Tetrahedron Vol. 45, No. 4, pp. 1119 to 1130, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00

ORGANOBORATION OF 3-(TRIMETHYLSTANNYL)-2-PROPYNYL-1-ETHERS

Bernd Wrackmeyer* and Gudrun Guldner
Laboratorium für Anorganische Chemie, Universität Bayreuth
Postfach 10 12 61 - D- 8580 Bayreuth - F.R.G.
and
Sultan T. Abu-Orabi
Department of Chemistry - Faculty of Sciences
Yarmouk University
Irbid - Jordan

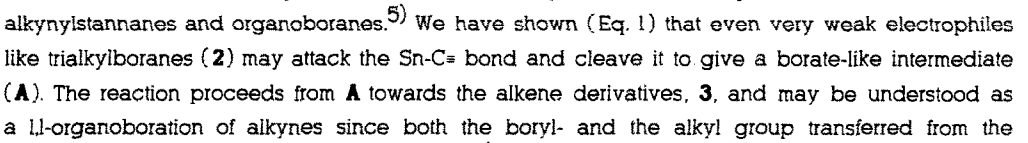
(*Received in Japan* 8 *August* 1988)

Abstract

The reaction of 3-(trimethylstannyl)-2-propynyl-1-ethers (**4**, **5**) with trialkylboranes (**2**, **7**) leads to different products, depending on the substituents at boron, on the presence of a Me_3SnO-group as well as on the substituents at the C-1 carbon atom. In the case of the CH_2OSnMe_3 group (**4a**), the reaction with trimethyl- or triethylborane (**2a,b**) gives the new heterocycles, 2,3,3-trialkyl-4,4-bis(trimethylstannyl)-1,2-oxaborolanes, **12**, in quantitative yield (alkyl = Me, Et). In contrast, in the presence of a MeO-group (**5**) an alkene derivative, **18**, is obtained with the stannyl- and the boryl group in *cis*-position. The analoguous products (**14**, **15a,b,c**) are formed in the reaction between **4a** and trisopropylborane (**2c**) or B-alkyl-9-borabicyclo[3.3.1]nonane (**7**). If there are one or two alkyl groups as substituents at C-1 (**4b**, **c**, **d**) the reaction with triethylborane (**2b**) leads also to such alkenes, **16**. However, exchange of alkyl groups between the stannyl and the boryl groups takes place, leading to the alkenes **17 b,c,d** in which a $Me_2(Et)Sn$- and a B(Me)Et group are in *cis*-position. ^1H-, ^{11}B-, ^{13}C- and ^{119}Sn NMR data are given.

Until recently organotin- and organoboron chemistry have shared only a few points of contact, like the formation of a boron-carbon bond via the exchange reaction between a boron halide and tetraorganylstannanes.[1] At present, however, there are several interesting applications involving both organoboron- and organotin compounds: Hydrostannation of alkynylboranes,[2] triethylborane-induced hydrostannation of alkynes,[3] the reaction of alkynylborates with triorganotin halides,[4] and the organoboration of alkynylstannanes[5] may be regarded as examples for this development.

Alkynylstannanes (e.g. **1**) are attractive reagents in organometallic synthesis[6] and our interest is focused on the reactivity of the Sn-C≡ bond, in particular with respect to reactions between alkynylstannanes and organoboranes.[5] We have shown (Eq. 1) that even very weak electrophiles like trialkylboranes (**2**) may attack the Sn-C≡ bond and cleave it to give a borate-like intermediate (**A**). The reaction proceeds from **A** towards the alkene derivatives, **3**, and may be understood as a 1,1-organoboration of alkynes since both the boryl- and the alkyl group transferred from the boron atom end up at the same carbon atom.[5]



(1)

In most cases the reactions are stereospecific and the alkenes **3** with the stannyl- and the boryl group in *cis*-position are formed quantitatively.[7] These results remind of the reaction of

alkynyltriorganylborates with electrophiles.[8] If the electrophiles are triorganotin halides, products similar to **3** can be obtained.[4]

The presence of functional groups at the tin atom (e.g. NEt_2, Cl) increases the synthetic potential of the organoboration products.[9] For the same reason we are currently studying the influence of functional groups in R^1 in the alkynylstannanes **1** upon the course of the organoboration reaction. In this work we report on the reaction between some 3-(trimethylstannyl)-2-propynyl-1-ethers (**4**, **5**), 4-(trimethylstannyl)-3-butynyl-1-trimethylstannylether (**6**) and trialkylboranes **2** [R_3B: R = Me (**2a**), Et (**2b**), ^{i}Pr (**2c**), **7** (B-alkyl-9-borabicyclo-[3.3.1]nonane; Alkyl = R = Me, **7a**, Et, **7b**, ^{i}Pr, **7c**).

RESULTS AND DISCUSSION

Synthesis of the alkynylstannanes

The Sn-N bond of stannylamines is cleaved by terminal alkynes to give the alkynylstannane and amine.[10] This reaction works also with various yn-ols and propargylmethylether. By treatment of these compounds with two or one equivalent of diethylaminotrimethylstannane (Me_3Sn-NEt_2, **8**) the corresponding alkynes, **4**, **5**, **6**, are obtained in essentially quantitative yield (Eq. 2).

$$R^1\text{-}C{\equiv}C\text{-}H \;+\; n\ Me_3Sn\text{-}NEt_2 \longrightarrow Me_3Sn\text{-}C{\equiv}C\text{-}R^1 \qquad (2)$$

(**8**; $-n\ HNEt_2$; **4**, **5**, **6**)

R^1 =	CH_2OSnMe_3	$CH(Me)OSnMe_3$	CMe_2OSnMe_3	$CMe(Et)OSnMe_3$	$C(CH_2)_5OSnMe_3$	CH_2OMe	$CH_2CH_2OSnMe_3$
n =	2	2	2	2	2	1	2
Nr.	**4a**	**4b**	**4c**	**4d**	**4e**	**5**	**6**

The alkyne derivatives **4**, **5**, **6** are colourless, oily liquids (**4b**,**c**,**d**, **5**) or waxy solids (**4a**,**e**,**6**) which are sensitive to traces of moisture. They dissolve readily in hydrocarbons, ethers and chlorinated hydrocarbons without decomposition. ^{1}H-, ^{13}C- and ^{119}Sn NMR data (Table 1) serve for the characterization of the alkynes. If the yn-ols are treated with only one equivalent of **8** the trimethylstannyl ethers, **9**, are formed exclusively, e.g. **9d**:

$$H\text{-}C{\equiv}C\text{-}CMe(Et)\text{-}O\text{-}SnMe_3 \quad \mathbf{9d}$$

The reaction between the yn-ols with hexamethyldisilazane [$(Me_3Si)_2NH$] readily affords the trimethylsilyl ethers, **10**, corresponding to **9**, e.g. **10d** and **11**, respectively. However, we did not

$H\text{-}C{\equiv}C\text{-}CMe(Et)\text{-}O\text{-}SiMe_3$ (**10d**) $\qquad$ $H\text{-}C{\equiv}C\text{-}CH_2CH_2\text{-}O\text{-}SiMe_3$ (**11**)

succeed in converting **10d** or **11** into the 3-(trimethylstannyl)- and 4-(trimethylstannyl)-derivatives by treatment of **10d** or **11** with **8**. Instead mixtures of various compounds containing the Me_3Sn-C≡ and Me_3Sn-O units were found which have not been further investigated.

Reactions of the alkynes with trialkylboranes

All reactions between the alkynes **4**, **5**, **6** and the trialkylboranes **2**, **7** have been carried out under comparable conditions, by adding the boranes to a hexane solution of the alkynes at -78°C and warming the mixture to room temperature. The progress of the reaction has been monitored by recording ^{11}B- and ^{119}Sn NMR spectra of the reaction solutions. Since the alkynes reacted with the boranes to give rather different types of products, the reactions are discussed separately for each alkyne.

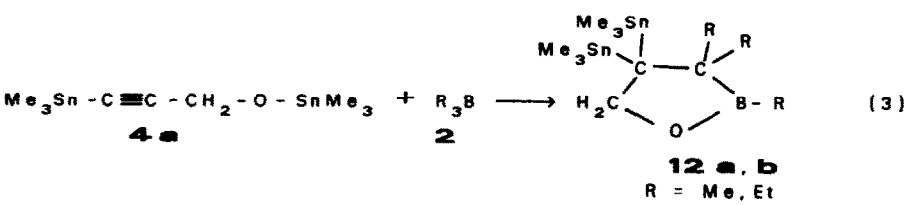
Organoboration of **4a**

As shown in Eq. 3 the reaction between **4a** and **2a**,**b** gives the 1,2-oxaborolanes, **12**, in high

Table 1 ^{13}C- and ^{119}Sn NMR data of the alkynylstannanes **4**, **5**, **6** and other alkynes for comparison

		$\delta^{13}C$							$\delta^{119}Sn$	
Nr.	R^1	Sn-C≡	≡C-	R^1			Me_3Sn-C	Me_3Sn-O	Me_3Sn-O	Me_3Sn-C
4a	CH_2OSnMe_3	87.5 [454.5]	112.8 [86.7; <2.0]	54.6[b] [9.4]			-8.3 [404.9]	-3.8 [398.0]	+135.3	-70.4
4b	$CH(Me)OSnMe_3$	85.6 [455.0; 4.0]	116.6 [84.0; 16.3]	61.8[b] [26.2; 8.7]	27.6 [19.0]		-8.2 [403.8]	-3.3 [397.2]	+119.0	-70.8
4c	CMe_2OSnMe_3	83.7	119.2	67.8[b]	34.8		-8.2	-2.2	+103.5	-70.3
4d	$CMe(Et)OSnMe_3$	85.2 [455.0]	118.4 [86.1; 19.1]	71.2[b] [30.5; 7.5]	32.8 [<4]	39.2[c] [14.2]	9.2[d] [<4]	-8.1 [405.0]	-2.2 [400.5]	+100.9 -71.2
4e	$C(CH_2)_5OSnMe_3$	86.1 [462.0]	118.4 [86.1; 19.1]	71.2[b] [30.5; 7.5]	43.4[e] [12.0]	26.1 [<3]	24.2 [<3]	-8.1 [403.2]	-2.1 [398.9]	+102.1 -70.7
5	CH_2OMe	89.5 [437.1]	105.7 [87.2]	60.6[b] [8.7]	57.0[f] [<2]			-8.2 [405.4]	--	-- -68.9
6	$CH_2CH_2OSnMe_3$	83.0	109.2	64.8[b]	26.9			-8.0 [405.4]	-4.6 [397.0]	+141.9 -70.1
9d	$CMe(Et)OSnMe_3$	71.5	90.6 [18.6]	70.2[b] [28.5]	31.6 [9.2]	38.3[c] [12.0]	9.2[d] [<2]	--	-2.3 [399.0]	+116.3 --
10d	$CMe(Et)OSiMe_3$	71.4	88.2	68.5[b]	29.5	36.7[c]	9.1[d]	--	2.7[g]	-- --
11	$CH_2CH_2OSiMe_3$	69.9	81.5	61.4[b]	23.0			--	-0.5[g]	-- --

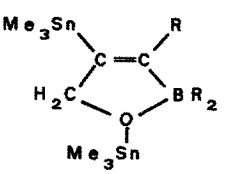
[a] In C_6D_6 (~ 10 %) at 27-28°C, $\delta^{13}C$ relative to Me_4Si ($\delta^{13}C_{C_6D_6}$ = 128.0), $\delta^{119}Sn$ relative to external Me_4Sn; values for coupling constants $^nJ(^{119}Sn^{13}C)$ are given in [ ]. [b] ≡C-***C***-O. - [c] ≡C-CMe(***CH***$_2$-CH_3). - [d] ≡C-CMe(CH_2-***CH***$_3$). - [e] ≡C-C(***CH***$_2$-. - [f] ≡C-CH_2-O***CH***$_3$. - [g] O-Si(***CH***$_3$)$_3$.



(3)

12 a, b
R = Me, Et

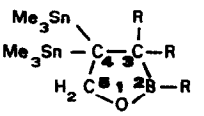
yield. The compounds **12a, b** are air- and moisture-sensitive, colourless, waxy solids which can be distilled under reduced pressure without decomposition. It is conceivable that an intermediate **13** rearranges into **12** by migration of a trimethylstannyl group and an alkyl group transfer from the



13

boron to the neighbored carbon atom. The comparison with Eq. 1 shows that the stereochemistry of the organoboration is different, leading primarily to the product with the stannyl- and the boryl group in *trans*-position as indicated in **13**. Taking into account the results for the reaction between **4a** and **7** as well as for the reactions between **4b-e** and **2b** (vide infra), it is suggested that a weak coordinative O-B bond between **4a** and **2a** or **2b** is involved in the early stage of the formation of **12**.

Table 2 ^{11}B-, ^{13}C- and ^{119}Sn NMR data[a,b] for the 1,2-oxaborolanes **12a, b**



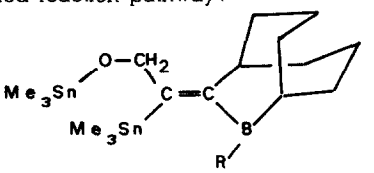
Nr.	R	$\delta^{13}C^{2',2''}$	$\delta^{13}C^{3-3''}$	$\delta^{13}C^{4-4''}$	$\delta^{13}C^{5}$	$\delta^{11}B$	$\delta^{119}Sn$
12a	Me	3.2	39.4	39.6	77.4	61.0	9.9
		(br)	(br)	[292.6]	[7.0]		
			23.6	-7.1			
			[41.4; 34.4]	[303.0]			
12b	Et	11.4	47.3	41.3	78.1	61.2	5.8
		(br)	(br)	[293.2]	[5.0]		
		8.2	27.3	-6.1			
			[41.4; 34.0]	[299.2]			
			11.1				
			[<3]				

a) In C_6D_6 (~10 %) at 27-28°C, $\delta^{13}C$ relative to Me_4Si ($\delta^{13}C_{C_6D_6}$ = 128.0), $\delta^{11}B$ relative to external BF_3-OEt_2, $\delta^{119}Sn$ relative to external Me_4Sn.

b) (br) denotes the broad ^{13}C resonance of a carbon atom linked directly to boron.

c) Values for coupling constants $^{n}J(^{119}Sn^{13}C)$ are given in [ ].

The reaction between **4a** and the more bulky triisopropylborane (**2c**) or B-alkyl-9-borabicyclo[3.3.1]- nonanes, **7**, takes a different course. The structure of the products **14** and **15 a,b,c** which could be assigned by ^{1}H-, ^{11}B-, ^{13}C- and ^{119}Sn NMR corresponds to the usual stereochemistry of the organoboration reaction (see Eq. 1,4). The enlargement of the bicyclic system is in accord with the kinetically controlled reaction pathway.[11]

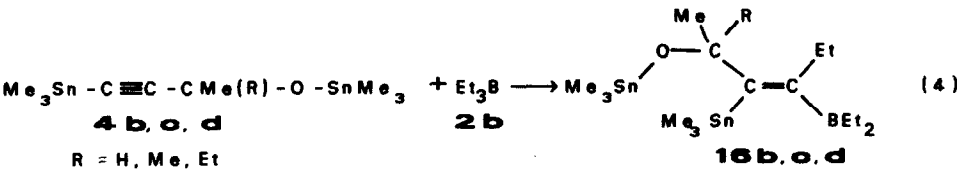


15 a, b, c
R = Me, Et, ^{i}Pr

The alkene derivative **14** is remarkably stable in solution, even after heating for 8h to 80°C or UV irradiation for 2h. In contrast, **15 a,b** decomposes already after several hours at room temperature in benzene solution, leading to a various unidentified products, whereas **15c** is again stable in solution for several weeks.

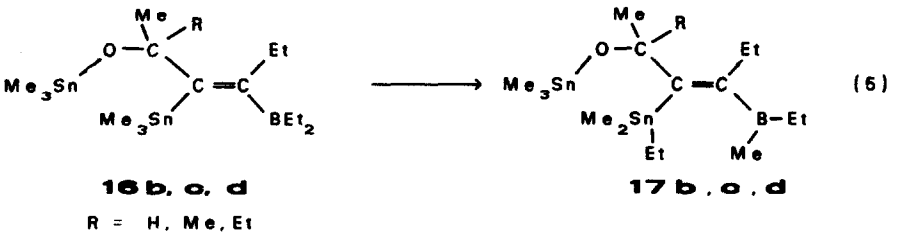
***Organoboration of* 4b, c, d, e**

The alkynes **4b, c, d** react with triethylborane (**2b**) to give alkenes (**16**) analogous to **14** with the stannyl- and the boryl group in *cis*-position at the C-C double bond (Eq. 4). In contrast, **4e** does not react with **2a,b** at room temperature and extensive decomposition is observed after keeping **4e** with **2b** in boiling hexane for 1h.



(4)

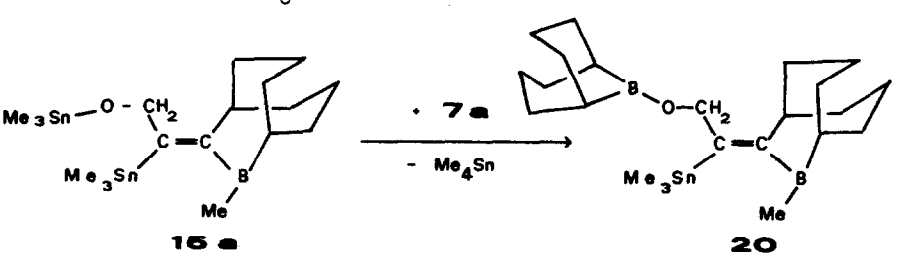
The compounds **16** are stable in benzene solution for several hours. They decompose by various routes one of which starts with the exchange of alkyl groups between the boron and the tin atom (Eq. 5). In the case of **16b** there is no other compound present in solution for about 24 h. After that NMR spectra prove that ethyl- and methyl groups are exchanged between boron and tin. In the case of **16 c, d** this exchange occurs already below room temperature during the synthesis of these compounds and mixtures of **16c/17c** and **16 d/17 d** is obtained instead of pure compounds **16c,d**. These mixtures are stable for several days



(5)

at room temperature. When heated to 60°C in hexane solution the compounds **16**, **17** decompose into numerous unidentified products.

The decomposition proceeds only slowly if there are bulky groups at the boron atom (see **14**, **15c**). Therefore, an intermolecular transfer of a B-organyl group to the tin atom of the Me_3Sn-O group has to be considered. This has been studied in the case of **15a** which was left in solution at room temperature in the presence of large excess of **7a** for several hours. Already after 2 h the ^{11}B NMR spectra show a very broad signal at $\delta^{11}B$ = 57, characteristic for a B-oxo-borabicyclo[3.3.1]-nonane unit.[12] The ^{119}Sn NMR spectra are even more instructive since they show that the ^{119}Sn resonances for **15 a** ($\delta^{119}Sn$ = +129.7; -64.8) decrease in intensity and two new ^{119}Sn resonances are growing at the same rate: One signal ($\delta^{119}Sn$ = 0) proves the formation of Me_4Sn (transfer of the B-Me group from **7a** to the Me_3Sn-O group in **15c**) and the other signal ($\delta^{119}Sn$ = -53.8) is found



(6)

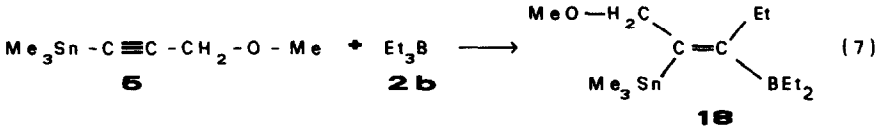
Relevant ^{13}C NMR data for 20 (see also Table 3):

Me_3Sn-C=	=C-BR_2	$CH_2OBC_8H_{14}$	R
151.8	165.0	67.5 24.8	37.4, 31.7
[517.7]	(br)	[29.5] (br)	[79.0] [6.3]
-5.0	34.3, 15.8	33.5, 20.4	30.4, 22.9
[338.3]	(br) (br)		

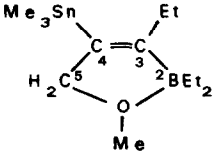
B-Me group from **7a** to the Me_3Sn-O group in **15c**) and the other signal ($\delta^{119}Sn$ = -53.8) is found in the typical region for alkenylstannanes[13] (see **18**, $\delta^{119}Sn$ = -53.3). The ^1H- and ^{13}C NMR spectra support the proposed structure of compound **20**.

***Organoboration of* 5**

The reaction of **5** with triethylborane (**2b**) gives a single product, **18**, in quantitative yield (Eq. 7) which is stable for weeks in solution and can be distilled without decomposition.



The treatment of the alkynylborate $Na[Et_3B\text{-}C{\equiv}C\text{-}CH_2OMe]$ with dimethylsulfate has been reported[14] to give a mixture of (Z/E)-isomers, where the (Z)-isomer as a minor component corresponds to compound **18**. In the (E)-isomer a coordinative O-B bond is present. Since thermal isomerization of **18** did not occur, a solution of **18** in hexane was irradiated with UV-light. This caused partial decomposition (~ 20%) together with partial (~30%) isomerization of **18** into **19**, as proved by the NMR data (vide infra).



19

Relevant ^{11}B-, ^{13}C- and ^{119}Sn NMR data (see also Table 3):						
$\delta^{13}C^{1'}$	$\delta^{13}C^{2',2''}$	$\delta^{13}C^{3-3''}$	$\delta^{13}C^{4-4'}$	$\delta^{13}C^{5}$	$\delta^{11}B$	$\delta^{119}Sn$
56.0	13.5 (br)	-- (br)	125.7	87.5	21.9	-69.3
	10.4	32.0 ; 14.0 [50.6] [8.2]	-8.7 [335.7]			

***Organoboration of* 6**

Although the alkynylstannane **6** reacts readily with triethylborane (**2b**) no definite product has been isolated so far from the complex mixture present in the reaction solution. There are some indications from the ^{11}B- and ^{119}Sn NMR spectra of the reaction solution that the course of the reaction is similar, at least partly, to that for the organoboration of **4a**. This is supported by the ^{13}C NMR spectra which shows only weak ^{13}C resonances for olefinic carbon atoms.

The different behaviour of **4a** and **5** towards trialkylboranes (Eq. 3 and 6) proves that the Me_3Sn-O group takes a significant influence upon the course of the reaction. The oxygen atom in **4a** may be a better donor than in **5** towards the three-coordinate boron atom in **2a,b**. The major change in the product distribution in the reactions of **4a** and **4b** with triethylborane (Eq. 3 and 4) has to be attributed to the increase in steric hindrance preventing the formation of a weak adduct with a coordinative O-B bond in the beginning of the reaction. The argument concerning the steric hindrance is supported by the observation that **4e** does not react with **2** at room temperature. An exchange of alkyl groups between boron and tin in the alkenes **3** has been observed only once so far, when the substituent R^1 in **3** has been a 2-pyridyl group.[15] In that case, it has been suggested that a weak intramolecular N-Sn interaction plays an important role. In the present case it is also possible that weak intramolecular coordinative O-Sn bonding has to be considered (see the discussion of the $\delta^{119}Sn$ values). Furthermore, the increasing bulkiness of R^1 in going from **4b** to **4d** will force the Me_3Sn- and the Et_2B-group in close spatial contact.

NMR spectra

Table 1 contains NMR data for the alkynylstannanes **4**, **5**, **6** and other alkynes for comparison. Table 2 lists the NMR data for the 1,2-oxaborolanes **12** and Table 3 contains NMR data for the alkenes **14**, **15**, **16**, **17**, **18**. Data for **19**, **20** are given together with the proposed structures and some relevant ^{1}H NMR data are given in the experimental part.

^{1}H- and ^{13}C NMR

The assignment of the ^{13}C resonances is based on the usual techniques,[16] in most cases also on the magnitude of the coupling constants $^{n}J(^{119}Sn^{13}C)$,[13] and on the broadening of the ^{13}C resonances caused by scalar relaxation of the second kind if a boron atom (^{11}B, I = 3/2; ^{10}B, I = 3) is linked directly to a carbon atom.[12,17] The ^{1}H- and ^{13}C NMR data prove convincingly the proposed structures. Examples are the heterocycles **12** (e.g. the absence of olefinic ^{13}C resonances and the $^{3}J(^{119}Sn^{1}H)$ values of 68.3 and 57.6 Hz to the OCH_2-protons), the alkenes **15** where the ^{13}C NMR spectra show the enlarged bicyclic system (^{13}C resonances for the -C-CH- and the B-R units instead of ^{13}C resonances for a -C-R group), and the alkenes **17b,c,d** for which the presence of a SnEt-, a BMe group and diadstereotopic Sn-Me groups (not for **17c**, because there is no chiral centre) could be observed.

^{11}B NMR

Preliminary information on the organoboration reaction can be gained by studying reaction solutions and ^{11}B NMR spectra can be recorded within seconds even for very diluted solutions. Furthermore, the $\delta^{11}B$-values are rather characteristic for a particular surrounding of the boron atom.[12,18] Thus, the $\delta^{11}B$-values for the compounds **12** are found in the usual range for 1,2-oxaborolanes proving the structural unit O-B $\begin{smallmatrix} C \\ C \end{smallmatrix}$. Similarly, the $\delta^{11}B$-values for the alkenes **14**, **15**, **16**, **17**, **18** are in the typical range for triorganylboranes with little (pp)π-CB interaction.[12,18] The increase in ^{11}B-nuclear shielding in **19** ($\delta^{11}B$ 21.9) with respect to **17** ($\delta^{11}B$ 84.1) supports the cyclic structure with a coordinative O-B bond since there are several examples in the literature with a comparable structure and similar $\delta^{11}B$-values.[12,17]

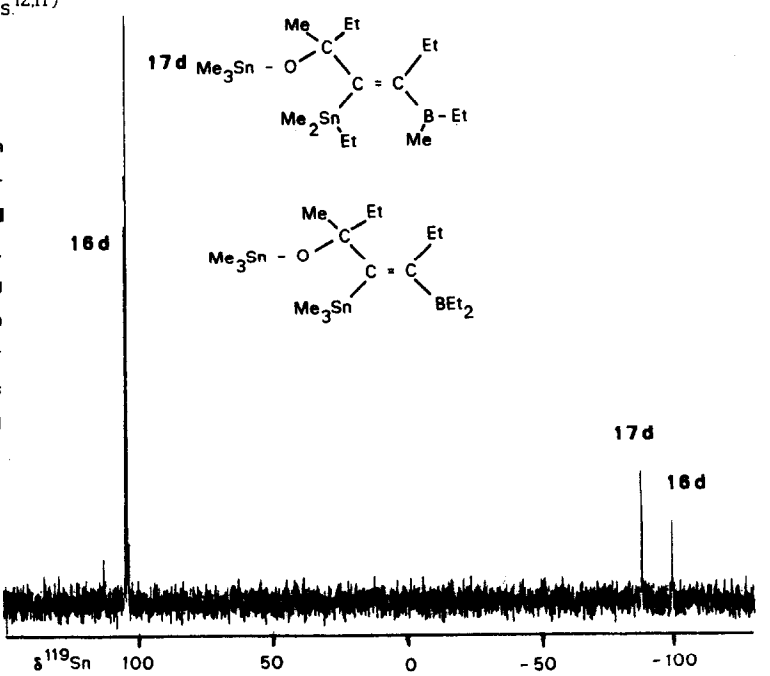


Fig. 1
74.63 MHz $^{119}Sn\{^{1}H\}$ NMR spectrum (NOE-suppressed[13]) of the reaction solution (organoboration of **4d** with triethylborane) in hexane, taken immediately after warming the reaction mixture to room temperature. The integral ratio for the respective ^{119}Sn resonances for the Me_3Sn-O-, Me_3Sn-C=, and $Me_2(Et)Sn$-C= groups is 1:1. The ^{119}Sn resonances for the Me_3Sn-C= and the $Me_2(Et)Sn$-C= groups are broadened by partially relaxed scalar coupling $^{3}J(^{119}Sn^{11}B)$.[19]

Table 3 ^{11}B-, ^{13}C- and ^{119}Sn NMR data of the alkene derivatives **14**, **15**, **16**, **17**, **18**

Nr.	R^1	R	$\delta^{13}C$ Me_3Sn-C=	=C-BR_2	R^1	R	$\delta^{11}B$	$\delta^{119}Sn$[c]
14	CH_2OSnMe_3	^iPr	148.7	160.0	67.0[e]	32.4 22.5	84.0	+128.7
			[577.2; 42.5]	(br)	[19.6; 19.6]	[97.0] [7.1]		- 81.4
			-4.7[h]	25.9 19.8	-5.3			[17.8]
			[334.6]	(br)	[393.5]			
15a	CH_2OSnMe_3	C_8H_{14}[d]	161.5	161.7	66.2[e]	37.5[f] 32.0[g]	85.0	+129.7
		Me	[553.7, 33.3]	(br)	[27.2, 19.6]	[79.6] [5.4]		-64.8
			-4.1	34.0, 16.0[i]	-5.2[j]	30.3[g] 23.6[g]		
			[335.5]	(br) (br)	[391.8]			
15b	CH_2OSnMe_3	C_8H_{14}[d]	158.5	161.3	66.3[e]	37.1[f] 31.6[g]	84.0	+130.2
		Et		(br)	[26.0; 26.0]	[80.8]		- 63.6
			-5.2[h]	31.0, 20.0, 9.8[i]	-4.4[j]	30.1[g] 23.2[g]		
			[332.0]	(br) (br)	[396.0]			
15c	CH_2OSnMe_3	C_8H_{14}[d]	157.8	160.6	66.4	37.1[f] 31.3[g]	83.5	+129.9
		^iPr	[560.2, 32.7]	(br)	[26.2, 19.6]	[79.6] [5.6]		- 64.7
			-4.2	30.3, 27.4, 20.7[i]	-5.0[j]	29.3[g] 23.1[g]		
			[334.0]	(br) (br)	[392.4]			
16b	$CH(Me)OSnMe_3$	Et	153.4	155.7	71.8[e] 27.2[k]	24.5 14.2	83.5	+119.9
			[573.3]	(br)	[24.0; 19.6] [9.3]	[93.7] [8.7]		-77.9
			-4.4[h]	22.7 9.5	-4.3[j]			
			[329.2]	(br)	[393.5]			
16c	CMe_2OSnMe_3	Et	157.9	158.6	78.7[e] 33.0[k]	24.7 14.4	84.0	+98.5
			[611.0]	(br)	[24.8, 16.9] [10.0]	[108.9] [10.0]		-102.8
			-2.2[h]	22.8 9.7	-3.0[j]			
			[333.0]	(br)	[395.6]			
16d	$CMe(Et)OSnMe_3$	Et	154.4	156.3	81.2[e] 33.1[k]	24.3 13.4	82.5	+97.7
			[612.5]	[70.0] (br)	[25.0; 17.4] [10.5]	[111.2] [9.8]		-103.4
			-3.4[h]	22.6 9.5	37.1[m] 9.3[m]			
			[331.3]	(br)	[13.0; 5.4] [<3]			
					-2.2[j]			
					[394.6]			
17b	$CH(Me)OSnMe_3$	Et	153.8	157.6	71.5[e] 27.1[k]	24.4 14.6	83.5	+120.1
		Me		(br)				-68.5
			-6.3[n] -6.4[n]	22.5 9.4 14.3[o]	-4.3[j]			
			7.3[p] 11.1[p]	(br) (br)	[393.5]			

Table 3, continued

17c CMe_2OSnMe_3	Et	158.3	158.6	78.5[e]	32.9[k]	24.8	14.8	84.0	+96.5
	Me	[586.0]	(br)	[25.0, 17.5]	[10.0]	[101.4]	[10.0]		-91.5
		-4.7[h]	22.8 9.5 15.0[o]	-2.2[j]					
		[303.0]	(br) (br)	[395.6]					
		8.5[p] 11.4[p]							
		[391.8] [20.0]							
17d $CMe(Et)OSnMe_3$	Et	154.8	158.7	80.9[e]	32.9[k]	24.4	13.9	82.5	+97.0
	Me	[585.9]	[68.0](br)	[25.0; 18.3]	[10.5]	[104.0]	[10.9]		-92.4
		-5.3[n] -5.4[n]	22.6 9.5 14.9[o]	37.2[m]	9.5[m]				
		[331.3] [305.2]	(br) (br)	[13.0; 5.4]	[<2]				
		8.0[p] 10.9[p]		-2.2					
		[395.6] [22.9]		[394.6]					
18 CH_2OMe		139.1	162.1	73.7[e]	57.7[q]	23.8	13.9	84.1	-53.3
		[532.0]	(br)	[30.0]	[<2]	[81.2]	[9.0]		
		-7.4[h]	21.5 8.9						
		[315.0]	(br)						

a,b) See Table 2. - c) The ^{119}Sn resonance of Me_3SnO-group is found at high frequency (+) and that of the Me_3Sn-C≡ group at low frequency (-). - d) C_8H_{14} corresponds to the enlarged bicyclic system, see text. - e) ≡C-***C***-O. - f) ≡C-***CH*** . - g) CH_2-groups of the enlarged bicyclic system. - h) $(CH_3)_3Sn$-C≡ or $(CH_3)_2Sn$ group. - i) B***CH*** and B-***R*** . - j) $(CH_3)_3Sn$-O. - k) ≡C-C***CH***$_3$. - l) n.m. = not measured. - m) ≡C-CH_2***CH***$_3$. - n) diastereotopic ***CH***$_3$ Sn groups. - o) ***CH***$_3$B group. - p) SnCH_2***CH***$_3$ group. - q) $\equiv CCH_2O$-***CH***$_3$.

^{119}Sn NMR

The reaction solutions can also be studied by ^{119}Sn NMR,[13] although this is somewhat more time consuming than ^{11}B NMR. However, the information gained can be very useful in particular if mixtures of closely related compounds are involved (see Fig.1). In the case of the 1,2-oxaborolanes **12** the information from ^{119}Sn NMR is complementary to the ^{11}B NMR data, as the absence of the Me_3Sn-C• and Me_3Sn-O groups is proved by the $\delta^{119}Sn$-values. In the alkenes **14** to **20** the presence of Me_3Sn-C• (or $Me_2(Et)Sn$-C•) and Me_3Sn-O units follows from the ^{119}Sn NMR spectra. The formation of the mixtures **16** /**17** is readily apparent from the ^{119}Sn NMR spectra of the reaction solutions (see Fig. 1) whereas the ^{11}B NMR spectra are not informative in this respect owing to the great line widths of the ^{11}B resonances.

The greater linewidth of the ^{119}Sn resonance ($h_{1/2}$• 45 Hz) for **19** with respect to **18** ($h_{1/2}$• 35 Hz) also indicates that the stannyl- and the boryl group are in *trans*-position, since the line-width is determined by the partially relaxed scalar ^{119}Sn-^{11}B coupling with $|^3J(^{119}Sn^{11}B)_{trans}| > |^3J(^{119}Sn^{11}B)_{cis}|$.[13,19] The changes in the $\delta^{119}Sn$ values for the Me_3Sn-O groups in **4**, **6**, **14** to **17** are induced by the substituents at the ether-carbon atom and correspond closely to the pattern observed in alkoxytrimethylstannanes, Me_3Sn-O-R[13] [$\delta^{119}Sn$ +129 (R•Me); +109 (R•^{i}Pr); +91 (R•^{t}Bu)]. There is also nothing unusual about the $\delta^{119}Sn$-values of the Me_3Sn-C≡ groups in **4**, **5**, **6** [$\delta^{119}Sn$ for Me_3Sn-C≡C-R^1 ranges from ~-60 to -85]. However, the $\delta^{119}Sn$-values for the Me_3Sn-C• groups in **14** to **18** display a somewhat unexpected pattern. Thus, the ^{119}Sn-nuclear shielding increases from **18** ($\delta^{119}Sn$ -53.3), **14b** ($\delta^{119}Sn$ -63.6), **16b** ($\delta^{119}Sn$ -77.9), **14** ($\delta^{119}Sn$ -81.4) to **16d** ($\delta^{119}Sn$ -103.4). The

comparsion with δ^{119}Sn-values for the alkenes **3** shows that there is only a small shift to low frequency between **3** with R^1 = ^{n}Bu (δ^{119}Sn -49.3) and R^1 = ^{t}Bu (δ^{119}Sn -54.6). Therefore, it is tempting to attribute the low frequency shift of the ^{119}Sn resonances e.g. for **16d** with weak coordinative O-Sn interactions. This would be in accord with the observation that Me/Et - exchange proceeds most readily in the case of **16 c, d** less readily for **16 b** and no exchange of this kind has been observed for **16**. The increase in the bulkiness of the stannyl group [Me_2(Et)Sn-C-, once the Me/Et - exchange has taken place] reduces the amount of O-Sn interactions which in turn impedes further exchange reactions, as found experimentally. The same effect is produced if the bulkiness of the boryl group increases (e.g. in **14a**). The decreasing strength of the coordinative O-Sn interaction in **17** with respect to **16** may be deduced from the decrease in ^{119}Sn-nuclear shielding between **16** and **17** [e.g. δ^{119}Sn(**15d**) -103.4 and δ^{119}Sn(**17 d**) -92.4]. This effect is larger than expected for a single step of Me/Et- substitution.[13]

The ^{119}Sn NMR spectra of compound **14** have been measured between -90 to +27°C. The ^{119}Sn-resonance of the Me_3SnO-group remains almost unchanged as a sharp signal at δ^{119}Sn +128.7 ± 0.3, whereas the ^{119}Sn-nuclear shielding of the Me_3Sn-C- group increases steadily as the temperature decreases from δ^{119}Sn -81.4 (27°C) to δ^{119}Sn -87.3 (-90°C) and the ^{119}Sn-resonance for this group becomes much broader at lower temperature. These observations are also in support of weak O-Sn coordinative interactions.

EXPERIMENTAL

All reactions and manipulations were performed under nitrogen by standard techniques. Gaseous trimethylborane (**2a**) was kept in a flask connected to a vacuum line. Solvents were dried and freshly distilled under nitrogen. The various yn-ols and the propargylmethylether were used as commercial products. The diethylaminotrimethylstannane (**8**)[20] and the boranes **2a**,[21] **c**,[22] **7a**, **c**[23] were prepared by published routes. NMR spectra were recorded with Jeol FX 90Q and Bruker AC 300 spectrometers (see Tables 1 to 3) Elemental analyses have been performed at the Max Planck Institute, Mülheim, and by Mikronalytisches Labor Pascher. All new compounds gave satisfactory elemental analytical data and the molecular masses were confirmed by EI-mass spectra (Finnigan MAT CH5).

The *alkynylstannanes* **4** to **6** were prepared by the following typical procedure:

In a 100 ml Schlenk flask 7.07 g (30 mmoles) of the diethylaminotrimethylstannnane (**8**) were dissolved in 50 ml of hexane. The solution was cooled to -78°C and 15 mmoles of the yn-ols, or 30 mmoles of the propargylmethylether were added. After warming to room temperature the mixture was stirred for 2 h and then heated to reflux for 1 h. The solvent and the diethylamine were removed *in vacuo* and the colorless oily or solid residues were identified as the pure compounds **4** to **6**, ready for further use. Attempts at the distillation of the alkynes **4, 6** led to extensive decomposition. In the case of **5** fractional distillation gave 6.0 g (86 %) **5** as a colorless liquid (bp 75-80°C/12 Torr). The stepwise reaction between 3-methyl-4-pentyn-3-ol and **8** (ratio 1:1) gave pure **9d** and treatment of **9d** with a second equivalent of **8** gave pure **4d**.

^{1}H NMR in C_6D_6: δ^1H [$^nJ(^{119}Sn^1H)$] **4a** 0.16 [60.2] s, 9H, $Me_3SnC\equiv$, 0.28 [57.6] s, 9H, Me_3SnO, 4.57 [9.0] s, 2H, OCH_2. - **4b** 0.13 [60.2] s, 9H, $Me_3SnC\equiv$, 0.32 [57.8] s, 9H, Me_3SnO, 1.51 d, 3H, OCMe, 4.76 q, 1H, OCH. - **4c** 0.10 [60.5] s, 9H, $Me_3SnC\equiv$, 0.45 [57.8] s, 9H, Me_3SnO, 1.53 s, 6H, $OCMe_2$. - **4d** 0.13 [60.0] s, 9H, $Me_3SnC\equiv$, 0.36 [58.0] s, 9H, Me_3SnO, 1.49 s, 3H, OCMe, 1.71 m, 1.11 t, 5H, OCEt. - **4e** 0.15 [60.0] s, 9H, $Me_3SnC\equiv$, 0.38 [57.8] s, 9H, Me_3SnO, 1.1 - 2.05 m, 10H, $OC(CH_2)_5$. - **5** 0.11 [60.6] s, 9H, $Me_3SnC\equiv$, 3.16 s, 3H, OMe, 3.92 [9.4] s, 2H, OCH_2. - **6** 0.1 [60.3] s, 9H, $Me_3SnC\equiv$, 0.30 [57.8] s, 9H, Me_3SnO, 2.36 t, 2H, $\equiv CCH_2$, 3.56 t, 2H, OCH_2. - **9d** 0.30 [58.0] s, 9H, Me_3SnO, 1.23 s, 3H, OCMe, 1.43 m, 0.82 t, 5H, OCEt, 2.30 s, 1H, $\equiv$CH.

The *trimethylsilylethers* **10d** and **11** were obtained as follows:

Solutions of 100 mmoles of the 3-methyl-4-pentyn-3-ol, or of the 3-butyn-1-ol, in 50 ml of hexane were cooled to -78°C and then 8.05 g (50 mmoles) of hexamethyldisilazane were added. The reaction mixtures were allowed to warm up to room temperature and heated to reflux for 3 h until the evolution of NH_3 had ceased. The solvent was removed *in vacuo* and from the residues the compounds **10d** (bp 46-52°C/20 Torr, 13.1 g, 77 %) and **11** (bp 36-42°C/20 Torr, 12.9 g, 91 %) were isolated by fractional distillation as colorless liquids.

^{1}H NMR in C_6D_6: δ^{1}H **10d** -0.02 s, 9H, Me_3SiO, 1.35 s, 3H, OCMe, 1.43 m, 0.82 t, 5H, OCEt, 2.21 s, 1H, ≡CH. - **11** -0.01 s, 9H, Me_3SiO, 2.21 d,t, 2H, $\equiv CCH_2$, 3.52 t, 2H, OCH_2, 1.81 t, 1H, ≡CH.

Organoborations

Typically, 5 mmoles of the alkynylstannane were dissolved in 20 ml of hexane, cooled to -78°C, then the trialkylboranes **2b, c, 7a, b, c** (~6 to 8 mmoles) and the mixtures were allowed to warm up to room temperature. Trimethylborane was handled in a vacuum line and the required amount was condensed at -196°C into the reaction vessel containing the frozen solution of the alknylstnnane in hexane. The reaction vessel was allowed to warm up until the vapour pressure started to rise. Then the pressure was increased to ~600 Torr with nitrogen gas and the mixture was warmed to room temperature. Except for three cases all reactions were complete after 20 min at room temperature (monitored by ^{11}B- and ^{119}Sn NMR). It was necessary to heat the reaction solution containing **4a** and **2c** for 10 min to 60°C and no reaction took place between **4c** and **2a, b** at room temperature. Heating the mixture of **4c** and **2b** in hexane caused extensive decomposition. As soon as the reaction were found to be complete the solvent and the small excess of the boranes were removed *in vacuo*, leaving the products as pure oily liquids or waxy solids (**12a, b**) which were all extremely sensitive towards traces of moisture and oxygen.

The heterocycles **12a** (bp 62-65°C/0.05 Torr), **12 b** (bp 85-88°C/0.05 Torr) and the alkene **18** (bp 58-61°C/0.05 Torr) could be distilled without noticeable decomposition.

UV irradiation of **14** (2 h, Hg-vapour lamp, Hanau TQ 718, 700 W, using quartz glassware) did not induce decomposition or rearrangements. The same treatment of **18** produced a mixture containing ~ 30 % of the alkene **19** together with **18**.

Some relevant ^{1}H NMR data (in C_6D_6) : δ^{1}H [$^nJ(^{119}Sn^1H)$] **12a** 0.09 [50.0] s, 18H, $C(SnMe_3)_2$, 0.47 s, 3H, BMe, 0.93 [3.5] s, 6H, CMe_2, 4.42 [67.4, 56.8] s, 2H, OCH_2. - **12b** 0.08 [50.2] s, 9H, $C(SnMe_3)_2$, 0.95 m, 1.10 t, 5H, BEt, 1.60 m, 1.31 m, 0.78 t, 10H, CEt_2, 4.43 [68.3, 57.6] s, 2H, OCH_2. - **14** 0.17 [52.5] s, 9H, Me_3SnC=, 0.16 [57.2] s, 9H, Me_3SnO, 1.66 sept, 1.12 d (broad), 14H, B^iPr_2, 2.47 [7.3] sept, 1.03 d, 7H, $=C^iPr$, 4.59 [46.0, 22.4] s, 2H, OCH_2. - **15a** 0.12 [52.3] s, 9H, Me_3SnC=, 0.10 [57.0] s, 9H, Me_3SnO, 0.89 s, 3H, BMe, 3.06 m, 1H, ≡CH, 4.41 [45.1, 22.6] s, 2H, OCH_2. - **15b** 0.28 [52.1] s, 9H, Me_3SnC=, 0.14 [58.0] s, 9H, Me_3SnO, 3.05 m, 1H, ≡CH, 4.55 [44.3, 21.1] s, 2H, OCH_2. - **15c** 0.21 [52.1] s, 9H, Me_3SnC=, 0.16 [57.2] s, 9H, Me_3SnO, ~1.70 m, 1.14 d, 7H, B^iPr, 3.12 m 1H, ≡CH, 4.49 [45.2, 22.8] s, 2H, OCH_2. - **16b** 0.20 [52.0] s, 9H, Me_3SnC=, 0.18 [57.2] s, 9H, Me_3SnO, 1.23 d, 3H, OCMe, 4.83 [66.1, ≤ 3] q, 1H, OCH . - **16d** -0.04 [51.0] s, 9H, Me_3SnC=, 0.38 [56.8] s, 9H, Me_3SnO, $=CCH_2$-, 1.36 [3.5] 3H, OCMe. - **17d** 0.12 [48.0] s, 0.14 [48.6] s, 6H, Me_2SnC=, 0.38 [56.8] s, 9H, Me_3SnO, $=CCH_2$-, 1.34 [3.5] s, 3H, OCMe. - **18** -0.07 [52.8] s, 9H, Me_3SnC=, 1.16 m, 0.86 t, 10H, BEt_2, 1.95 q, 0.81 t, 5H, =CEt, 3.2 s, 3H, OMe, 4.1 s, 2H, OCH_2.

ACKNOWLEDGEMENT

We thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for support of this work. S.T.A-O. is grateful to the *DAAD* for a research grant. We owe thanks to *Prof. R. Köster* for generous gifts of triethylborane and B-ethyl-9-borabicyclo(3.3.1)nonane, as well as for some analytical work (mass spectra and elemental analyses).

REFERENCES

1. K.Niedenzu, *Organomet.Chem.Rev.* 1966, **1**, 305.
2. a) B. Wrackmeyer and H. Nöth, *Z.Naturforsch., Teil B,* 1974, **29**, 564. - b) H.-O. Berger, H. Nöth, G.Rub and B. Wrackmeyer, *Chem. Ber.* 1980, **113**, 1235.
3. K. Nozaki, K. Oshima and K. Utimoto, *J.Am.Chem.Soc.* 1987, **109**, 2547.
4. a) J. Hooz and R. Mortimer, *Tetrahedron Lett.* 1966, 305. - b) K.K. Wang and K.-H. Chu, *J.Org.Chem.* 1984, **49**, 5175. - c) K.-H. Chu and K.K. Wang, *J.Org.Chem.* 1986, **51**, 767.
5. a) B. Wrackmeyer, *Rev.Silicon-,Germanium-, Tin-, Lead Compds.* 1982, **6**, 82. - b) B. Wrackmeyer, in *Boron Chemistry - Proceedings of the 6th International Meeting on Boron Chemistry (IMEBORON VI),* (S. Hermanek, Ed.), World Scientific, Singapore 1987, p. 387-415.
6. C. Cauletti, C. Furlani and A. Sebald, *Gazz.Chim.Ital.* 1988, **118**, 1.
7. G. Menz and B. Wrackmeyer, *Z.Naturforsch., Teil B,* 1977, **32**, 1400.
8. a) R. Köster, *Pure Appl. Chem.* 1977, **49**, 281. - b) A. Pelter, *Chem.Soc.Rev.* 1982, **11**, 191. - c) A. Suzuki, *Acc.Chem.Res.* 1982, **15**, 178.
9. a) S. Kerschl and B. Wrackmeyer, *Z.Naturforsch., Teil B,* 1985, **40**, 845. - b) S. Kerschl and B. Wrackmeyer, *J.Chem.Soc.Chem.Commun.* 1986, 403. - c) S. Kerschl and B. Wrackmeyer, *Z.Naturforsch., Teil B,* 1986, **41**, 890. - d) S. Kerschl and B. Wrackmeyer, *J.Chem.Soc.Chem.Commun.* 1986, 1170. - e) S. Kerschl, B. Wrackmeyer, A. Willhalm and A. Schmidpeter, *J.Organomet.Chem.* 1987, **319**, 49. - f) S. Kerschl and B. Wrackmeyer, *Z.Naturforsch., Teil B,* 1987, **42**, 1047. - g) S. Kerschl and B. Wrackmeyer, *J.Organomet. Chem.* 1988, **338**, 195.
10) K. Jones and M.F. Lappert, *J.Organomet.Chem.* 1965, **3**, 295.
11) a) C. Bihlmayer and B. Wrackmeyer, *Z.Naturforsch., Teil B,* 1981, **36**, 1265. - b) C. Bihlmayer, S.T. Abu-Orabi and B. Wrackmeyer, *J.Organomet.Chem.* 1987, **322**, 25.
12. B. Wrackmeyer, *Annual Rep. NMR Spectrosc.* 1988, **20**, 61-203.
13. B. Wrackmeyer, *Annual Rep. NMR Spectrosc.* 1985, **16**, 73-185.
14. P. Binger and R. Köster, *Synthesis,* 1974, 350.
15. B. Wrackmeyer, K. Wagner and S.T. Abu-Orabi, *J.Organomet.Chem.* 1988, **348**, 333.
16. H.-O. Kalinowski, S.Berger and S. Braun, *^{13}C NMR Spektroskopie,* Thieme, Stuttgart 1984.
17. B. Wrackmeyer, *Progr. NMR Spectrosc.* 1979, **12**, 227.
18. a) H. Nöth and B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds,* in *NMR - Basic Principles and Progress* (P. Diehl, R. Fluck and R. Kosfeld, Eds.), Vol. 14, Springer Verlag, Berlin 1978. - b) B. Wrackmeyer and R. Köster, in *Houben-Weyl-Müller - Methoden der Organischen Chemie* (R.Köster, Ed.), Vol. XIII/3c, Thieme, Stuttgart 1984, p. 377-611.
19. B. Wrackmeyer, *Polyhedron,* 1986, **5**, 1709.
20. K. Jones and M.F. Lappert, *J.Chem.Soc.* 1965, 1944.
21. R. Köster, P. Binger and W.V. Dahlhoff, *Synth.React.Inorg.Metal-org.Chem.* 1973, **3**, 359.
22. E. Krause and P. Nobbe, *Chem.Ber.* 1931, **64**, 2112.
23. G.W. Kramer and H.C. Brown, *J.Organomet.Chem.* 1974, **73**, 1.