-on π Coordination to C \equiv C Bonds

ARTICLE in *BERICHTE DER DEUTSCHEN CHEMISCHEN GESELLSCHAFT* · FEBRUARY 1994

Impact Factor: 2.94 · DOI: 10.1002/cber.19941270209

CITATIONS

26

READS

7

4 AUTHORS, INCLUDING:



Wolfgang Milius

University of Bayreuth

338 PUBLICATIONS 4,116 CITATIONS

SEE PROFILE



Roland Boese

University of Duisburg-Essen

986 PUBLICATIONS 15,184 CITATIONS

SEE PROFILE

Stabilization of Triorganotin Cations – Competition between Intramolecular Coordinative O–, S– or N–Sn Bonds and Side-on π Coordination to $C\equiv C$ Bonds

Bernd Wrackmeyer^{*a}, Sabine Kundler^a, Wolfgang Milius^a, and Roland Boese^b

Laboratorium für Anorganische Chemie der Universität Bayreuth^a,
D-95440 Bayreuth

Institut für Anorganische Chemie der Universität-GH Essen^b,
Universitätsstraße 1–4, D-45141 Essen

Received August 13, 1993

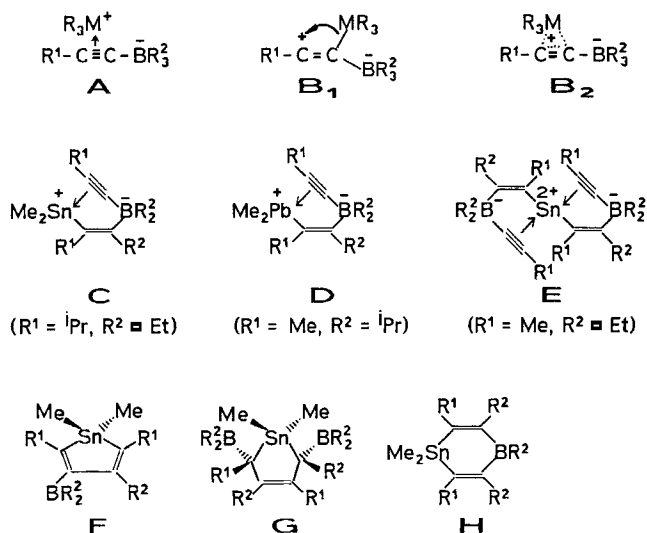
Key Words: Tin cations, triorgano / Coordination, σ and π / 1,1-Organoboration / 1-Alkynyltin compounds, functionally substituted

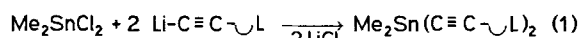
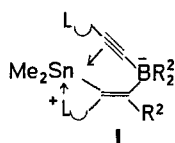
Di-1-alkynyltin compounds **1** of the type $Me_2Sn(C\equiv C_L)_2$ [L_U = 2-pyridyl (**a**), Me_2NCH_2 (**b**), $MeOCH_2$ (**c**), $MeOCH=CH$ (**d**), $EtSCH_2$ (**e**)] were prepared and the 1,1-organoboration of **1** with triethyl- (**2a**) and triisopropylborane (**2b**) has been studied. The first detectable intermediates were in all cases zwitterionic compounds **3** (from Et_3B) and **4** (from iPr_3B) with a cationic triorganotin fragment, stabilized by coordinative σ L–Sn bonds and by side-on coordination to the $C\equiv C$ bond of an alkynylborate moiety. The nature of this stabilization has been established by three X-ray analyses (**3b**, **4b**, and **4d**) in the solid state and by multinuclear NMR (1H -, ^{11}B -, ^{13}C -, ^{15}N -, ^{119}Sn NMR) in solution. The comparison of the molecular structure of **3b**, **4b**, and **4d** with that of intermedi-



ates without functional groups shows that the distance of the tin atom to the $C\equiv C$ bond is elongated. However, the planar arrangement of all relevant atoms proves that the side-on coordination of the tin atom to the $C\equiv C$ bond is still present. These intermediates **3** and **4** rearrange to stannoles **5**, **6** and/or to 1-stanna-4-bora-2,5-cyclohexadienes **9**, **10**. In the case of **3b** and **3e**, ^{119}Sn NMR indicates that dialkenyltin compounds **7b** and **7e** are also formed as minor products. In the case of **3e**, the 3-stannolene **8e** is one of the final products. In the stannoles **5** and **6** a coordinative L–B bond is evident, and there is NMR spectroscopic evidence of a weak coordinative L–Sn bond.

Free triorganoelement cations of silicon, germanium, tin, and lead, $[R_3M]^+$, have been in the centre of a controversial debate for a long time^[1]. However, there are many examples of stabilization of such species by more or less strong donor-acceptor interactions $[R_3M-L]$ where the donor L in general offers a lone pair of electrons for M–L σ interactions^[2]. In order to explain the course of 1,1-organoboration reactions of alkynylmetal compounds^[3] we have proposed that the cleavage of the $M-C\equiv$ bond leads to zwitterionic intermediates of the type A. The triorganoelement cation in A is stabilized by side-on coordination to the $C\equiv C$ bond of the alkynylborate group. In principle, this can also be understood as hyperconjugative^[4] β -metal-stabilization of a vinyl cation (**B₁**)^[5a–c], as a bridged structure (**B₂**), or even more general as σ – π delocalization^[5d]. Recently, we have shown that such intermediates can be isolated and fully characterized when di-1-alkynyltin^[6], -lead^[7], or tetra-1-alkynyltin compounds^[8,9] are treated with triethyl- or triisopropylborane (see X-ray analyses of compounds of the type C^[6], D^[7], and E^[8]). These species are very reactive and tend to rearrange, in some cases already at $-20^\circ C$, into various cyclic compounds such as stannoles (F) or plumboles^[10], 3-plumbolenes^[11], or 3-stannolenes G (in the presence of excess of R_3^2B), 1-plumba^[17] or 1-stanna-4-bora-2,5-cyclohexadienes^[6] (H), or into various spirocompounds^[9,12,13] (starting from the intermediate E).

In this work, we report on the attempts to prepare intermediates of type I ($R^1 = L_U$) which are stabilized by π coordination and/or intramolecular O–, S–, and N–Sn coordination (functional substituent in L). Starting point is

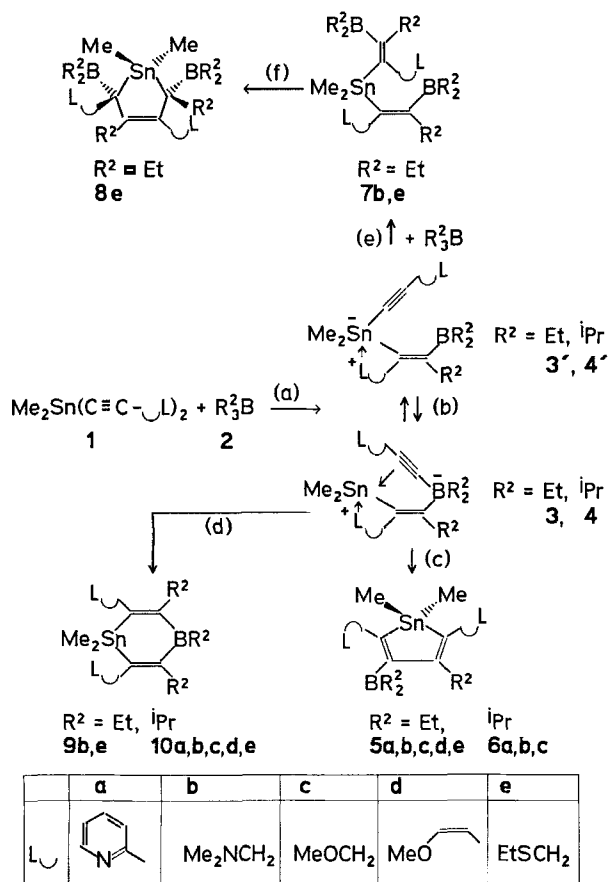




	a	b	c	d	e
LC		Me_2NCH_2	MeOCH_2	MeO 	EtSCH_2

The 1,1-organoboration of **1** with Et₃B or *i*Pr₃B (**2a,b**) should afford the intermediates **3** (from Et₃B) or **4** (from *i*Pr₃B). Furthermore, it was of interest to find out whether the final products of the 1,1-organoboration reactions correspond to those found for di-1-alkynyltin compounds without functional groups in R^{1[6]} (Scheme 1). Multi-nuclear NMR (¹H-, ¹¹B-, ¹³C-, and ¹¹⁹Sn NMR) in solution served for monitoring the progress of the reactions and to identify the final products. In three cases X-ray analyses were carried out in order to determine the molecular structure of the intermediates **3b**, **4b** and **4d**.

Scheme 1. 1,1-Organoboration of functionally substituted di-1-alkynyldimethyltin compounds **1a–e**



The synthesis of the di-1-alkynyltin compounds **1** is straightforward, according to eq. (1) (see Table 1 for ^{13}C - and ^{119}Sn -NMR data).

Table 1. ^{13}C , ^{119}Sn -, and ^{15}N -NMR data of dialkynyln tin compounds **1a–e**^[a,b]

L_{\cup}	2-Py 1a [c]	CH_2NMe_2 1b [d]	CH_2OMe 1c	$CH=CHOMe$ 1d [e]	CH_2SeEt 1e [f]
Me_2Sn	-6.5 [500.3]	-6.3 [499.2]	-7.1 [501.4]	-6.5 [498.6]	-6.6 [499.7]
$Sn-C\equiv$	90.6 [573.3]	84.9 [612.9]	86.1 [592.9]	93.0 [619.1]	82.4 [609.3]
$L_{\cup}C\equiv$	107.5 [117.2]	105.1 [123.4]	105.0 [119.4]	103.3 [133.0]	105.2 [124.8]
L_{\cup}	142.3 (2) [15.8] 122.5 (3)	48.9 [11.4] 44.0	59.6 [11.4] 56.6	84.7 [16.3] 156.8	19.4 [12.5] 24.8
$\delta^{119}Sn$	-145.5	-156.8	-152.5	-151.5	-153.5
$\delta^{15}N$	-63.5	-358.9			

[a] Ca. 20–40% in CDCl_3 at $26 \pm 1^\circ\text{C}$. – [b] $\eta_{\text{J}}(^{119}\text{Sn}, ^{13}\text{C})$ in Hz are given in []. – [c] Other $\delta^{13}\text{C}$ values: 135.6 (C-4), 126.7 (C-5), 149.4 (C-6). – [d] ^{13}C -INADEQUATE: $^1J(=^{13}\text{C}^{13}\text{CH}_2) = 62.5$, $^1J(^{13}\text{C}\equiv^{13}\text{C}) = 124.1$ Hz. – [e] Other $\delta^{13}\text{C}$ values: 60.1 (OCH_3). – [f] Other $\delta^{13}\text{C}$ values: 13.7 (CH_3).

In order to determine the proper reaction conditions for the formation and isolation of intermediates at a larger scale, all reactions between the di-1-alkynyltin compounds **1** and the trialkylboranes **2** were at first carried out in NMR tubes, using a 1:1 ratio of **1** and **2** and also a five- to tenfold excess of the trialkylborane **2**. The components were mixed in an inert solvent such as chloroform, dichloromethane, or toluene between -60 and -78°C , and two samples were made of each mixture. One sample was allowed to reach ambient temperature and the second sample with the same composition was slowly warmed until ^{119}Sn NMR (see Figure 1) showed that the reaction had started.

Keeping the reaction mixture at that temperature, the first detectable intermediates are **3** and **4**. A stereoselective intermolecular 1,1-organoboration of one of the two 1-alkynyl groups in **1** has taken place, and the second 1-alkynyl group has already migrated from the tin to the boron atom. In the case of **4**, these compounds were isolated as air- and moisture-sensitive, colorless solids. The compounds **3** are much less stable and rearrange further at room temperature. However, it proved possible to get crystalline material suitable for an X-ray analysis of **3b** and also of the compounds **4b** and **4d** (vide infra). The characterization of all other compounds **3** and **4** is based on the consistent ^1H -, ^{11}B -, ^{13}C -, and ^{119}Sn -NMR data set (see Experimental and Tables 2, 3).

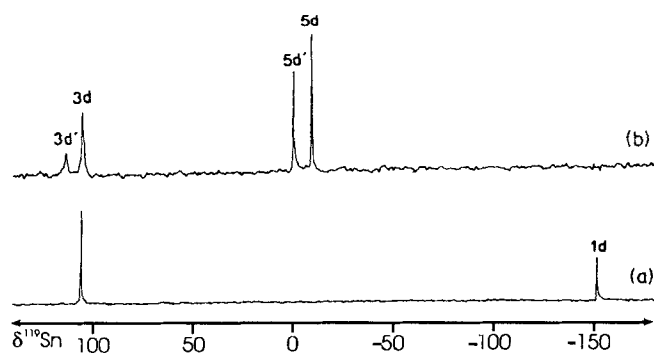


Figure 1. 33.3 MHz ^{119}Sn -NMR spectra of the reaction solution in CDCl_3 containing the di-1-alkynyltin compound **1d** and Et_3B . (a) ^1H inverse-gated decoupled ^{119}Sn -NMR spectrum, measured at -65°C immediately after mixing of the starting compounds. (b) ^{119}Sn -NMR spectrum (refocused INEPT with ^1H decoupling) measured after three days at room temperature. The appearance of the ^{119}Sn -NMR signal for **3d'** shows that the SnMe/BEt exchange takes place in the zwitterionic intermediate

With the exception of **3c,e** and **4c,e**, the derivatives **3** and **4** appear to be more stable than their counterparts of type **C**^[6]. The final products (**5**, **6**, **8**, **9**, **10**) of the twofold 1,1-organoboration are very similar to those found previously without functional substituents in R^1 ^[6]. Clearly, the formation of **7e** and, finally, **8e** requires the equilibrium (b) in Scheme 1 where **3'**, with the 1-alkynyl group linked to the tin atom, must be available for the intermolecular reaction with Et_3B . The donor stabilization does not prevent the electrophilic attack of the stannyl group at the $\text{C}\equiv\text{C}$ bond of the alkynylborate moiety [Scheme 1 (c, d)], and, depending on the substituents R^2 and L_\cup , either the stannoles **5**, the 1-stanna-4-bora-2,5-cyclohexadienes **9**, or mixtures of both are formed (see Experimental). One major difference to previous work on organoboration of di-1-alkynyltin compounds^[6] concerns the exchange of alkyl groups between tin and boron, e.g. in **3d** (not in **4!**) as shown in Figure 1. It appears that a donor L_\cup is necessary [eq. (2)] since a similar behaviour has been observed previously in the 1,1-organoboration of functionally substituted monoalkynyltin compounds^[14,15].

We regard this as a chemical indication of a weakened π coordination to the tin atom in **3** because the BEt/SnMe exchange requires alkyl groups to move into the bridging position, at least for a very short time. Unfortunately, this exchange is a complicating factor for isolating pure compounds. Therefore, depending on the reaction time required for the rearrangement of **3** to **5** or **9**, pure compounds **5** or mixtures of **5** and **9** may also contain some isomers resulting from the BEt/SnMe exchange reaction. All products **5** to **10** are identified on the basis of their characteristic NMR data (see Experimental and Tables 4, 5).

NMR Spectra

Di-1-alkynyltin Compounds (1): Chemical shifts $\delta^{13}\text{C}$ and $\delta^{119}\text{Sn}$ as well as coupling constants $J(^{119}\text{Sn}^{13}\text{C})$ (Table 1) for the di-1-alkynyltin compounds **1** are similar to those of comparable derivatives without functional substituents^[16].

Table 2. ^{13}C -, ^{119}Sn -, ^{11}B -, and ^{15}N -NMR data of $(\eta^2\text{-alkyne})\text{tin}$ compounds **3a–e**^[a,b]

L_\cup	2-Py 3a ^[c]	CH_2NMe_2 3b	CH_2OMe 3c ^[f]	$\text{CH}=\text{CHOMe}$ 3d ^[g]	CH_2SEt 3e ^[h]
Temp.(K)	258	243	243	243	243
Me_2Sn	1.3 [362.9]	-0.2 [308.4]	1.3 [304.1]	-0.8 [358.6]	1.1 [304.1]
$\text{SnC}\equiv$	139.9 [864.9]	138.2 [877.9]	136.0 [779.8]	126.9 [745.5]	141.0 [819.6]
$\text{BC}\equiv$	194.0 [br]	177.9 [br]	177.4 [br]	185.0 [br]	183.0 [br]
$\text{BC}\equiv$	125.7 [br]	127.2 [br]	125.0 [br]	115.9 [br]	116.3 [br]
$\text{B}-\text{C}\equiv\text{C}$	107.1 [38.7]	97.9 [49.6]	103.5 [54.5]	111.2 [27.8]	106.3 [44.7]
BEt_2	17.1 [br]	16.2 [br]	16.5 [br]	17.8 [br]	16.7 [br]
	12.6	12.4	12.2	12.2	12.2
$\text{Et}-\text{C}\equiv$	26.4 [145.0]	25.6 [169.5]	26.4 [153.7]	25.0 [134.1]	25.1 [135.1]
	12.9 [17.4]	13.9 [20.2]	13.2 [19.1]	14.9 [16.9]	14.0 [18.5]
$\text{L}_\cup\text{C}\equiv$	159.0 [86.1]	62.9 [83.4]	75.3 [58.3]	110.8 [114.4]	33.6 [122.1]
	121.0 [74.0]	46.0	58.1	140.3 [21.8]	25.1
$\text{L}_\cup\text{C}\equiv$	142.4 122.5	49.6 43.2	60.0 56.9	81.8 162.5	18.9 24.4
$\delta^{119}\text{Sn}$	114.1	127.7	207.1	105.1	169.0
$\delta^{11}\text{B}$	-8.7	-10.2	-8.7	-7.1	-4.6
$\delta^{15}\text{N}$ $\text{L}_\cup\text{C}\equiv$	-101.4 ^[d]	-334.4 ^[e]			
$\text{L}_\cup\text{C}\equiv$	-64.9	-357.6			

[a] Ca. 20% in CDCl_3 . – [b] $^1J(^{119}\text{Sn}, ^{13}\text{C})$ in Hz are given in []; [br] denotes broad ^{13}C resonances of boron-bound carbon atoms; [n.o.] = not observed; $\delta^{11}\text{B}$ values ± 0.3 . – [c] Other $\delta^{13}\text{C}$ values: 139.1 [14.7], 145.3 [10.4], 119.4 ($\text{L}_\cup\text{C}\equiv$), 136.0, 128.4, 149.5 ($\text{L}_\cup\text{C}\equiv$). – [d] $\delta^{15}\text{N}$ at 238 K. – [e] $\delta^{15}\text{N}$ at 298 K. – [f] $\delta^{13}\text{C}$ values in C_7D_8 at 243 K: 1.3 [306.3] (Me_2Sn), 136.4 [779.4] ($\text{SnC}\equiv$), 178.1 [br] ($\text{BC}\equiv$), 125.5 [br] ($\text{BC}\equiv$), 104.7 [55.6] ($\text{B}-\text{C}\equiv\text{C}$), 17.3 [br], 12.7 (BEt_2), 26.9 [154.8], 13.6 [17.4] ($\text{EtC}\equiv$), 75.8 [61.0], 57.1 ($\text{L}_\cup\text{C}\equiv$), 60.0, 56.9 ($\text{L}_\cup\text{C}\equiv$). – [g] Other $\delta^{13}\text{C}$ values: 59.0, 61.0 (OCH_3). – [h] Other $\delta^{13}\text{C}$ values: 13.5, 13.8 (SCH_2CH_3).

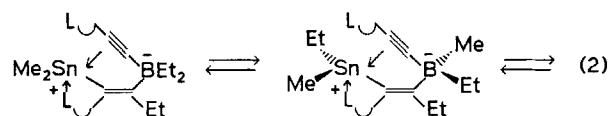
Using the phenyl derivative for comparison with **1a** and the ethyl derivative^[6] for comparison with **1b**, **1c**, and **1e**, it turns out that the magnitude of the coupling constants $^1J(^{119}\text{Sn}^{13}\text{C}\equiv)$ is smaller in the functionally substituted compounds **1**, whereas there is a slight increase in the magnitude of $^1J(^{119}\text{Sn}^{13}\text{C}_{\text{Me}})$ in **1** (see Table 6).

(η^2 -Alkyne)tin Compounds (3, 4): The formation of the zwitterionic compounds **3** and **4** in the respective reaction solutions is evident from the $\delta^{11}\text{B}$ values in a typical range^[17] for tetracoordinate boron atoms and from the deshielding of the ^{119}Sn nuclei by >200 ppm as compared to

Table 3. ^{13}C , ^{119}Sn , ^{11}B -, and ^{15}N -NMR data of (η^2 -alkyne)tin compounds **4a–e**^[a,b]

L	2-Py 4a ^[c]	CH_2NMe_2 4b	CH_2OMe 4c	$\text{CH}=\text{CHOMe}$ 4d ^[d]	CH_2SEt 4e ^[e]
Me_2Sn	0.8 [372.8]	−0.7 [305.2]	0.8 [307.9]	−0.9 [355.9]	0.8 [304.1]
Sn–C=	141.4 [894.2]	138.7 [889.9]	136.1 [808.7]	127.6 [754.2]	142.5 [840.3]
B–C=	198.9 [br]	182.4 [br]	181.1 [br]	189.2 [br]	186.6 [br]
BC=	122.7 [br]	122.6 [br]	121.7 [br]	114.5 [br]	112.9 [br]
B=C=C	110.0 [37.4]	103.2 [52.3]	107.2 [50.1]	114.5 [23.4]	110.3 [41.4]
BiPr_2	21.1 [br] 22.5	19.9 [br] 21.8 22.2	19.8 [br] 21.6 21.9	21.2 [br] 22.0	20.0 [br] 21.7
iPr–C=	32.9 [141.7] 20.3 [n.o.]	32.4 [177.1] 21.4 [17.4]	32.6 [161.3] 20.9 [16.8]	32.9 [147.1] 22.5 [13.5]	32.5 [155.9] 21.6 [15.3]
$\text{L}_2\text{C}=\text{C}$	158.4 [80.7] 123.2	64.9 [80.7] 45.9	76.1 [52.9] 57.8	113.4 [109.5] 139.1 [28.3]	37.0 [116.6] 25.9
$\text{L}_2\text{C}=\text{C}$	142.7 122.4	49.9 43.8	60.0 57.1	82.7 162.3	25.2 20.1
$\delta^{119}\text{Sn}$	70.9	108.7	175.3	78.3	137.4
$\delta^{11}\text{B}$	−3.1	−4.6	−3.6	0.5	−1.5
$\delta^{15}\text{NL}_2\text{C}=\text{C}$	−99.0	−331.0			
$\text{L}_2\text{C}=\text{C}$	−69.3	−357.6			

[a] Ca. 20% in CDCl_3 at $298 \pm 1\text{ K}$. – [b] $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ in Hz are given in []; [br] denotes broad ^{13}C resonances of boron-bound carbon atoms; [n.o.] = not observed; $\delta^{11}\text{B}$ values ± 0.3 . – [c] Other $\delta^{13}\text{C}$ values: 138.4 [16.3], 119.0, 144.5 [10.9] ($\text{L}_2\text{C}=\text{C}$), 135.9, 128.2, 149.5 ($\text{L}_2\text{C}=\text{C}$). – [d] Other $\delta^{13}\text{C}$ values: 59.0, 60.9 (OCH_3). – [e] Other $\delta^{13}\text{C}$ values: 13.7, 13.9 (SCH_2CH_3).



the di-1-alkynyltin compounds **1**. The ^{13}C -NMR spectra of **3** and **4** are also fully in accord with the proposed structures (Figure 2) and reveal several indications of a coordinative N–, O–, or S–Sn bond in solution. The magnitude of all coupling constants $^1J(^{119}\text{Sn}, ^{13}\text{C})$ is greater than in compounds of type **C** [**C**: $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 625.6$; $^1J(^{119}\text{Sn}, ^{13}\text{C}_{\text{Me}}) = 240.8\text{ Hz}$]. This is the typical behaviour if the coordination number of tin is increased^[18]. The trend

Table 4. ^{13}C -, ^{119}Sn -, and ^{11}B -NMR data of stannoles **5** and **6**^[a,b]

L	2-Py 5a ^[c,d]	2-Py 6a ^[e]	$\text{CH}_2\text{NMe}_2\text{CH}_2\text{NMe}_2$ 5b	$\text{CH}_2\text{OMeCH}_2\text{OMe}$ 6b	$\text{CH}_2\text{OMeCH}_2\text{OMe}$ 5c ^[f]	$\text{CH}_2\text{OMeCH}_2\text{OMe}$ 6c	$\text{CH}=\text{CHOMe}$ 5d ^[g]	CH_2SEt 5d'	CH_2SEt 5e ^[h]
Me_2Sn	−7.4 [364.5]	−6.7 [371.5]	−8.8 [323.8]	−8.5 [322.9]	−8.5 [334.0]	−8.1 [335.2]	−8.5 [380.0]	−9.8 [365.6]	−8.5 [323.7]
C-2	141.6 [335.7]	138.7 [n.o.]	133.5 [388.3]	135.9 [363.3]	133.0 [388.3]	134.2 [368.4]	134.1 [415.4]	134.0 [391.8]	136.3 [n.o.]
C-3	207.6 [br]	208.9 [br]	179.2 [br]	178.1 [br]	172.2 [35.0]	172.5 [br]	166.0 [br]	164.1 [br]	175.1 [br]
C-4	158.4 [70.4]	160.6 [63.0]	154.7 [83.1]	157.7 [78.8]	151.6 [78.0]	154.2 [73.6]	151.2 [108.3]	151.7 [100.4]	156.2 [86.1]
C-5	150.8 [578.7]	148.1 [n.o.]	142.1 [528.2]	144.8 [540.0]	141.3 [527.3]	142.0 [530.8]	129.7 [456.8]	129.6 [435.1]	142.9 [526.4]
BEt_2 , BiPr_2	17.7 [br] 10.3	[e] 19.5 20.5	12.5 [br] 10.5	18.4 [br] 20.3	14.9 [br] 10.5	18.8 [br] 20.4 20.6	[g] 9.2	[g] 10.8	22.6 [br] 10.2
Et, iPr	26.0 [57.5] 13.6 [11.1]	33.8 [47.3] 22.8 [n.o.]	24.3 [58.9] 14.6 [10.9]	31.0 [65.5] 22.2 [9.8]	25.2 [59.3] 14.2 [11.3]	33.6 [63.8] 21.4 [8.7]	26.4 [47.2] 14.6 [n.o.]	26.3 [45.3] 14.8 [n.o.]	
L_2C^2	163.1 [95.1]	161.8 [112.2]	73.4 [105.5]	74.7 [100.4]	87.0 [123.2]	86.8 [119.9]	110.8 [57.1]	111.0 [53.1]	
L_2C^5	159.6 [45.8]	164.2 [50.2]	61.2 [51.2] 45.9 [n.o.]	62.7 [n.o.] 46.0 [n.o.]	74.3 [38.4] 58.0 [14.7]	74.7 [28.3] 58.8	108.5 [51.2] 144.8 [9.8]	108.5 [50.2] 145.8 [9.8]	
$\delta^{119}\text{Sn}$	−36.9	−12.4	−35.2	−30.3	−18.1	−9.1	−8.2	+0.9	−40.5
$\delta^{11}\text{B}$	+3.7	+5.6	+6.1	+9.2	+25.5	+47±1	+0.5	+0.5	+13.3

[a] Ca. 20% in C_7D_8 (**5e**), in CDCl_3 (**5b**, **6b**, **5d**), in C_6D_6 (**5a**, **5c**, **6c**). – [b] $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ in Hz are given in []; [br] denotes broad ^{13}C resonances of boron-bound carbon atoms; [n.o.] = not observed; $\delta^{11}\text{B}$ values ± 0.5 , if not noted otherwise. – [c] Other $\delta^{13}\text{C}$ values: 149.6, 140.6, 138.3, 136.3, 121.7, 120.9, 120.2, 117.3. – [d] $\delta^{15}\text{N}$ in CDCl_3 : −58.5, −130.9. – [e] Other $\delta^{13}\text{C}$ values: 148.5, 141.4, 138.1, 135.1, 122.2, 120.2, 119.1, 116.6 (CH_2Py). Other signals were not assigned owing to overlap with signals from **10a**. – [f] $\delta^{13}\text{C}$ values at 183 K (in CD_2Cl_2): −8.9 [337.3] (Me_2Sn), 132.2 [401.6] (C-2), 170.9 [31.6, br] (C-3), 151.0 [77.9] (C-4), 139.6 [506.3] (C-5), 13.9 [br] 10.0 (BEt_2), 24.4 [53.4] 13.6 (Et), 86.7 [124.3] (C-5), 55.7 ($\text{C}^2\text{-CH}_2\text{OMe}$), 73.2 [38.1], 57.6 ($\text{C}^5\text{-CH}_2\text{OMe}$). – [g] The assignment of the signals to **5d** and **5d'** can be reversed. Other signals were not assigned owing to overlap. – [h] Other signals are not assigned owing to overlap with signals from **9e**.

of nuclear shielding of the alkynyl carbon atoms is inverted as compared to that observed for the triorganotin cations of type **C** [**C**: $\delta^{13}\text{C}(\text{B}-\text{C}\equiv) = 106.1$; $\delta^{13}\text{C}(\equiv\text{C}-) = 123.3$]. This points towards a rather different bonding situation. Nevertheless, π coordination is retained to some extent because long-range coupling constants $|J(^{119}\text{Sn}\equiv^{13}\text{C}-\text{L})|$ (23 to 55 Hz) can be measured. In the absence of π coordination, this would be a coupling across six bonds which is not likely to be detected. The structures **J** and **K** describe the extremes of the bonding situation in **3** or **4**. The relative contribution of these structures should be reflected by the magnetic shielding of the carbon atom which carries the formal positive charge, similar to vinyl cations^[5b]. In comparison with **C**, the shielding of $^{13}\text{C}(\equiv\text{C}-)$ and the deshielding of the $^{13}\text{C}(\text{B}-\text{C}\equiv)$ nuclei indicate an increasing contribution of the structure **K**.

The ^{15}N -NMR spectra of **3a** and **4a** provide additional proof of σ coordination. One ^{15}N signal is close to that in

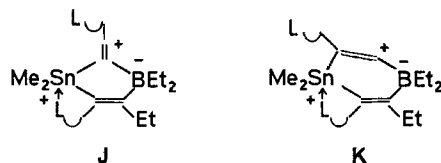
Table 5. ^{13}C - and ^{119}Sn -NMR data of 1-stanna-4-bora-2,5-cyclohexadienes **9**, **10**^[a,b]

L	2-Py 10a ^[c]	CH ₂ NMe ₂ 9b	CH ₂ NMe ₂ 10b	CH ₂ OMe 10c	CH=CHOMe 10d ^[d]	CH ₂ SEt 9a ^[e]	CH ₂ SEt 10e ^[f]
Me ₂ Sn	-8.5 [337.7]	-7.5 [379.5]	-3.2 [317.0]	-6.2 [379.3]	-8.4 [397.8] -5.5 [425.1]	-6.7 [374.0]	-9.4 (br) -4.0 (br)
C-2,6	144.3 [413.3]	159.6 [448.0]	146.4 [435.1]	145.4 [433.8]	135.5 [428.9]	156.2 [463.2]	141.7 [450.1]
C-3,5	171.3 (br)	161.1 (br)	167.7 (br) [31.5]	166.9 (br)	167.6 (br)	162.9 (br) [32.7]	169.5 (br) [36.0]
BET, BIPr	26.0 (br) 20.8	15.6 (br) 8.6	25.5 (br) 20.8	25.6 (br) 21.0	25.2 (br) 20.4	17.0 (br) 8.5	25.1 (br) 20.4
Et, iPr	32.4 [60.0] 23.3	24.8 [60.6] 15.3 [9.8]	31.4 [67.0] 23.1 [5.9]	32.6 [64.9] 23.1 [6.0]	31.0 [58.3] 22.8 [n.o.]	23.5 [54.5] 15.6 (br)	30.4 [62.1] 22.7 (br) 23.5 (br)
L	163.0 [32.5]	62.5 [32.3] 45.8	62.8 [27.6] 45.6	75.1 [39.2] 57.8	108.7 [34.3] 144.9 [15.8]	34.5 [48.0] 23.7	35.0 [41.4] 24.2
$\delta^{119}\text{Sn}$	-117.3	-143.5	-122.8	-118.2	-120.7	-137.3	-121.5

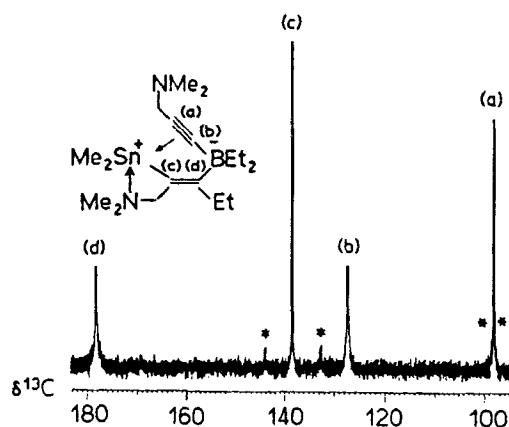
[a] Ca. 20% in C₇D₈ (**9e**), in CDCl₃ (**9b**, **10b**, **10e**), in C₆D₆ (**10c**); all ^{11}B -NMR signals are extremely broad: $\delta^{11}\text{B} \approx +70 \pm 2$. — [b] $^nJ(^{119}\text{Sn}^{13}\text{C})$ in Hz are given in []; (br) denotes broad ^{13}C resonances of boron-bound carbon atoms; (br) denotes broad ^{13}C resonance signals due to dynamic effects. — [c] Other $\delta^{13}\text{C}$ values: 148.7, 135.4, 121.6, 119.3 (CH, Py). — [d] Other $\delta^{13}\text{C}$ values: 59.2 (OMe); ^{13}C NMR (SnMe₂) at 238 K. — [e] Other signals were not assigned owing to overlap with signals from **6e**. — [f] Other $\delta^{13}\text{C}$ values: 14.1 (SCH₂CH₃).

Table 6. Comparison between coupling constants $^1J(^{119}\text{Sn}^{13}\text{C})$ and chemical shifts $\delta^{119}\text{Sn}$ for some di-1-alkynyltin compounds with and without functional substituents at the C≡C bond

	1a	Me ₂ Sn(C≡CPh) ₂	1b	1c	1e	Me ₂ Sn(C≡CEt) ₂
$^1J(^{119}\text{Sn}^{13}\text{C}_{\equiv})$	573.3	602.7	612.9	592.9	609.3	640.9
$^1J(^{119}\text{Sn}^{13}\text{C}_{\text{Me}})$	500.3	497.0	499.2	501.4	499.7	497.0
$\delta^{119}\text{Sn}$	-145.5	-147.6	-156.8	-152.5	-153.5	-156.7

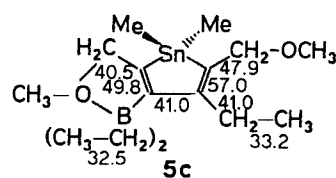


1a and the second one is shifted to lower frequencies, in accord with $\delta^{15}\text{N}$ of pyridine derivatives where the lone pair of electrons at the nitrogen atom is engaged in coordinative bonding^[19]. There are also two ^{15}N -NMR signals each for **3b** and **4b**, but the $\delta^{15}\text{N}$ values of this type of nitrogen atom are not characteristic for coordinative bonds^[19b]. The $\delta^{119}\text{Sn}$ data of **3** and **4** are found in the range between +70 to +210 with higher ^{119}Sn nuclear shielding in the com-

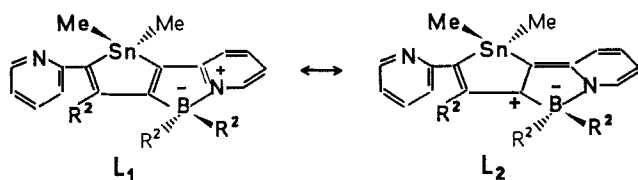
Figure 2. 75.5 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (-30°C in CDCl₃) of the zwitterionic intermediate **3b**, showing the range of olefinic and alkynyl carbon atoms. $^{117/119}\text{Sn}$ satellites are marked by asterisks

pounds **4** [$\Delta^{119}\text{Sn}$: -43 (**4a**), -19 (**4b**), -32 (**4c**), -27 (**4d**), -32 (**4e**)]. Our understanding of ^{119}Sn nuclear shielding of such compounds is still rather limited, although the rather large range can be qualitatively interpreted as a function of greatly varying σ and π interactions between tin and the respective ligands. The increase in ^{119}Sn nuclear shielding in **4** as compared to **3** is similar to the situation observed for the compounds of type C. However, in the case of C the temperature dependence of the $\delta^{119}\text{Sn}$ data^[6] indicated a significant contribution of the equilibrium shown in Scheme 1(b), whereas there is no appreciable change in the $\delta^{119}\text{Sn}$ data of the compounds **3** and **4** between -65 and $+10^\circ\text{C}$. Therefore, the equilibrium in Scheme 1(b) plays a minor role, in agreement with the experimental evidence. Compounds of type **7** and **8** were observed and identified by their ^{119}Sn -NMR signals in reaction mixtures as minor products only in the case of **7b** ($\delta^{119}\text{Sn} = -87.1$), **7e** ($\delta^{119}\text{Sn} = -86.4$), and **8e** ($\delta^{119}\text{Sn} = +67.8$).

Stannoles (5, 6): The structure of the stannoles **5** and **6** is proposed because of the typical pattern of olefinic ^{13}C resonance signals^[6,20] with three sharp signals of which two show $^{117/119}\text{Sn}$ satellites according to $^1J(^{117/119}\text{Sn}^{13}\text{C})$ and one broad signal owing to partially relaxed scalar ^{13}C - ^{11}B coupling. Furthermore, the assignments are supported by the results of 2D $^{13}\text{C}/^1\text{H}$ heteronuclear shift correlations based both on $^1J(^{13}\text{C}^1\text{H})$ and long-range coupling constants $^nJ(^{13}\text{C}^1\text{H})$. In the case of **5c**, the carbon-carbon connectivity has also been established by the determination of $^1J(^{13}\text{C}^{13}\text{C})$ coupling constants (INADEQUATE).

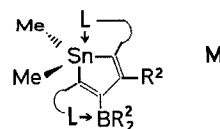
Coupling constants $^1J(^{13}\text{C}^{13}\text{C})$ in Hz

The presence of the functional groups L_U leads to the question for coordinative $L-B$ and $L-Sn$ bonds in the stannoles. The $\delta^{11}B$ values are in accord^[17] with coordinative $N-B$, $O-B$, and $S-B$ bonds in the compounds **5** and **6**, although the $O-B$ bond in **5c** ($\delta^{11}B = +25.5$), and particularly in **6c** ($\delta^{11}B = +47$), appears to be weak. ^{15}N -NMR spectra of **5a** show two ^{15}N resonance signals, one at low frequency ($\delta^{15}N = -130.9$), typical of the nitrogen atom engaged in the coordinative $N-B$ bond^[19], the other one at high frequency ($\delta^{15}N = -58.6$). This $\delta^{15}N$ value does not indicate a significant $N-Sn$ interaction. The $^{13}C-3$ resonance signals of the stannoles **5** and **6** are all shifted to higher frequencies as compared to stannoles **F** without functional groups in 2,5-positions. However, the deshielding of $^{13}C-3$ nuclei in **5a** and **6a** is rather extreme ($\Delta \approx 47$ with respect to the 2,5-diphenyl derivative^[6]). This is readily explained by taking into account the second important canonical zwitterionic structure L_2 in which the carbocationic character of C-3 becomes apparent.



The comparison of the $\delta^{119}Sn$ data for **5** and **6** with those of other stannoles^[6] is not straightforward because of the tetracoordinate boron atoms. However, the marked shift to lower frequency for most ^{119}Sn resonance signals in **5** and **6** [e.g. compare $\delta^{119}Sn$ of **5a** (-36.9) with the 2,5-diphenyl derivative ($+14.6$ ^[6]) or that of **5b** (-35.3) with the 2,5-dipropyl derivative (-3.5 ^[6])] points towards weak coordinative $L-Sn$ interactions arising from the L_U group in 5-position. There is a significant influence of the ring size on $\delta^{119}Sn$ ^[18]. If the coordinative $L-Sn$ bond involves a five-membered ring like in **5d**, the expected increase in ^{119}Sn nuclear shielding may be compensated by the deshielding influence of the five-membered ring. The most reliable proof for the increase in the mean coordination number of the tin atom should be revealed by the relative magnitude of the coupling constants $|^1J(^{119}Sn^{13}C)|$. The values $|^1J(^{119}Sn^{13}C_{Me})|$ in **5** and **6** are always larger than in stannoles **F** without functional groups in 2,5-positions^[6]. The difference in the magnitude of the coupling constants $|^1J(^{119}SnC^2)|$ and $|^1J(^{119}SnC^5)|$ in **5** and **6** is much larger than in stannoles of type **F**. Although a small part of this difference can be traced to the influence of the tetracoordinate boron atom, the large increase of the values $|^1J(^{119}Sn^{13}C^5)|$ must be related to an increase in the mean coordination number of the tin atom, as shown in **M** where the C-5 atom adopts one of the equatorial positions of a trigonal bipyramid whereas one of the axial positions is taken by the C-2 atom of the stannol ring. Similar to $|^1J(^{119}Sn^{13}C)|$ values in $[SnMe_5]^-$ ^[21] and in some other hypervalent tin compounds with four organic substituents^[22],

this model explains the increase and decrease in the magnitude of $|^1J(^{119}Sn^{13}C^5)|$ and $|^1J(^{119}Sn^{13}C^2)|$, respectively.



X-Ray Analyses of **3b**, **4b**, and **4d**

Experimental data for the X-ray analyses are given in Table 7^[23]. The structure determination of **4d** was carried out at room temperature because the crystal was destroyed below 220 K, probably because of a phase transition. An analogous behaviour was observed in the case of **3b** in an attempt to measure responses at temperatures below 200 K. Table 8 contains selected bond distances and bond angles together with those of **C** for comparison. The molecular structures of **3b** and **4b** are depicted in Figure 3, and Figure 4 shows the molecular structure of **4d**.

Table 7. Data for the X-ray analyses of compounds **3b**, **4b**, and **4d**

	3b	4b	4d
Crystal size [mm ³]	0.24x0.23x0.07	0.28 x 0.26 x 0.26	0.18x0.20x0.50
Space group; Z	P2 ₁ /c; 4	P2 ₁ /n; 4	P2 ₁ /c; 4
a, b, [Å]	16.043(5), 9.460(4)	8.629(2), 20.968 (4)	9.746(2), 15.130(3)
c [Å]	15.552(5)	14.042 (3)	16.005(3)
β [°]	113.99(2)	104.97(3)	94.97(3)
Volume [Å ³]	2157 (1)	2454.4 (9)	2351.3 (8)
Density (calcd.) [Mg/m ³]	1.263	1.226	1.274
Absorption coeff. [mm ⁻¹]	1.18	1.047	1.097
Diffractometer	Nicolet R3m/v	Siemens P4	Siemens P4
Radiation	MoK α ($\lambda = 0.71073$ Å);	graphite	monochromator
Temperature [K]	200	201	296
2 θ range [°]	3–50	2–55	2–50
Scan type	Wyckoff	ω	ω
Independent reflections	3380	5571 ($R_{int} = 2.44\%$)	4138 ($R_{int} = 2.17\%$)
Observed reflections	2768 ($F > 4.0\sigma(F)$)	4915 ($F > 2.0\sigma(F)$)	4138 ($F > 0.0\sigma(F)$)
Solution	Direct methods	Direct methods	Direct methods
Weighting scheme	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$
Parameters refined	210	227	227
R indices (all data)	4.04 %, $R_w = 4.47\%$	3.09 %, $R_w = 3.55\%$	4.87 %, $R_w = 2.69\%$
Largest diff. peak [e/Å ³]	0.44	0.46	0.39
Largest diff. hole [e/Å ³]	-0.70	-0.48	-0.82

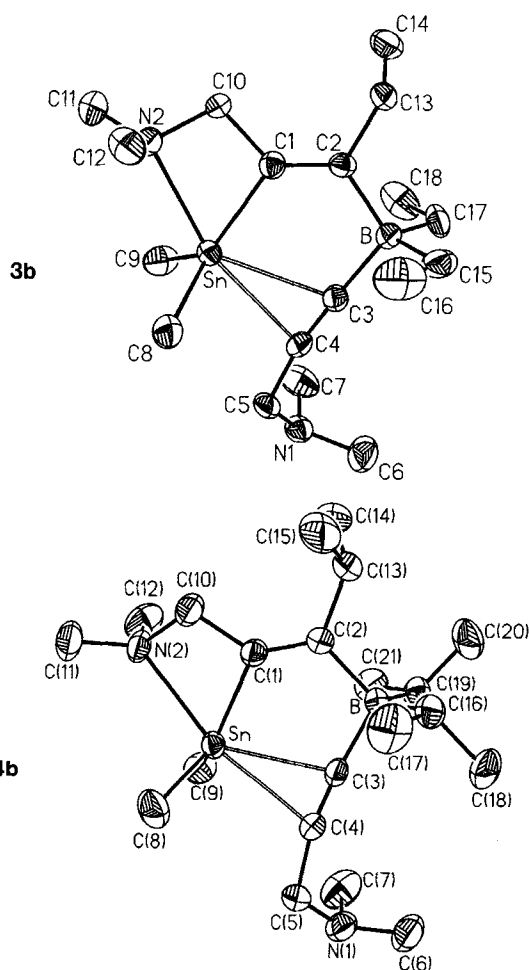
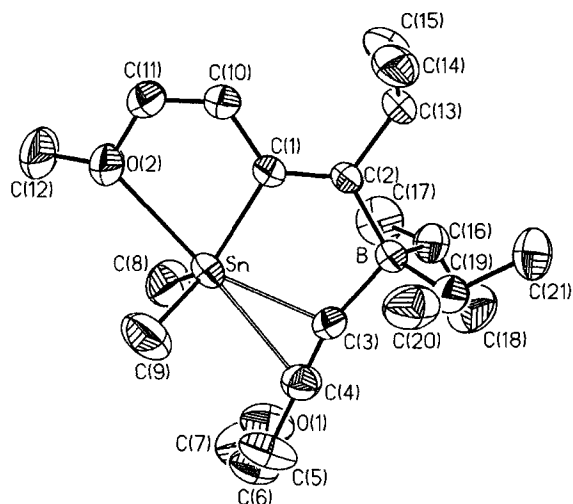
In the light of the NMR spectroscopic differences between the *B*-ethyl (**3**) and *B*-isopropyl derivatives (**4**) in solution (e.g., see $\delta^{119}Sn$ values in the Tables 2 and 3) and of the structural differences between **3b** and **4d** (vide infra) it was necessary to determine the molecular structure of **4b**. The strong similarity of the molecular structures of **3b** and **4b** proves that differences in some NMR data of **3** and **4** are induced by the properties of the compounds in solution, and that structural differences between **3b** and **4b** (vide infra) in the solid state are not caused by the different influence of isopropyl and ethyl groups. The common feature of all three molecular structures is the plane formed by the atoms N or O (in L_U), Sn, C1, C2, B, C3, and C4. This is shown for compound **4d** in Figure 5 where, because of the nature of L_U , even more atoms lie in one plane. This planar arrangement strongly supports the side-on π coordination

Table 8. Selected bond distances [\AA] and bond angles [$^\circ$]^[a]

	C	3b	4b	4d
Sn-C1	2.116(4)	2.104(5)	2.114(3)	2.127(3)
Sn-C3	2.339(4)	2.626(6)	2.554(2)	2.373(3)
Sn-C4	2.523(5)	2.604(5)	2.589(3)	2.661(3)
Sn-C8	2.128(5)	2.142(8)	2.132(3)	2.113(5)
Sn-C9	2.136(5)	2.134(7)	2.135(3)	2.111(5)
B-C2	1.616(6)	1.629(8)	1.638(4)	1.643(4)
B-C3	1.651(6)	1.627(7)	1.630(4)	1.650(5)
C1-C2	1.334(6)	1.342(8)	1.334(4)	1.353(4)
C1-C10	1.529(6)	1.512(8)	1.523(4)	1.462(4)
C3-C4	1.213(6)	1.220(7)	1.212(4)	1.221(5)
C4-C5	1.483(7)	1.500(7)	1.492(5)	1.432(6)
Sn-L		2.521(4)	2.481(3)	2.592(2)
C1-Sn-C3	84.2(2)	75.3(2)	76.5(1)	82.9(1)
C1-Sn-C4	112.6(2)	102.1(2)	103.4(1)	110.2(1)
C3-Sn-C4	28.6(1)	27.0(2)	27.3(1)	27.3(1)
C1-Sn-C8	118.1(2)	124.2(2)	119.8(1)	122.7(2)
C1-Sn-C9	119.1(2)	122.0(3)	125.2(1)	119.0(2)
C8-Sn-C9	113.9(2)	111.8(3)	112.5(1)	113.6(2)
C2-B-C3	110.1(3)	109.1(5)	109.3(2)	109.8(2)
Sn-C1-C2	114.5(3)	125.4(4)	124.4(2)	116.5(2)
B-C2-C1	125.2(4)	122.8(4)	121.7(2)	123.8(3)
Sn-C3-B	105.5(2)	106.7(3)	107.0(2)	106.9(2)
B-C3-C4	170.1(4)	177.8(6)	174.9(2)	163.5(3)
C3-C4-C5	174.0(5)	171.0(6)	169.6(3)	179.2(4)
C3-Sn-C8	107.3(2)	100.7(2)	106.9(1)	104.6(1)
C4-Sn-C8	95.7(2)	88.4(2)	90.1(1)	90.3(1)
C3-Sn-C9	108.6(2)	110.0(2)	103.9(1)	105.0(2)
C4-Sn-C9	90.9(2)	93.0(2)	91.5(1)	90.3(2)
L-Sn-C1		61.8(2)	62.1(1)	74.0(1)
L-Sn-C3		136.6	138.4(1)	156.9(1)
L-Sn-C4		163.6	165.6(1)	175.7(1)
L-Sn-C8		98.3(2)	98.0(1)	86.7(1)
L-Sn-C9		98.3(2)	96.3(1)	88.2(2)

^[a] L = N (**3b**, **4b**) or O (**4d**) in $\text{L}_2\text{C}\equiv$.

between the $\text{C}\equiv\text{C}$ bond and the tin atom, in spite of the fairly long $\text{Sn}-\text{C}\equiv$ distances. One of the major differences between the molecular structures of **3b**, **4b**, **d**, and **C** concerns the distance between the tin atom and the alkynyl carbon atoms C3 and C4 (Table 8). The shortest distances $d_{\text{Sn}-\text{C3}}$ and $d_{\text{Sn}-\text{C4}}$ are observed in the case of **C**, the distance to C3 being much shorter than to C4. In compound **4d**, both distances become slightly longer than in **C**, and the nature of bonding seems to be different if one compares the bond angle $\text{B}-\text{C3}-\text{C4}$ which deviates significantly from 180° in **4d** [$163.5(3)^\circ$], much more than in **C** [$170.1(4)^\circ$] or in **3b** [$177.8(6)^\circ$] and **4b** [$174.9(2)^\circ$]. In **3b** and **4b**, the distances between the tin atom and the alkynyl carbon atoms C3 and C4 are almost equal, and the distance to C3 is significantly longer than in **4d** or in **C**. The competition between the $\text{L}-\text{Sn}$ σ bond and π coordination is also evident from the arrangement of the other ligands around the tin atom. The sum of bond angles (not including the $\text{C}\equiv\text{C}$ bond) at the tin atom in **C** (351.1°) shows that a pyramidal geometry is adopted, the tin atom being oriented towards the $\text{C}\equiv\text{C}$

Figure 3. Molecular structures of compound **3b** and **4b**Figure 4. Molecular structure of compound **4d**

bond. In the case of **4d**, the surrounding of the tin atom can be described as a distorted trigonal bipyramid where the tin atom is shifted out of the equatorial plane in the direction of the $\text{C}\equiv\text{C}$ bond. In contrast, in **3b** and **4b** the

trigonal bipyramidal surrounding of the tin atoms is distorted by a shift of the tin atom away from the C≡C bond towards the nitrogen atom in L_U . Similar to the anion $[BET_4]^-$, the relevant bond angles in **3b** [BC15C16 = 116.2(7) and BC17C18 = 117.1(5)°] are fairly large^[24].

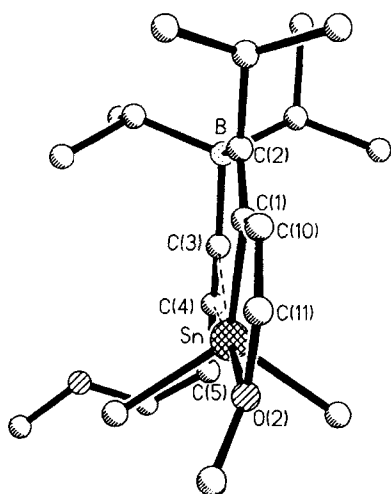


Figure 5. Side view of the molecular structure of **4d** showing the planar arrangement of the bicyclic system (mean deviation from best plane 3.4 pm)

We gratefully acknowledge support of this work by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. We also thank Prof. Dr. R. Köster (Mülheim a.d. Ruhr) for a generous gift of triethylborane.

Experimental

All compounds were handled under N_2 by using carefully dried glassware and solvents. Deuterated solvents were stored over molecular sieves and saturated with N_2 . Starting materials such as solutions of butyllithium (1.6 M) in hexane (Aldrich) and most terminal alkynes were commercial products. Me_2SnCl_2 was prepared from Me_4Sn and $SnCl_4$ and purified by recrystallization from hexane. – Elemental analyses: Pascher, Remagen. – IR: Perkin-Elmer 983. – MS: EI-MS (70 eV), Varian MAT CH-7 with direct inlet. – $^1H/^{13}C$ NMR: Bruker AC 300 (300.13/75.5 MHz), Bruker AM 500 (500.13/125.8 MHz), Jeol JNM-EX 270E (270.67/67.94 MHz). – ^{11}B NMR: Bruker AC 300 (96.3 MHz) and Jeol FX 90Q (28.7 MHz), $Et_2O \cdot BF_3$ as external standard [$\Xi(^{11}B)$ = 32.083971 MHz]. – ^{119}Sn NMR: Bruker AC 300 (111.8 MHz) and Jeol FX 90Q (33.3 MHz), $SnMe_4$ as external standard [$\Xi(^{119}Sn)$ = 37.290665 MHz]. – ^{15}N NMR: Bruker AC 300 (30.4 MHz) and Bruker AM 500 (50.7 MHz), neat CH_3NO_2 as external standard [$\Xi(^{15}N)$ = 10.136767 MHz].

Starting materials: Ethyl propargyl thioether^[25], triethylborane^[26], and triisopropylborane (**2b**)^[27] were prepared according to literature procedures.

Dialkynylstannanes (1). – *General Procedure:* A freshly prepared suspension of 85 mmol of the respective lithiated alkyne in 100 ml of toluene is stirred at $-78^\circ C$ before 8.3 g (38 mmol) of Me_2SnCl_2 is added in one portion. The mixture is warmed to room temp., stirred for 12 h, and filtered. After removal of the solvent in vacuo (0.1 Torr), the residues are purified either by fractional distillation, sublimation, or recrystallization to give pure products in 46–78% yield (see Table 1 for ^{119}Sn -, ^{15}N -, and ^{13}C -NMR data).

1a: Yield 6.2 g (46%); decomp. at $97^\circ C$. – IR ($CHCl_3$): $\tilde{\nu}$ = 2253 cm^{-1} [$\nu(C\equiv C)$]. – 1H NMR ($CDCl_3$): δ [$^nJ(^{119}Sn, ^1H)$] = 0.55 [68.7 Hz] [s, 6H, $Sn(CH_3)_2$]; 7.35 (m, 2H), 7.51 (m, 2H), 7.10 (m, 2H), 8.44 (m, 2H). – MS, m/z (%): 354 (10) [M^+], 339 (100), 324 (5), 222 (7), 120 (1).

1b: Yield 8.6 g (72%); m.p. $29-31^\circ C$. – IR ($CHCl_3$): $\tilde{\nu}$ = 2154, 2162 cm^{-1} [$\nu(C\equiv C)$]. – 1H NMR ($CDCl_3$): δ [$^nJ(^{119}Sn, ^1H)$] = 0.39 [69.1 Hz] [s, 6H, $Sn(CH_3)_2$]; 3.17 [10.7] (s, 4H, CH_2); 2.20 [s, 12H, $N(CH_3)_2$]. – MS, m/z (%): 232 (100) [$M^+ - C\equiv CCH_2NMe_2$], 120 (7), 82 (100), 58 (52).

1c: Yield 6.8 g (62%); b.p. $69^\circ C/0.2$ Torr. – IR ($CHCl_3$): $\tilde{\nu}$ = 2157, 2250 cm^{-1} [$\nu(C\equiv C)$]. – 1H NMR ($CDCl_3$): δ [$^nJ(^{119}Sn, ^1H)$] = 0.23 [69.8 Hz] [s, 6H, $Sn(CH_3)_2$]; 3.83 [10.7] (s, 4H, CH_2); 3.10 (s, 6H, OCH_3). – MS, m/z (%): 273 (100) [$M^+ - 15$], 189 (44), 135 (45), 120 (26), 69 (53). – $C_{10}H_{16}O_2Sn$ [286.9]: calcd. C 41.86, H 5.62; found C 41.72, H 5.66.

1d: Yield 7.9 g (67%); m.p. $83-86^\circ C$. – IR ($CHCl_3$): $\tilde{\nu}$ = 2127, 2243 cm^{-1} [$\nu(C\equiv C)$]. – 1H NMR ($CDCl_3$): δ [$^nJ(^{119}Sn, ^1H)$] = 0.24 [69.1 Hz] [s, 6H, $Sn(CH_3)_2$]; 4.31 (d, 2H, $CH=$); 6.09 (d, 2H, $=CH-O$); 3.55 (s, 6H, OCH_3). – MS, m/z (%): 297 (100) [$M^+ - 15$], 201 (8), 135 (9), 120 (5). – $C_{12}H_{16}O_2Sn$ [311.0]: calcd. C 46.35, H 5.62; found C 46.17, H 5.34.

1e^[28]: Yield 10.3 g (78%); b.p. $123^\circ C/0.2$ Torr. – IR ($CHCl_3$): $\tilde{\nu}$ = 2154 cm^{-1} [$\nu(C\equiv C)$]. – 1H NMR ($CDCl_3$): δ [$^nJ(^{119}Sn, ^1H)$] = 0.26 [69.1 Hz] [s, 6H, $Sn(CH_3)_2$]; 3.11 [11.5] (s, 4H, $\equiv CCH_2$); 2.49 (q, 4H, CH_2CH_3); 1.08 (t, 6H, CH_2CH_3). – MS, m/z (%): 348 (8) [M^+], 333 (26), 249 (70), 135 (45), 120 (18), 99 (199), 71 (73), 29 (45).

Stannoles 5, 6 and 1-Stanna-4-bora-2,5-cyclohexadienes 9, 10. – *General Procedure:* A solution of 4 mmol of **1b–e** in 8 ml of CH_2Cl_2 (**1c, d**) or toluene (**1a, b, e**) is cooled to $-78^\circ C$, then 4 mmol of **2** is added in one portion; the mixture is warmed to room temp. and stirred (**1a+2a**: 5 h/ $65^\circ C$; **1a+2b**: 14 h/ $60^\circ C$; **1b+2a**: 5 h/ $60^\circ C$; **1b+2b**: 12 h/ $60^\circ C$; **1c+2a**: 12 h/ $25^\circ C$; **1c+2b**: 2 d/ $25^\circ C$; **1d+2a**: 14 d/ $25^\circ C$, **1d+2b**: 90 d/ $25^\circ C$; **1e+2a**: 2 d/ $25^\circ C$; **1e+2b**: 3 d/ $25^\circ C$). After removal of volatile materials in vacuo the compounds **5, 6, 9**, and **10** are obtained in quantitative yield as oily yellow liquids or solids (**5a**) (see Tables 4 and 5 for ^{119}Sn -, ^{15}N -, ^{11}B -, and ^{13}C -NMR data).

5a: 1H NMR ($CDCl_3$): δ [$^nJ(^{119}Sn, ^1H)$] = 0.51 [59.7 Hz] [s, 6H, $Sn(CH_3)_2$]; 0.77 (m), 0.34 (t) (10H, BEt_2); 2.97 (q), 1.26 (t) (5H, Et); 6.91 (m), 7.11 (m), 7.19 (m), 7.27 (m), 7.60 (m), 8.01 (m), 8.48 (m) (8H, Py). – MS, m/z (%): 423 (2) [$M^+ - 29$], 393 (5), 366 (5), 264 (26), 236 (31), 185 (45), 174 (45), 158 (100), 144 (84), 130 (48), 117 (53), 93 (50), 78 (39); 57 (43), 43 (31). – $C_{22}H_{29}BN_2Sn$ (451.0): calcd. C 58.59, H 6.48, N 6.21; found C 55.54, H 5.45, N 5.43.

5c: 1H NMR ($CDCl_3$): δ [$^nJ(^{119}Sn, ^1H)$] = 0.23 [57.0 Hz] [6H, $Sn(CH_3)_2$]; 0.40 (m), 0.58 (m) (10H, BEt_2); 2.11 (q), 0.87 (t) (5H, Et); 4.57 (s), 3.43 (s) (5H, 2- CH_2OMe); 4.18 [41.8] (s), 3.23 (s) (5H, 5- CH_2OMe). – MS, m/z (%): 357 (100) [$M^+ - 29$], 325 (32), 255 (92), 207 (60), 151 (68), 135 (25), 105 (18). – $C_{16}H_{31}BO_2Sn$ [385.0]: calcd. C 49.93, H 8.12; found C 50.42, H 8.21.

5b/9b (mixture): $C_{18}H_{37}BN_2Sn$ (411.1): calcd. C 52.60, H 9.07; found C 51.65, H 8.93.

10d: 1H NMR ($CDCl_3$ at $-35^\circ C$): δ [$^nJ(^{119}Sn, ^1H)$] = 0.24 [64.8 Hz], -0.06 [55.2] [s, 6H, $Sn(CH_3)_2$]; 1.78 (m), 0.96 (d) (7H, $BiPr$); 2.89 (m), 1.18 (d) (14H, iPr); 5.67 [84.5] (d), 5.84 (d), 3.56 (s) (5H, $CH=CHOMe$).

10e: 1H NMR ($CDCl_3$): δ [$^nJ(^{119}Sn, ^1H)$] = 0.16 [58.5 Hz] [s, 6H, $Sn(CH_3)_2$]; 2.44 (m), 2.45 (m), 0.89 (d) (7H, $BiPr$); 2.76 (m), 1.04,

1.05 (br) (14H, *i*Pr); 3.93 (br), 3.47 (br), 3.00 (br), 2.30 (q), 1.13 (t) (7H, CH₂SEt). – MS, *m/z* (%): 445 [*M*⁺ – 43] (31), 215 (39), 211 (100), 174 (86), 151 (31), 131 (45), 93 (15), 43 (17), 41 (31). – C₂₁H₄₁BS₂Sn (487.2): calcd. C 51.77, H 8.48; found C 51.48, H 8.32.

Mixtures of compounds are obtained for **5b/9b** (≈1:1), **5d/5d'** (≈1:1.3), **5e/9e** (≈1:1, with **7e** and **8e** as minor components), **6a/10a** (≈1.5:1), **6b/10b** (≈1:2), and **6c/10c** (≈1:2).

(η^2 -Alkyne)tin Compounds **3**, **4**. – *General Procedure*: A solution of 10 mmol of **1** in 6 ml of CHCl₃ (**3c**, **3d**, **3e**, **4b**, **4c**, **4d**, **4e**) or CH₂Cl₂ (**3a**, **3b**, **4a**) is cooled to –78°C, then 10 mmol of **2a** or **2b** is added in one portion. The following solutions were warmed to room temp.: **1d**+**2a** (30 min), **1a**+**2b** (2 d), **1b**+**2b** (6 h), **1d**+**2b** (4 d). The solvents are removed in vacuo at 20°C. The successful preparation of the other compounds depends critically on the reaction conditions in Table 9 which were optimized by using NMR spectroscopy for monitoring of the progress of the reaction.

Table 9. Reaction conditions for preparing some (η^2 -alkyne)tin compounds **3** and **4**

Com- pound	Conditions			
	solvent	first warming up to [°C]	cooling down to [°C]	removal of solvent [°C]
3a	CH ₂ Cl ₂	+20/5min	–35/3h	0
3b	CH ₂ Cl ₂	+25/20min	0/1h	0
3c	CHCl ₃	–35/1d	–	–30
3e	CHCl ₃	25/1min	–35/2d	–30
4c	CHCl ₃	25/3min	–35/14d	0
4e	CHCl ₃	25/3min	–35/14d	0

Compounds **3b**, **4b**, and **4d** were recrystallized from pentane (**3b**) and CH₂Cl₂ (**4b**, **4d**). All compounds were obtained in quantitative yield and must be stored at –35°C (see Tables 2 and 3 for ¹¹⁹Sn-, ¹⁵N-, ¹¹B-, and ¹¹⁹Sn-NMR data).

3a: ¹H NMR (CDCl₃/25°C): $\delta^r J(^{119}\text{Sn}, ^1\text{H}) = 0.82$ [60.4 Hz] [s, 6H, Sn(CH₃)₂]; 0.51 (q), 0.89 (t) (10H, BEt₂); 2.54 (q), 1.15 (t) (5H, =CEt); 6.97 (m), 7.15 (m), 7.40 (m), 7.48 (m), 7.58 (m), 8.11 (m) (8H, Py).

3b: ¹H NMR (CDCl₃/–30°C): $\delta^r J(^{119}\text{Sn}, ^1\text{H}) = 0.44$ [51.3 Hz] [s, 6H, Sn(CH₃)₂]; 0.51 (dq), 0.86 (t) (10H, BEt₂); 2.01 (q, br), 0.96 (t) (5H, =CEt); 3.08 [80.2] (s), 1.94 (s) (8H, =CCH₂NMe₂); 3.08 (s), 2.07 (s) (8H, =CCH₂NMe₂).

3c: ¹H NMR (CDCl₃/–30°C): $\delta^r J(^{119}\text{Sn}, ^1\text{H}) = 0.55$ [53.4 Hz] [s, 6H, Sn(CH₃)₂]; 0.19 (q, br), 0.67 (t) (10H, BEt₂); 1.84 (q, br), 0.86 (t) (5H, =CEt); 4.30 [47.8] (s), 3.62 (s) (5H, =CCH₂OMe); 4.17 (s), 3.28 (s) (5H, =CCH₂OMe).

3d: ¹H NMR (CDCl₃/–30°C): $\delta^r J(^{119}\text{Sn}, ^1\text{H}) = 0.58$ [58.1 Hz] [s, 6H, Sn(CH₃)₂]; 0.22 (q, br), 0.69 (t) (10H, BEt₂); 2.07 (q, br), 0.88 (t) (5H, =CEt); 5.88 [183.4] (d), 5.78 (d), 3.60 (s) (5H, =CCH=CHOMe); 6.49 (d), 4.46 (d), 3.75 (s) (5H, =CCH=CHOMe).

3e: ¹H NMR (CDCl₃/–30°C): $\delta^r J(^{119}\text{Sn}, ^1\text{H}) = 0.72$ [52.1] [s, 6H, Sn(CH₃)₂]; 0.16 (q, br), 0.64 (t, br) (10H, BEt₂); 1.84 (q, br), 0.81 (t) (5H, =CEt); 3.44 [83.2] (s), 2.45 (q), 1.16 (t) (7H, =CCH₂SEt); 3.29 (s), 2.59 (q), 1.16 (t) (7H, =CCH₂SEt).

4a: ¹H NMR (CDCl₃/25°C): $\delta^r J(^{119}\text{Sn}, ^1\text{H}) = 0.61$ [46.2] [s, 6H, Sn(CH₃)₂]; 0.83 (d) [12H, B(CH(CH₃)₂)₂]; BCH was not observed

because of overlap with other signals; 3.16 (m), 1.18 (t) (7H, *i*Pr); 7.0 (m), 7.16 (m), 7.42 (m), 7.58 (m), 7.74 (m), 8.08 (m), 8.52 (m) (8H, Py).

4b: ¹H NMR (CDCl₃/25°C): $\delta^r J(^{119}\text{Sn}, ^1\text{H}) = 0.57$ [51.4 Hz] [s, 6H, Sn(CH₃)₂]; 0.80 (m), 0.79 (d), 0.84 (d) (14H, BiPr₂); 2.53 (m), 0.96 (d) (7H, =CiPr); 3.49 [87.9] (s), 2.23 (s) (8H, =CCH₂NMe₂); 3.26 (s), 2.37 (s) (8H, =CCH₂NMe₂).

4c: ¹H NMR (CDCl₃/25°C): $\delta^r J(^{119}\text{Sn}, ^1\text{H}) = 0.64$ [54.1 Hz] [s, 6H, Sn(CH₃)₂]; 0.78 (m, br), 0.78 (d) (14H, BiPr₂); 2.53 (m), 0.96 (d) (7H, =CiPr); 4.45 [54.6] (s), 3.40 (s) (5H, =CCH₂OMe); 4.15 (s), 3.31 (s) (5H, =CCH₂OMe).

4d: ¹H NMR (CDCl₃/25°C): $\delta^r J(^{119}\text{Sn}, ^1\text{H}) = 0.58$ [55.3 Hz] [s, 6H, Sn(CH₃)₂]; 0.84 (m), 0.83 (d) (14H, BiPr₂); 2.76 (m), 1.17 (d) (7H, =CiPr); 6.17 [208.7] (d), 5.71 [12.8] (d), 3.60 (s) (5H, =CCH=CHOMe); 6.45 (s), 4.50 (s), 3.78 (s) (5H, =CCH=CHOMe).

4e: ¹H NMR (CDCl₃/25°C): $\delta^r J(^{119}\text{Sn}, ^1\text{H}) = 0.74$ [52.1 Hz] [s, 6H, Sn(CH₃)₂]; 0.80 (d) [12H, B(CH(CH₃)₂)₂]; BCH was not assigned because of overlap with other signals; 2.52 (m), 1.23 (d) (7H, =CiPr); 3.69 [90.1] (s), 2.57 (q), 1.22 (t) (7H, =CCH₂SEt); 3.32 (s), 2.67 (q), 1.24 (t) (7H, =CCH₂SEt).

- [1] [1a] R. J. P. Corriu, M. Henner, *J. Organomet. Chem.* **1974**, *74*, 1–28. – [1b] J. B. Lambert, W. J. Schulz, Jr., J. A. McConnell, W. Schilf, *J. Am. Chem. Soc.* **1988**, *110*, 2201–2210. – [1c] J. B. Lambert, W. Schilf, *J. Am. Chem. Soc.* **1988**, *110*, 6364–6367. – [1d] M. Okano, K. Mochida, *Chem. Lett.* **1991**, 819–822. – [1e] G. A. Olah, G. Rasul, L. Heilinger, J. Bausch, G. K. S. Prakash, *J. Am. Chem. Soc.* **1992**, *114*, 7737–7742. – [1f] T. Birchall, V. Manivannan, *J. Chem. Soc., Dalton Trans.* **1985**, 2671–2675. – [1g] J. B. Lambert, B. Kuhlmann, *J. Chem. Soc., Chem. Commun.* **1992**, 931–932.
- [2] [2a] H. C. Clark, J. O'Brien, *Inorg. Chem.* **1963**, *2*, 1010–1012. – [2b] V. G. K. Das, W. Kitching, *J. Organomet. Chem.* **1967**, *10*, 59–69. – [2c] I. R. Beattie, G. P. McQuillan, *J. Chem. Soc.* **1963**, 1519–1523. – [2d] K. L. Leighton, R. E. Wasylishen, *Can. J. Chem.* **1987**, *65*, 1469–1473. – [2e] T. S. B. Baul, D. Dey, D. D. Mishra, W. Basaiawmoit, E. Rivaola, *J. Organomet. Chem.* **1993**, *447*, 9–13. – [2f] A. Vij, S. Singh, R. D. Verma, *J. Fluorine Chem.* **1992**, *58*, 43–51.
- [3] [3a] B. Wrackmeyer, *Rev. Silicon, Germanium, Tin, Lead Compds.* **1982**, *6*, 75–148. – [3b] B. Wrackmeyer, *Boron Chemistry – Proceedings of the 6th International Meeting on Boron Chemistry (IMEBORON VI)* (Ed.: S. Hermanek), World Scientific, Singapore, **1987**, p. 387–415.
- [4] [4a] J. B. Lambert, *Tetrahedron* **1990**, *46*, 2677–2689. – [4b] K. A. Nguyen, M. S. Gordon, G. Wang, J. B. Lambert, *Organometallics* **1991**, *10*, 2798–2803. – [4c] G. A. McGibbon, M. A. Brook, J. K. Terlouw, *J. Chem. Soc., Chem. Commun.* **1992**, 360–362.
- [5] [5a] P. J. Stang, Z. Rappoport, M. Hannack, L. R. Subramanian, *Vinyl Cations*, Academic Press, New York, **1979**. – [5b] H.-U. Siehl, F.-P. Kaufmann, Y. Apeloig, V. Braude, D. Danovich, A. Berndt, N. Stamatis, *Angew. Chem.* **1991**, *103*, 1546–1549; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1479. – [5c] C. Dallaire, M. A. Brook, *Organometallics* **1993**, *12*, 2332–2338. – [5d] P. Buzek, P. v. Rague Schleyer, S. Sieber, *Chem. Unserer Zeit* **1992**, *28*, 116–128. – [5e] A. Berndt, *Angew. Chem.* **1993**, *105*, 1034–1058; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 985–1009.
- [6] B. Wrackmeyer, S. Kundler, R. Boese, *Chem. Ber.* **1993**, *126*, 1361–1370.
- [7] B. Wrackmeyer, K. Horchler, R. Boese, *Angew. Chem.* **1989**, *101*, 1563–1565; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1500–1501.
- [8] B. Wrackmeyer, G. Kehr, R. Boese, *Angew. Chem.* **1991**, *103*, 1374–1376; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1370–1372.
- [9] B. Wrackmeyer, G. Kehr, A. Sebald, J. Kümmerlen, *Chem. Ber.* **1992**, *125*, 1597–1603.
- [10] B. Wrackmeyer, K. Horchler, *J. Organomet. Chem.* **1990**, *339*, 1–10.
- [11] B. Wrackmeyer, K. Horchler, *Z. Naturforsch., Teil B*, **1990**, *45*, 437–446.

- [12] B. Wrackmeyer, G. Kehr, *Polyhedron* **1991**, *10*, 1497–1506.
- [13] R. Köster, G. Seidel, I. Klopp, C. Krüger, G. Kehr, J. Süß, B. Wrackmeyer, *Chem. Ber.* **1993**, *126*, 1385–1396.
- [14] B. Wrackmeyer, K. Wagner, S. T. Abu-Orabi, *J. Organomet. Chem.* **1988**, *346*, 333–340.
- [15] B. Wrackmeyer, G. Guldner, S. T. Abu-Orabi, *Tetrahedron* **1989**, *45*, 1119–1130.
- [16] B. Wrackmeyer, K. Horchler, *Progr. NMR Spectrosc.* **1990**, *22*, 209–253.
- [17] [17a] H. Nöth, B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds in NMR – Basic Principles and Progress*, vol. 14 (Eds.: P. Diehl, E. Fluck, R. Kosfeld), Springer, Berlin, **1978**. – [17b] B. Wrackmeyer, R. Köster in *Houben-Weyl, Methoden der Organischen Chemie*, vol. 13/3c (Ed.: R. Köster), Thieme, Stuttgart, **1984**, pp. 377–611. – [17c] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61–203.
- [18] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73–186.
- [19] [19a] G. J. Martin, M. L. Martin, J.-P. Gouesnard, *¹⁵N NMR Spectroscopy in NMR – Basic Principles and Progress*, vol. 18 (Eds.: P. Diehl, E. Fluck, R. Kosfeld), Springer, Berlin, **1981**. – [19b] M. Witanowski, L. Stefaniak, G. A. Webb, *Annu. Rep. NMR Spectrosc.* **1986**, *18*, 1.
- [20] [20a] L. Killian, B. Wrackmeyer, *J. Organomet. Chem.* **1978**, *148*, 137–146. – [20b] C. Bihlmayer, S. T. Abu-Orabi, *J. Organomet. Chem.* **1987**, *322*, 25–32. – [20c] S. Kersch, B. Wrackmeyer, *J. Organomet. Chem.* **1988**, *338*, 195–204. – [20d] B. Wrackmeyer, *J. Organomet. Chem.* **1989**, *364*, 331–342.
- [21] H. J. Reich, N. H. Phillips, *J. Am. Chem. Soc.* **1986**, *108*, 2102–2103.
- [22] R. Köster, G. Seidel, B. Wrackmeyer, K. Horchler, D. Schlosser, *Angew. Chem.* **1989**, *101*, 945–946; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 918–919.
- [23] Further details of the crystal structure analyses are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-57792, the names of the authors, and the journal citation.
- [24] R. Boese, D. Bläser, N. Niederprüm, W. A. Brett, P. v. Rague Schleyer, M. Bühl, N. J. R. van Eikema Hommes, *Angew. Chem.* **1992**, *104*, 356–358; *Angew. Chem. Int.* **1992**, *31*, 314–316.
- [25] L. Brandsma, *Preparative Acetylenic Chemistry*, 2nd Ed., Elsevier, Amsterdam, **1988**, p. 267–268.
- [26] R. Köster, P. Binger, W. V. Dahlhoff, *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*, 359–367.
- [27] E. Krause, P. Nobbe, *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2112–2116.
- [28] G. O. Tsetlina, V. A. Pestunovich, M. G. Voronkov, E. E. Liepin'sh, V. N. Cherkasov, E. T. Bogorodovskii, V. S. Zagorodnii, A. A. Petrov, *Dokl. Akad. Nauk. SSSR* **1979**, *245*, 400–403.

[271/93]