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1,1-Organoboration of alkynylsilicon, -germanium, -tin and -lead compounds

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Abstract

In the course of 1,1-organoboration reactions the metal—carbon bond in 1-alkynylmetal compounds ($L_nM{-}C{\equiv}CR^1$) is cleaved by a triorganoborane (R_3B), followed by a selective

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new C—C bond formation via a 1,2 shift of a group R from boron to carbon. Mono-1-alkynyl derivatives of silicon, germanium, tin and lead react with R_3B via 1,1-organoboration to give organometallic-substituted alkenes in high yield and stereoselectively, in most cases, with the R_2B group and M (M = Si, Ge, Sn, Pb) in *cis* position at the C=C bond. These alkenes can again be used for 1,1-organoboration reactions which lead either to allenes or to dienes and 3-borolenes. The same type of reaction can be applied to di-1-alkynylmetal derivatives. The first step in the twofold 1,1-organoboration is an intermolecular 1,1-organoboration, followed by an intramolecular 1,1-vinyloboration which leads exclusively, in the case of M = Si and Ge, to siloles and germoles. In the same way stannoles and plumboles can be prepared; however, depending on R (e.g. R = ^{i}Pr) in R_3B and on R^1 (e.g. R^1 = Me) in the alkyne other heterocycles (e.g. 1,4-stannabora-2,5-cyclohexadiene or 1,4-plumbabora-2,5-cyclohexadiene derivatives) may also be obtained. Tetra-1-alkynyl derivatives of silicon and germanium react with R_3B to give selectively *spiro* compounds with two silole or germole rings. Starting from $Sn(C{\equiv}CR^1)_4$ and R_3B various types of *spiro* compounds are obtained, depending on R and R^1. In all compounds derived from 1,1-organoboration reactions numerous reactive element—carbon bonds are available for further transformations. The mechanism of the 1,1-organoboration is revealed by the nuclear magnetic resonance spectroscopic analysis in solution and in the solid state as well as by direct structural characterization of several zwitterionic intermediates in which a cationic triorganotin or triorganolead fragment is weakly coordinated to the C≡C bond of an alkynylborate.

Keywords: Alkynylsilicon; Alkynylgermanium; Alkynyltin; Alkynyllead; 1,1-organoboration

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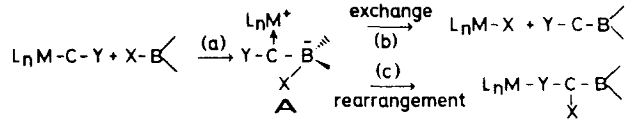
1. Introduction

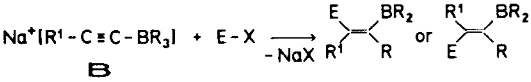
Organometallic chemistry of group 14 elements (M = Si, Ge, Sn, Pb) on the one hand and of boron on the other hand has been extensively studied, particularly in the last three to four decades. However, there are not many points of contact between these active research fields: the exchange reaction of boron halides with tetraorganyltin or -lead compounds has been used frequently to prepare organoboron halides [1]; boranes and borates with B—Si, B—Ge, B—Sn and B—Pb bonds have been described [2,3]; hydrostannation of alkynylboranes has been reported [4]; triethylborane has proved to be an efficient catalyst in hydrostannation [5] and hydrogermylation reactions [6]; 1,2-hydroboration of alkynyl- and alkenylsilanes has been studied using various borane reagents [7,8], including polyboranes [9]; a number of polyhedral boranes are known with organoelement groups as terminal or bridging ligands [10]; heteropolyboranes with silicon, germanium, tin or lead as heteroatoms have been known for some time [11].

The polarization of M—C bonds increases significantly from M = Si to Pb, and, depending on the nature of the organyl group, one can predict an alternative (Eq. (1), path c) to the widely used simple exchange reactions between organotin or -lead compounds and boranes [1] as shown in Eq. (1), path b. By taking into account that both the polarization of the M—C bonds and the electrophilic character of the boron atom can be finely tuned by selecting appropriate substituents, an alternative could open a new field of research. Following this line of thought, a cleavage of the M—C bond would also be required (Eq. (1), path a) in the first step to form an intermediate zwitterionic complex **A**. However, the subsequent rearrangement (Eq. (1), path c) of **A** would then afford a borane with a new carbon—X bond. If the group X is an organyl group a new C—C bond will be formed. This type of rearrangement has to be considered if the carbon atom, linked to M (M—C), is part of an unsaturated system such as in 1-alkynylmetal compounds ($L_nM-C{\equiv}CR^1$).



(1)

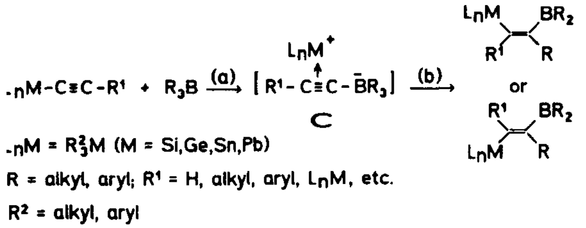
The reaction of alkalimetal trialkylalkynylborates (**B**) with various electrophiles [12] (Eq. (2)), including triorganosilicon [12,13] and -tin [13,14] chlorides, is a model reaction for the rearrangement described in Eq. (1), path c. It is also an extremely versatile method to form new C—C bonds. Depending on the electrophile, mixtures of E—Z isomers are obtained or the reaction proceeds stereoselectively, e.g. leading to the *E* isomer for E—X = Me_3Si—Cl [12b], Bu_3Sn—Cl [13].



(2)

What are the benefits of using 1-alkynylmetal compounds and triorganoboranes instead of trialkyl-1-alkynylborates and electrophiles? The products will also be organometallic-substituted alkenes which are important building blocks both in organic [12e,13b] and in organometallic [12b,14] chemistry. However, the work-up procedure is extremely simple since there is no need to remove salts, the reactions proceed essentially in a quantitative way and the stereochemistry of the reactions might be better defined. Furthermore, we can use di-, tri- and tetra-1-alkynylmetal compounds for the reaction with the boranes in order to arrive at various new heterocyclic systems which are not accessible via the alkynylborate route. Finally, there might be a chance to establish the reaction mechanism which, in principle, should be comparable with that of the reaction of alkynylborates with electrophiles.

If the fragment M—C—Y in Eq. (1) corresponds to an alkynylmetal group $M-C{\equiv}C-R^1$ and the reaction with a triorganoborane (R_3B) has taken place (Eq. (3), path a) we find a system closely analogous to that in Eq. (2): cleavage of the M—C≡ bond would provide a negatively charged alkynylborate fragment together with the L_nM^+ fragment which are expected to combine and to give a zwitterionic intermediate **C** (corresponding to **A**), in which the L_nM^+ fragment and the boron atom are bridged more or less symmetrically by the alkynyl group (see Section 9). This is the ideal starting position for further rearrangements which, in the most simple case, lead to alkene derivatives (Eq. (3), path b), with the boryl group in *cis* or in *trans* position with respect to the L_nM group (Eq. (3)). Since the R_2B group and R end up at the same carbon atom, this is called a 1,1-organoboration [14]. The products in Eq. (3) are analogous to those in Eq. (2) and therefore it can be assumed that the mechanism of the reaction shown in Eq. (2) involves a short-lived intermediate similar to **C** after elimination of NaX.



(3)

The synthetic potential of the 1,1-organoboration reactions, shown schematically in Eq. (3), depends mainly on the following factors:

(i) the formation of the new carbon—carbon bond must be highly stereoselective;
(ii) the 1,1-organoboration must tolerate a wide range of different groups R in the triorganoborane (R_3B) and of R^1 in the alkynyl group $C{\equiv}CR^1$;
(iii) the presence of other functional groups, including further alkynyl groups $C{\equiv}CR^1$ at Si, Ge, Sn or Pb, must also be tolerated;
(iv) boranes and 1-alkynylmetal compounds must be readily available;
(v) suitable analytical tools must be at hand for monitoring the progress of the reactions, characterizing the final products and analyzing mixtures.

If these conditions are fulfilled, 1,1-organoboration reactions are expected to become a powerful method in the stereospecific synthesis of organometallic-substituted alkenes or cyclic and non-cyclic dienes, to name just a few examples. It has already been shown that 1,1-organoboration can also be carried out with 1-alkynylplatinum(II) complexes [14b], and one can envisage widespread applications also to other 1-alkynylmetal compounds. Clearly, any compound obtained from 1,1-organoboration reactions possesses a number of reactive element—carbon bonds which can be exploited in many ways for further transformations. Furthermore, the presence of the boryl group and one or two other organometallic substituents linked to a C=C bond invites study of the behaviour of such compounds towards a large group of ambifunctional reagents which contain a nucleophilic site (for interaction with the three-coordinate boron atom) and an electrophilic site (in order to induce cleavage of polar element carbon bonds). The products of 1,1-organoboration reactions are also of interest for cycloaddition reactions since the electronic properties of the C=C bond in the alkenes or of the diene systems, e.g. in boryl-substituted metalloles, are greatly modified owing to the nature of the organometallic substituents. However, it is not in the scope of this review to deal with the chemistry of the products. Here, the emphasis is laid on the reactivity of the various 1-alkynylmetal compounds towards boranes and on the final products of the 1,1-organoboration reactions, together with mechanistic considerations.

In the following it will be shown that the five conditions stated above are fulfilled in many cases, although 1-alkynylgermanium compounds have received less attention than the 1-alkynylsilicon, -tin and -lead compounds. Most of the work reported here has been carried out in the group of the present author, and major progress which necessarily depended on firm evidence with regard to the reaction mechanism was achieved only during the last 6–7 years. The unequivocal evidence for the reaction mechanism is based on the isolation and structural characterization of intermediates corresponding to **C** (see Section 9). Zwitterionic compounds of this type in which an alkynyl group bridges a boron and a tin atom were unprecedented.

2. Availability of alkynyl group 14 element compounds and of boranes

2.1. *Alkynyl group 14 element compounds*

The major synthetic routes to alkynyl-group 14 element compounds have been summarized [15,16]. These compounds are readily available, in most cases, by application of standard preparative procedures. In the case of alkynylsilicon, -germanium and -tin compounds, the corresponding element halide is treated either with Grignard reagents, $R^1C{\equiv}C{-}Mg{-}X$, or with alkali metal alkynides, $LiC{\equiv}CR^1$, $NaC{\equiv}CR^1$ or $KC{\equiv}CR^1$ (Eq. (4)). For $R^1 = H$, the use of the Grignard reagent $HC{\equiv}C{-}Mg{-}Br$ in THF appears to be crucial [17]. Compounds of the type $R^2_3M{-}C{\equiv}C{-}MR^2_3$ are readily available from the reaction of the metal chloride with Li_2C_2 or the corresponding Grignard reagent (Eq. (5)). Tetra-1-alkynyllead compounds are prepared from K_2PbCl_6, as shown in Eq. (6). A very convenient access to 1-alkynyltin compounds, recommended for expensive alkynes, is provided by the reaction between dialkylaminotin compounds and terminal alkynes [15,18] (Eq. (7)).

$$R^2_{4-n}MCl_n + n\,|C{\equiv}C{-}R^1|^- \longrightarrow R^2_{4-n}M(C{\equiv}C{-}R^1)_n + n\,Cl^- \qquad (4)$$

R^1 = alkyl, aryl, $SiMe_3$, etc.
R^2 = alkyl, aryl

n =	1	2	3	4
M =	Si	Si	Si	Si
	Ge	Ge	Ge	Ge
	Sn	Sn	Sn	Sn
	Pb	Pb	-	-

$$2\,R^2_3MCl + [C{\equiv}C]^{2-} \longrightarrow R^2_3M{-}C{\equiv}C{-}MR^2_3 + 2\,Cl^- \qquad (5)$$

R^2 = alkyl, aryl

$$K_2[PbCl_6] + 4\,|C{\equiv}C{-}R^1|^- \longrightarrow Pb(C{\equiv}C{-}R^1)_4 + 2\,KCl + 4\,Cl^- \qquad (6)$$

R^1 = alkyl, aryl, $SiMe_3$, etc.

$$R^2_{4-n}Sn(NR^3_2)_n + n\,H{-}C{\equiv}C{-}R^1 \longrightarrow R^2_{4-n}Sn(C{\equiv}C{-}R^1)_n + n\,HNR^3_2 \qquad (7)$$

R^1 = alkyl, aryl, $SiMe_3$, etc.
R^2 = alkyl, aryl; R^3 = Me, Et

Most alkynylsilicon and -germanium compounds are stable towards air and water and can be stored for prolonged periods without decomposition. The tetraethynyl- and other tetra-1-alkynylsilicon and -germanium compounds should be handled with care during purification as they may explode. Alkynyltin and -lead compounds are sensitive to moisture. Ethynyltin compounds should not be stored in closed vessels at room temperature since ethyne may be formed, which is hazardous under pressure. Larger amounts of tetra-1-alkynyltin derivatives should be purified by crystallization rather than by distillation or sublimation. Ethynyllead derivatives are fairly unstable and cannot be stored for a prolonged time even at −78 °C. All other alkynyllead compounds are thermally more stable but should not be heated to above 80 °C.

2.2. *Boranes*

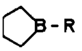
The synthesis of organoboranes has been described in great detail [19,20]. Thus, triorganoboranes R_3B of varied structure are readily available. Hydroboration of alkenes, reaction of Grignard reagents or organyllithium compounds with boron halides or methoxyboranes are the most common methods. In this review, many 1,1-organoboration reactions are described for triethyl- (**1**) or triisopropylborane (**2**) as typical examples of noncyclic trialkylboranes with very different steric demand of the organyl groups. Typical examples of cyclic or bicyclic borane reagents are boracylopentanes (**3**) or 9-bora-bicyclo[3.3.1]nonane derivatives (**4**).

Et_3B

1

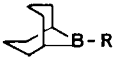
$^{i}Pr_3B$

2



3

R = alkyl, aryl



4

R = H, alkyl, aryl

3. Major analytical tools

Among the various physical methods available for the characterization of molecular compounds nuclear magnetic resonance (NMR) proved to be the most powerful analytical tool in studying 1,1-organoboration reactions. Advanced ^1H and ^{13}C one-dimensional (1D) and two-dimensional (2D) NMR techniques, routinely available on modern NMR instruments, enable unambiguous assignment of sophisticated structures of organic frameworks [21]. Together with information from NMR measurements of other nuclei such as ^{11}B, ^{29}Si, ^{119}Sn and ^{207}Pb (or ^{15}N, ^{19}F, ^{31}P, etc. if present) a fairly complete picture emerges both of the molecular structure in solution and also of the course of the reaction. Since the NMR sensitivity of ^{11}B, ^{29}Si, ^{119}Sn or ^{207}Pb is high (e.g. as compared with ^{13}C), reaction solutions can be studied under realistic conditions (e.g. deuterated solvents are not necessary; the solutions can be diluted as in experiments carried out on a larger preparative scale), from the beginning of the reactions at low temperature to room temperature or above and it becomes possible to detect intermediates and to determine optimum conditions.

^{11}B NMR spectra are ideal to look for a change in the coordination number of the boron atom. Thus, the intermediacy of complexes such as **A** or **C** should be revealed by a shift in the ^{11}B NMR signal to low frequency as compared with that of R_3B [22]. Since ^{11}B is a quadrupolar nucleus ($I = 3/2$) the resonance signals are rather broad, depending among other things on the local symmetry and molecular weight of the boron compounds. Therefore, if the chemical shifts $\delta(^{11}B)$ of the starting material and products are similar, a greater linewidth of the ^{11}B NMR signal of the product is observed.

The magnetic shielding of ^{29}Si [23] and particularly those of the heavier nuclei ^{119}Sn [24] and ^{207}Pb [25] are extremely sensitive to small changes in the environment of these nuclei. Therefore, ^{29}Si, ^{119}Sn (Fig. 1) and ^{207}Pb NMR spectra serve extremely well for monitoring the progress of the 1,1-organoboration reactions and also in the preliminary analysis even of complex mixtures. Since ^{29}Si, ^{119}Sn and ^{207}Pb are spin 1/2 nuclei (in contrast with ^{11}B), relatively sharp signals are detected under all conditions in solution provided that broadening owing to chemical exchange does not play a significant role.

Meaningful solid state NMR spectra of all types of nuclei other than ^1H, using magic angle spinning (MAS) or cross polarization (CP)–MAS techniques, are becoming more readily available. If direct structural information is accessible, e.g. from

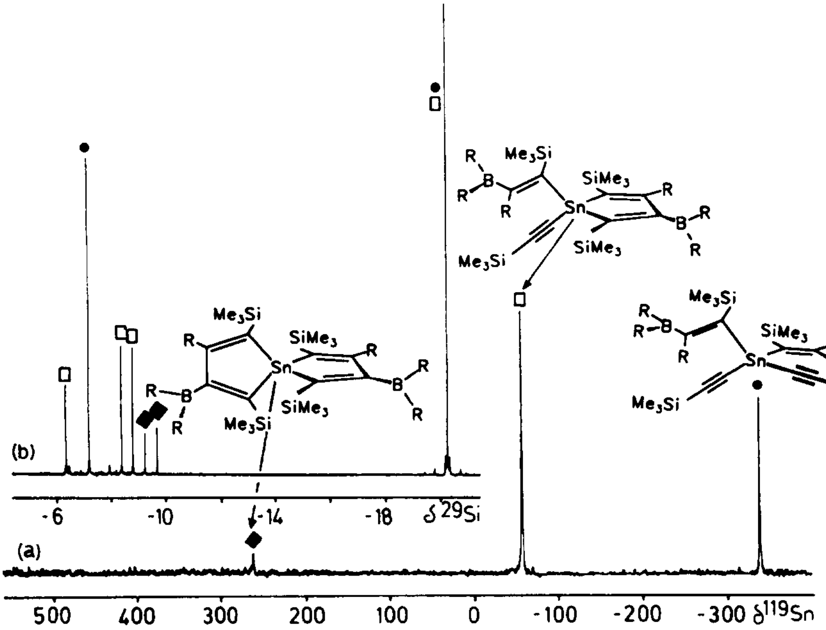


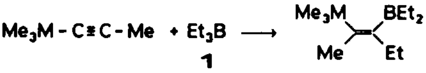
Fig. 1. Reaction between $Sn(C{\equiv}CSiMe_3)_4$ and an excess of R_3B (4, R = ^iPr) after 16 h at 80 °C in toluene, monitored by (a) ^{119}Sn NMR and (b) ^{29}Si NMR; there is no starting material left; after 8 days at 80 °C, all intermediates are converted to the *spiro* compound. (a) 33.5 MHz ^{119}Sn NMR spectrum (^1H inverse gated decoupled for suppression of the nuclear Overhauser effect (NOE)). (b) 59.6 MHz ^{29}Si NMR spectrum (refocused insensitive nuclei enhanced by polarization transfer (INEPT) pulse sequence, ^1H decoupled); with the exception of the $^{29}Si({\equiv}C\text{-}SiMe_3)$ resonances, all other ^{29}Si NMR signals are well separated and can be readily assigned owing to the characteristic changes in their intensity as a function of the reaction time.

X-ray analyses, the solid state NMR data are an important link to discuss the structure of the corresponding compound in solution [26,27].

4. General remarks on 1,1-organoboration reactions

4.1. Reaction conditions of 1,1-organoboration reactions

Since the cleavage of the M—C≡ bond in the presence of R_3B is the first major step in 1,1-organoboration reactions, a markedly different reactivity is observed for M = Si to Pb. Owing to the polarity of the M—C≡ bond, the 1,1-organoboration proceeds most readily for M = Pb and rather sluggishly for M = Si, as shown in



$$\mathrm{Me_3M{-}C{\equiv}C{-}Me} + \underset{\mathbf{1}}{\mathrm{Et_3B}} \longrightarrow \mathrm{(Me_3M)(Me)C{=}C(BEt_2)(Et)} \qquad (8)$$

M	Reaction starts at °C	Solvent	% conversion after 0.5 h
Si	>+95	Et_3B	< 5
Ge	+25	hexane	50
Sn	-40	hexane	100
Pb	-90	hexane	100

Eq. (8) for the trimethyl-1-propynyl element derivatives. The reaction conditions shown in Eq. (8) imply that 1,1-organoboration of alkynylsilanes has to be carried out with boranes which do not undergo dehydroboration reactions [28]. Therefore, Me_3B (to be used in an autoclave) and Et_3B will be the boranes of choice. Clearly, in the case of M = Si, it is also essential that the products can stand the rather harsh reaction conditions. For M = Ge, 1,1-organoborations with Et_3B are complete after several hours at room temperature or after a short time (minutes) of heating to reflux in hexane. This enables the use of a wider range of triorganoboranes since dehydroboration reactions normally require temperatures above 90 °C. For M = Sn, the 1,1-organoboration reaction is strongly exothermic when carried out at room temperature. Care must be taken to control the reaction conditions and this is also true and crucial in the case of M = Pb.

4.2. Stereochemistry of 1,1-organoborations

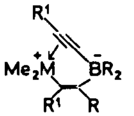
The stereochemistry of the 1,1-organoboration can be understood by inspection of the intermediate **C**. The L_nM fragment screens one side of the C≡C bond against a 1,2 shift of the group R from the boron to the alkynyl carbon atom. Therefore, the preferred product will be that with L_nM and the R_2B group in the *cis* position. There are very few exceptions:

(i) the group R^1 is itself an organometallic substituent (e.g. $R^1 = SiMe_3$, $GeMe_3$, $PbMe_3$, $B(NEt_2)_2$) which can take over the function of L_nM in **C**;

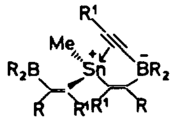
(ii) the steric requirement of the group R is low as in boracyclopentanes where the 1,1-organoboration takes place by ring extension, which usually leads to mixtures of E–Z-alkenes.

4.3. *1,1-organoboration of di-, tri- and tetra-1-alkynyl element compounds*

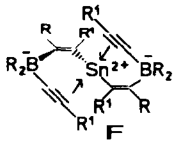
If there are two or more alkynyl groups linked to M (e.g. $Me_2M(C{\equiv}CR^1)_2$, $MeM(C{\equiv}CR^1)_3$ or $M(C{\equiv}CR^1)_4$) further intermolecular and intramolecular 1,1-organoborations may compete against each other, once the first intermolecular 1,1-organoboration has taken place. Since the intermolecular 1,1-organoboration is rather slow in the case of M = Si, Ge, further intramolecular 1,1-organoboration is dominant, even in the presence of a large excess of R_3B (e.g. Et_3B as solvent). In contrast, for M = Sn, Pb, further intermolecular 1,1-organoboration may readily occur and, in the absence of severe steric hindrance, it may even become the dominant process. This shows again that for M = Sn, Pb it is extremely important to adjust the experimental conditions with great care. Because of the mild reaction conditions for the 1,1-organoboration of alkynyltin and -lead compounds, it is possible to detect intermediates (see Section 9) corresponding to **C**. These are more stable if one starts with di-1-alkynyltin or -lead compounds (**D**) or with tri- (**E**) and tetra-1-alkynyltin compounds (**F**).



D



E

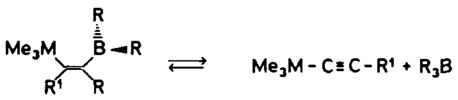


F

M = Sn, Pb; R = alkyl; R^1 = alkyl, aryl, etc.

4.4. *Reversibility of 1,1-organoboration reactions*

Frequently, 1,1-organoboration reactions are reversible. This can be explained by inspection of the preferred conformation **G** (Eq. (9)) looking at the arrangement of the R_2B group with respect to the C=C bond. For steric reasons, the C_2B plane of the R_2B group adopts an orthogonal position relative to the C=C—B plane. In this conformation σ—π interactions between the σ (=C—R) bond and the empty boron p_z orbital are conceivable. This causes weakening of the σ (=C—R) bond and appears to be a precondition for the process of deorganoboration (Eq. (9)). If R^1 is an organometallic substituent (e.g. $R^1 = Me_3Si$, Me_3Ge, Me_3Sn, Me_3Pb), the deorganoboration may occur already at room temperature or just above. This is important considering that the stereochemistry of the 1,1-organoboration is not well defined for this type of substituent (see Section 4.2). Any irreversible intramolecular process, following the intermolecular 1,1-organoboration, requires a certain stereochemistry (see the intermediates **D**, **E** and **F** and consider their precursors) and, therefore, reversibility of the intermolecular 1,1-organoboration is an important condition for shifting the equilibria finally in the desired direction.

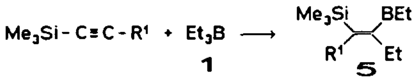


G

(9)

5. 1,1-organoboration of 1-alkynylsilanes

New alkene derivatives [29] and heterocyclic dienes [29–34] can be obtained by 1,1-organoboration of 1-alkynylsilanes using mainly triethylborane, Et_3B, or trimethylborane, Me_3B. In all cases it is necessary to use a large excess of the borane (it is recommended that the borane serves as the solvent) and to heat the mixtures for several days at least up to 100 °C. Under these conditions mono-1-alkynylsilanes are

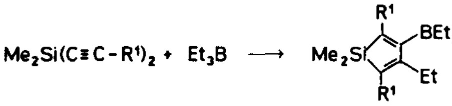


1 5

(10)

R^1 = alkyl, cycloalkyl, alkenyl, aryl

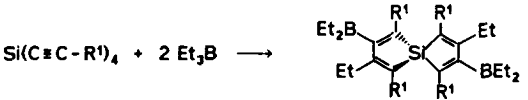
converted into the E-alkene derivatives **5** (Eq. (10)) in high yield (above 80%) [29]. Di-1-alkynylsilanes react with Et_3B (Eq. (11)) under the same conditions to give exclusively the silole derivatives **6** [31]. It was not possible to detect intermediates in which only one alkynyl group had reacted (the precursor of **D**). The harsh reaction conditions are responsible for a fast irreversible intramolecular 1,1-vinyloboration, once the intermolecular 1,1-ethyloboration has taken place.



R^1 = alkyl, aryl, $SiMe_3$ 6

(11)

Most tetra-1-alkynylsilanes react with Et_3B via fourfold 1,1-organoboration to

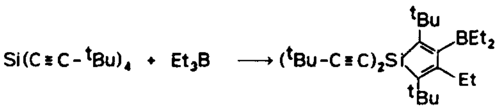


R^1 = alkyl, aryl, $SiMe_3$ 7

(12)

give the *spiro* compounds **7** as the final products (Eq. (12)) [32]. For some groups R^1 (e.g. R^1 = Ph, $SiMe_3$), the siloles of type **6** are observed as intermediates [32]. In the case of R^1 = ${}^tBu$, the reaction ends, even in the presence of a large excess of Et_3B, after twofold 1,1-organoboration at the stage of the silole **6** (Eq. (13)) [34].

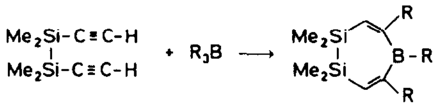
Of a large number of readily accessible alkynyldisilane derivatives only



6

(13)

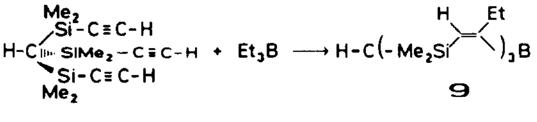
1,2-diethynyltetramethyldisilane has been studied so far with respect to 1,1-organoboration [30]. As shown in Eq. (14), this reaction leads straightforwardly to the 1,2,5-disilaborepines **8**. In this case the twofold (inter- and intramolecular) 1,1-alkyloboration takes place (in contrast to the formation of the siloles **6** [31] and the *spiro* compounds **7** [32], the second step of the reaction is not a 1,1-vinyloboration).



R = Me, Et **8**

(14)

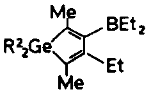
A macrobicyclic compound **9** becomes available via the threefold (intermolecular and twofold intramolecular) 1,1-ethyloboration of tris[ethynyl(dimethyl)silyl]methane according to Eq. (15) [35]. Monitoring of the reaction by ^{29}Si NMR indicates that the reaction mixture contains starting material and compound **9** but no potential intermediates. This proves again that in the case of alkynylsilanes the intramolecular 1,1-organoboration proceeds rapidly as compared with intermolecular 1,1-organoboration.



(15)

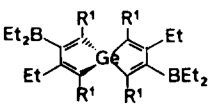
6. 1,1-organoboration of alkynylgermanium compounds

The 1,1-organoboration of alkynylgermanium compounds has not been studied extensively. However, the reactions proceed faster than in the case of alkynylsilanes and the same types of products can be prepared. This is shown in Eq. (8) for alkene derivatives [36]. Germoles (**10**) are obtained from the twofold 1,1-organoboration of di-1-propynylgermanium compounds, $Me_2Ge(C{\equiv}CMe)_2$ or $^nBu_2Ge(C{\equiv}CMe)_2$ [36a], and the *spiro* compounds (**11**) [32] corresponding to **7** are also readily accessible.



10

R^2 = Me, ^{n}Bu



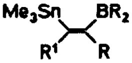
11

R^1 = Me, Ph

7. 1,1-organoboration of alkynyltin compounds

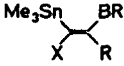
7.1. Mono-1-alkynyltin compounds

Mono-1-alkynyltin compounds react with one equivalent of a triorganoborane R_3B (R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu, ^{s}Bu, cycloalkyl, Ph) under mild reaction conditions (−78 °C to room temperature) by 1,1-organoboration of the C≡C bond to give a wide variety of alkene derivatives such as **12–14** stereoselectively and in quantitative yield. There may be a functional group X linked directly to the C=C bond (**13**), or the functional group is part of Y (**14**). For simplicity only formulae with Me_3Sn groups are shown; however, the 1,1-organoboration proceeds in the same way for Et_3Sn, Bu_3Sn or Ph_3Sn groups, to name just three prominent examples.



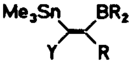
12

R^1 = H, alkyl, aryl, alkenyl, alkynyl



13

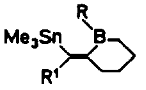
X = Cl, OEt, N(Me)Ph, PPh_2



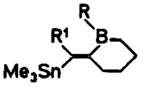
14

Y = CH_2Cl, CH_2OMe, $C(Me)HOSnMe_3$, CMe_2OSnMe_3, CH_2SEt, CH_2NH_2, CH_2NMe_2

For cyclic triorganoboranes, e.g. **3** or **4**, the question arises of which B—C bond is used to form the new C—C= bond. It appears that ring enlargement (**15** [37], **16** [38–40]) is the kinetically controlled process and, at least in the case of some derivatives of **4**, it is also possible to convert the product of kinetic control into the thermodynamically controlled reaction product (**17**) in which the 9-borabicyclo[3.3.1]nonane system is retained [39].



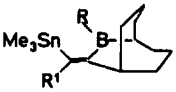
15



(Z)-15

R^1 = H, Me, $SnMe_3$

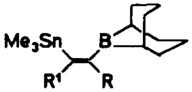
R = Me, Et, thexyl, Ph, 2-thienyl



16

R^1 = H, alkyl

R = alkyl, Ph

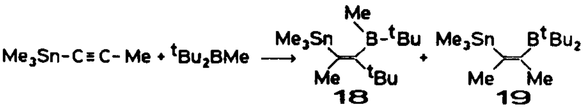


17

R^1 = Me

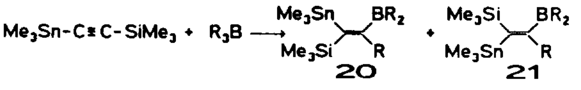
R = Me, Et

If non-cyclic triorganoboranes with different groups R and R′ (e.g. in R_2BR') are used in 1,1-organoborations, mixtures are obtained in which either R or R′ is transferred from boron to the neighbouring olefinic carbon atom. Since the product distribution is not statistical, kinetic effects may again be important: the reaction between $^{t}Bu_2BMe$ and trimethyl-1-propynyltin (Eq. (16)) affords the alkenes **18** and **19** in a 1:1 ratio [37]; this suggests that the transfer of the methyl group is faster than that of the *tert*-butyl group. The analogous reaction with dialkylborylferrocenes, $R_2B{-}Fc$ (R = Me, Et, ^iPr, ^tBu) affords alkenes preferably with new Fc—C= bonds (70%, if R = Me) or R—C= bonds (70%, if R = ^tBu) [41].



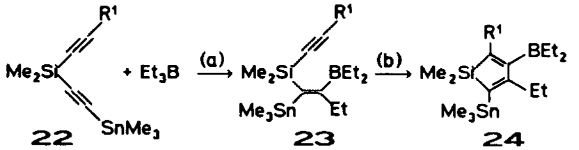
(16)

A different stereochemistry of the products from 1,1-organoboration reactions (with stannyl and boryl groups in mutual *trans* position) results if the group R in **3** is not sterically demanding (e.g. *Z*-**15**). With a bulky group R, e.g. R = CMe_2CMe_2H (thexyl), the *E* isomer **15** is obtained exclusively. The stereochemistry is not defined if R^1 is another organometallic group such as $R^1 = SiMe_3$, $GeMe_3$, $PbMe_3$ or $B(NEt_2)_2$ etc. In these cases, mixtures of alkenes are obtained (Eq. (17)), which, however, readily undergo deorganoboration (see Section 4.4). In the case of $R^1 = SiMe_3$, the mixture contains approximately 5% of **20** and 95% of **21** [42].



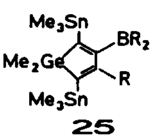
(17)

Since siloles are rather attractive metalloles [43], but di-1-alkynylsilanes are fairly unreactive towards R_3B (see Sections 4.1 and 5), compounds of type **22** were prepared in which the Me_3Sn-substituted alkynyl group reacts already below room temperature with R_3B (Eq. (18), path a). Once the boryl group has entered the molecule (**23**), the following intramolecular 1,1-vinyloboration (Eq. (18), path b) also proceeds under mild reaction conditions to give the organometallic-substituted siloles **24** [33]. Other metalloles can be prepared, following the route shown in Eq. (18) for $R^1 = SnMe_3$. Thus, germoles (**25**) [44] and a borole (**26**) [45] were isolated. Similarly, a 1,2,5-disilaborepine derivative (**27**) (analogous to **8**) is readily accessible [46].

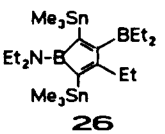


R¹ = alkyl, Ph, SnMe₃

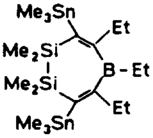
(18)



25
R = Me, Et

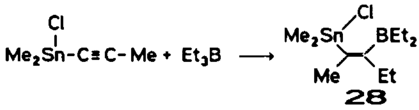


26

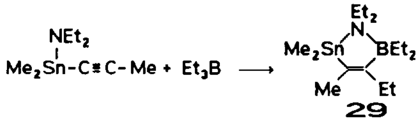


27

The synthetic potential of the new alkene derivatives can be further increased if a functional substituent at the tin atom is present instead of one of the organyl groups. This is shown in Eqs. (19) and (20) by the 1,1-organoboration of alkynyl(chloro)dimethyltin [47] and alkynyl(dialkylamino)dimethyltin respectively. The products **28** [47] and **29** [48] are versatile starting materials for further synthetic transformations [49–53].

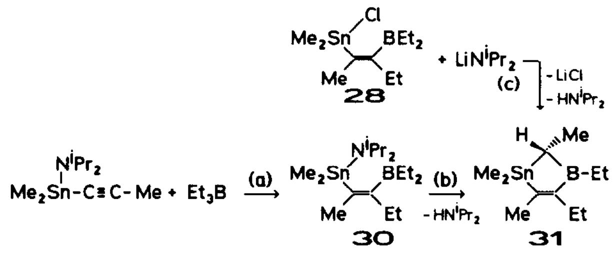


(19)



(20)

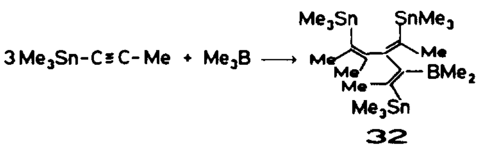
If the more bulky diisopropylamino group is used, the coordinative N—B bond is weak for steric reasons. However, compound **30** (Eq. (21), path a) cannot be isolated: the Sn—diisopropylamino group appears to be a very strong base and is able to abstract a proton from one of the B—CH_2 moieties. Diisopropylamine is eliminated, and a new Sn—C bond is formed to give the heterocyclic compound **31** (Eq. (21), path b). Alternatively, one can start with **28** and treat it with LiN^iPr_2 according to Eq. (20), path c. Numerous heterocycles analogous to **31** have been prepared by these routes [54,55].



(21)

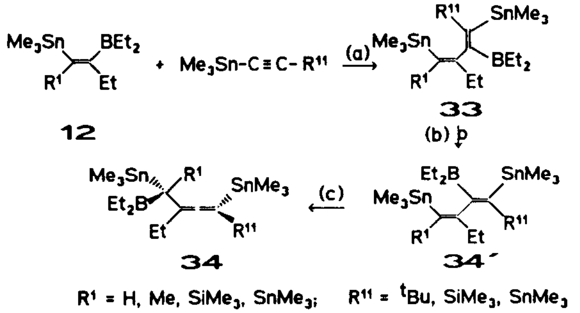
Compounds such as **12** are triorganoboranes of the type R_2BR' and therefore may also be active in 1,1-organoboration reactions (they may even compete with R_3B for the reaction with alkynyltin compounds). This aspect becomes particularly important if an excess of the alkynyltin compound is present. Thus, it was shown that Me_3B reacts with an excess of trimethyl-1-propynyltin (Eq. (22)) to give a mixture in which compound **32** was identified as a major product [56]. 1,1-Organoboration has taken place three times (starting with 1,1-methyloboration, followed by two 1,1-vinyloborations) with >98% (according to ^{1}H-, ^{13}C- and ^{119}Sn NMR) stereoselectivity.

The formation of the butadienes of type **33** (Eq. (23), path a) may be followed by rearrangement into allene derivatives (Eq. (23), path c). This rearrangement always takes place if a bulky group R^{11} is present in the alkynyltin compound



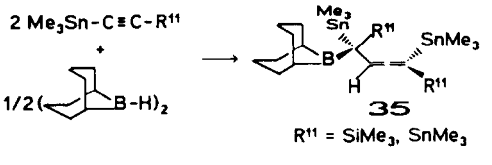
(22)

$Me_3Sn-C{\equiv}C-R^{11}$ which reacts with **12**. Because of the steric requirements of R^{11}, the *cis*-conformation of the butadienes **33** is unfavorable. Before the *trans* conformation **34'** is reached, the electron-deficient boron atom comes close to the electron-rich olefinic carbon atom bearing an Me_3Sn group and R^1. It is conceivable that this proximity of the two reactive centres is responsible for the rearrangement of **33** via **34'** to the allene system **34**. This is an efficient route to organometallic-substituted allenes [57–60].



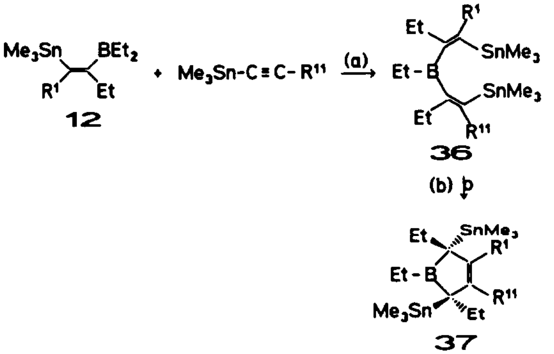
(23)

Interestingly, the reaction between dimeric 9-borabicyclo[3.3.1]nonane (a widely used 1,2-hydroborating agent) and the alkynyltin compounds $Me_3Sn-C{\equiv}C-R^{11}$ ($R^{11}=SiMe_3$, $SnMe_3$) does not proceed via the well-known 1,2-hydroboration, as with other alkynes, but via 1,1-hydroboration, followed by fast intermolecular 1,1-vinyloboration with a second equivalent of $Me_3Sn-C{\equiv}C-R^{11}$ and the rearrangement of the same type as shown in Eq. (23). The allene derivatives **35** (Eq. (24)) are formed quantitatively [59,60]. Their molecular structure is evident from extensive multinuclear NMR data [59,60] and also from the result of a single crystal X-ray analysis ($R^{11}=SnMe_3$) [61].



(24)

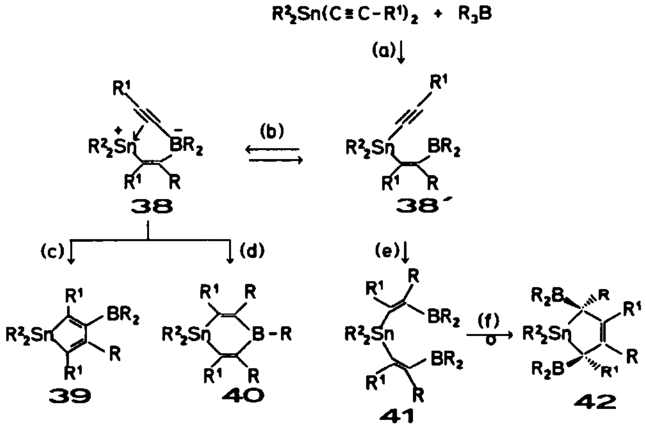
What happens if R^{11} in $Me_3Sn-C{\equiv}C-R^{11}$ is not a bulky group? Apparently the butadienes **33** are not particularly stable and their formation appears to be reversible via deorganoboration. An alternative to the 1,1-vinyloboration leading to **33** is 1,1-alkyloboration which would afford heteropentadiene derivatives of the type **36**. Again these compounds are unstable, this time with respect to an irreversible rearrangement to the 3-borolenes **37** (Eq. (25)) [62]. These 3-borolenes are fluxional compounds since the two Me_3Sn groups migrate by 2,4 or 5,3 shifts. At low temperature the 3-borolene is the preferred isomer if $R^1 = R^{11} = Me$ [62], whereas for $R^1 = R^{11} = H$ the structure of a 2-borolene is preferred [36a].



(25)

7.2. Di-1-alkynyltin compounds

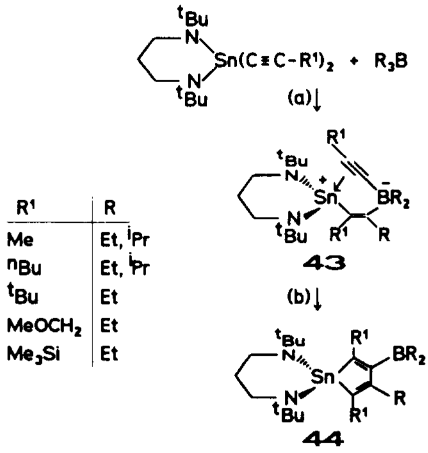
In principle, the 1,1-organoboration of di-1-alkynyltin compounds is similar to that of mono-1-alkynyltin compounds, at least as far as the first step is concerned (Eq. (26), path a), including all arguments regarding stereoselectivity and reversibility of the reaction. The second alkynyl group linked to tin opens the possibility for further intramolecular (Eq. (26), paths c and d) or, in the presence of an excess of R_3B, intermolecular 1,1-organoboration (Eq. (26), path e). The intramolecular reaction starts from the zwitterionic intermediate **38** [63] which is in equilibrium with **38′** (Eq. (26), path b). Intramolecular 1,1-vinyloboration affords the stannoles **39** (Eq. (26), path c), whereas intramolecular alkyloboration (R = alkyl) leads to the 1,4-stannabora-2,5-cyclohexadienes **40** (Eq. (26), path d).



(26)

The groups $R^2 = Me$, Et [64], ${}^iPr$, ${}^nBu$, ${}^tBu$ [36] have the expected effect on the reaction rate constants, but they exert little influence on the product distribution.

The stannoles **39** are formed selectively and quantitatively with $R^1=H$, $R=Et$, ${}^nPr$, ${}^iPr$, ${}^nBu$, ${}^iBu$ [36,64] and $R^1={}^tBu$ [65], PPh_2 [36b], $SiMe_3$ [65] and $R=Et$. The six-membered rings **40** result selectively and quantitatively with $R^1=Me$ and $R={}^iPr$ [66], ${}^iBu$, cpent [36]. Other combinations may lead to mixtures of **39** and **40** and also, depending on the reaction conditions, with products **41** and **42** [63,67]. Functional groups may be present in R^1 (e.g. $R^1=CH_2OMe$, $CH{=}CHOMe$, CH_2SEt, CH_2NMe_2, 2-pyridyl). In the case of $R^1=CH{=}CHOMe$, 2-pyridyl and $R=Et$, the 1,1-organoboration gives the corresponding stannoles only, whereas mixtures are obtained for other derivatives [68]. There appears to be a delicate balance between electronic and steric effects exerted by the substituents R and R^1 which may be related to the bonding in the zwitterionic intermediate **38**. It was found [69] that stannole formation (**44**) via the intermediate **43** is always favoured, independent of R^1, if the organic groups R^2 are replaced by a cyclic diamino group (Eq. (27)). Furthermore, kinetic effects play an important role, as is evident from the fact that stannoles **39** are always formed with $R^1=H$ and that it has not been possible to detect the corresponding intermediate **38** with $R^1=H$.

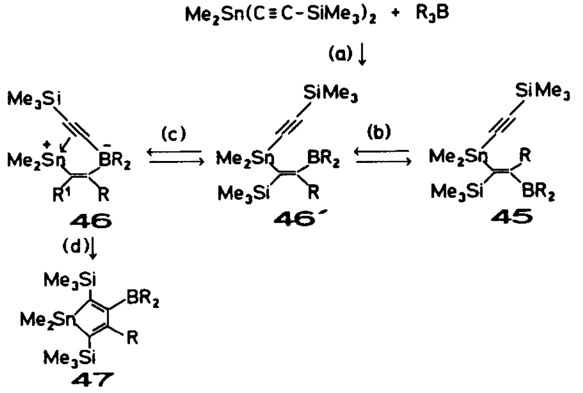


(27)

R^1	R
Me	Et, ${}^iPr$
${}^nBu$	Et, ${}^iPr$
${}^tBu$	Et
$MeOCH_2$	Et
Me_3Si	Et

If the steric requirements of R^1 and R are fairly small, the reaction rate for intramolecular 1,1-organoboration is not too fast (e.g. $R^1=Me$, $R=Me$, Et) and, if an excess of R_3B is present, the intermolecular 1,1-organoboration (Eq. (26), path d) becomes the dominant reaction pathway. This leads first to the bis(alkenyl)tin compounds **41** which finally (from −10 °C to room temperature) undergo a complex stereoselective rearrangement (note the substituent pattern of R and R^1) into the 2,5-diborylated 3-stannolenes [66,67,70]. Under these reaction conditions, there is apparently no direct route from **41** to the 1,4-stannabora-2,5-cyclohexadiene **40**. Instead, elimination of R_3B (deorganoboration) leads back to **38**′ and over **38** to either **39** or **40**.

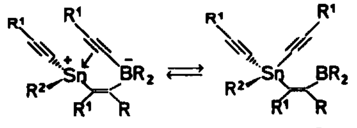
In the case of $R^1=SiMe_3$, the final product is exclusively the stannole system **47** [65,71], although the stereochemistry of the 1,1-organoboration is undefined (see Sections 4.2 and 7.1, compounds **20** and **21**). Thus, the presence of intermediates **45** with the "wrong" stereochemistry for stannole formation was proved by NMR data [71]. Since the intermolecular 1,1-organoboration is reversible (Eq. (28), path a), the equilibrium is shifted to the stannole by the irreversible intramolecular 1,1-vinyloboration (Eq. (28), path d) which takes place in the isomer with the "correct" stereochemistry (Eq. (28), path b and c) [71]. The intermediate **46** is extremely short lived as compared with that with R^1 = alkyl instead of $SiMe_3$. It could not be detected in this reaction but it was observed in the analogous 1,1-organoboration of $Me_2Pb(C{\equiv}CSiMe_3)_2$ [72] (see Section 8).



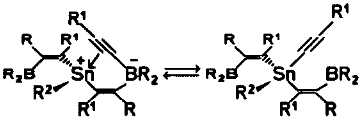
(28)

7.3. *Tri-1-alkynyltin compounds*

1,1-organoboration takes place readily with tri-1-alkynyltin compounds ($R^2Sn(C{\equiv}C{-}R^1)_3$; R^2 = Me, Et, ^nBu; R^1 = alkyl, $SiMe_3$) and has been studied with Et_3B and $^iPr_3B$ [73]. The system becomes more complex as compared with the di-1-alkynyltin compounds because of the greater number of potential reactive intermediates. Following the first intermolecular alkyloboration, the equilibrium between **48** and **48'** has to be considered. Further intramolecular alkyloboration leads to another zwitterionic intermediate **49** which is in equilibrium with **49'**. The existence of these intermediates and of the equilibria was shown by ^{13}C NMR at low temperature [73].

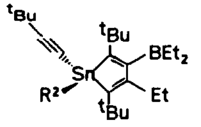


48 **48'**



49 **49'**

Starting from the compounds **48**, **48′** and **49**, **49′**, intramolecular 1,1-vinyloboration affords stannoles (**50**, **51**), whereas intramolecular alkyloboration leads to the 1,4-stannabora-2,5-cyclohexadienes (**52**, **53**). In the case of $R^1 = Me$ and $R = Et$, in the presence of a large excess of Et_3B, intermolecular 1,1-ethyloboration of the last C≡CMe group in **49′** generates the tris(alkenyl)tin compound **54** which rearranges into the 3-stannolene **55**. Only one of the possible diastereomers of **55** is formed; it has been assumed that this is the diastereomer with less steric interactions between the Et_2B groups and the alkenyl group. Attempts at the distillation of **55** cause deorganoboration and **56** is isolated, again as a single diastereomer [73].



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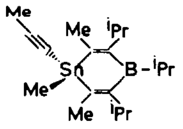

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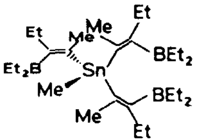

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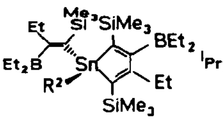

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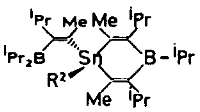

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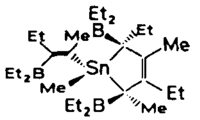

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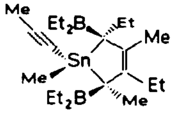

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7.4. Tetra-1-alkynyltin compounds

1,1-organoboration reactions of tetra-1-alkynyltin compounds, $Sn(C{\equiv}CR^1)_4$ ($R^1 = $ alkyl, Ph, $SiMe_3$), have been studied for various trialkylboranes [74–77] including 9-borabicyclo[3.3.1]nonane derivatives [77]. The intermolecular 1,1-alkyloboration leads first to the zwitterionic compounds **57** (Eq. (29), path a) and, after a second intermolecular 1,1-alkyloboration, to **58** (Eq. (29), path b). The dynamic equilibria between **57** and **57′** (Fig. 2) or **58** and **58′** were examined by temperature-dependent NMR studies [74,76]. In the case of **58** ($R^1 = Me$, $R = Et$), the molecular structure was determined by single-crystal X-ray analysis [74].

The main products from the 1,1-organoboration reactions of tetra-1-alkynyltin compounds are the *spiro* compounds **59** to **61**. The compounds **59** are formed selectively with $R^1 = Et$, ᵗBu, $SiMe_3$ and $R = Et$ [76,77]. The molecular structure of the *spiro* compound obtained by organoboration of $Sn(C{\equiv}CSiMe_3)_4$ with 9-$(CH_3)_3CCH_2$-9-borabicyclo[3.3.1]nonane has been determined [77] (Fig. 3), exhibiting a strongly distorted tetrahedral environment for the tin atom with small endocyclic bond angles (C(1)SnC(4), 84.2(2)°; C(5)SnC(8), 84.9(2)°). Mixtures of *spiro* compounds **59**, **60** and **61** are obtained with $R^1 = $ alkyl other than methyl and

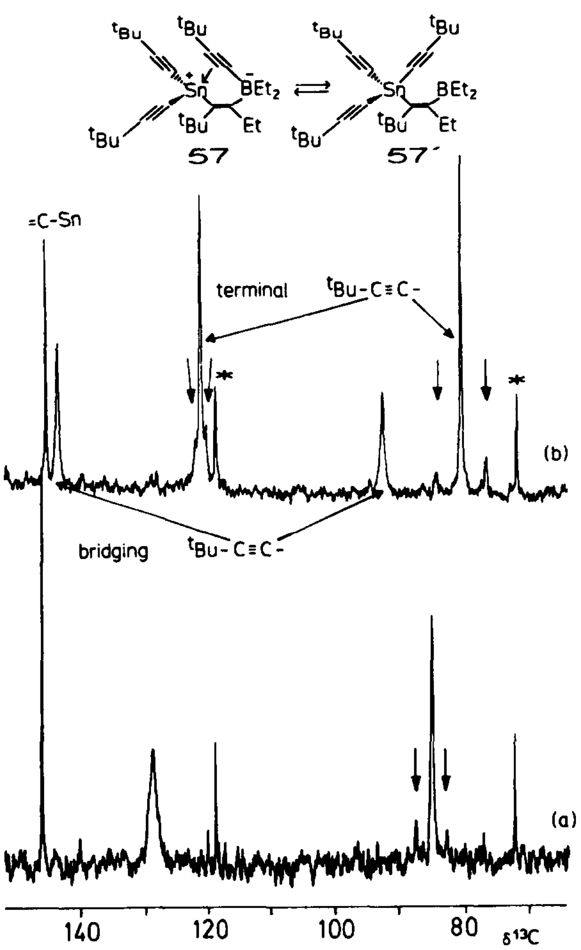


Fig. 2. 75.5 MHz $^{13}C(^1H)$ NMR spectra at various temperatures in CD_2Cl_2, demonstrating the dynamic behaviour of the zwitterionic intermediate **57** ($R^1 = {}^tBu$, $R = Et$); $^{117/119}Sn$ satellites are marked by arrows; the $^{13}C(C{\equiv}C)$ resonances belonging to a small amount of the starting material $Sn(C{\equiv}C^tBu)_4$ are marked by asterisks. (a) At −30 °C; there is rapid exchange between terminal and bridging alkynyl groups. (b) At −75 °C; the ^{13}C NMR signals for the alkynyl groups are now split in those for terminal and bridging groups as indicated.

$R = {}^iPr$. The formation of **61** is selective and quantitative for $R^1 = Me$ and $R = {}^iPr$ [75]. Similar to the 1,1-organoboration of di-1-alkynyltin compounds with $R^1 \neq H$, $SiMe_3$, six-membered rings are favoured if $^iPr_3B$ is used instead of Et_3B.

8. 1,1-organoboration of 1-alkynyllead compounds

1,1-organoboration of 1-alkynyllead compounds takes place under very mild reaction conditions (many of the reactions shown in Eq. (30), path a, are complete at

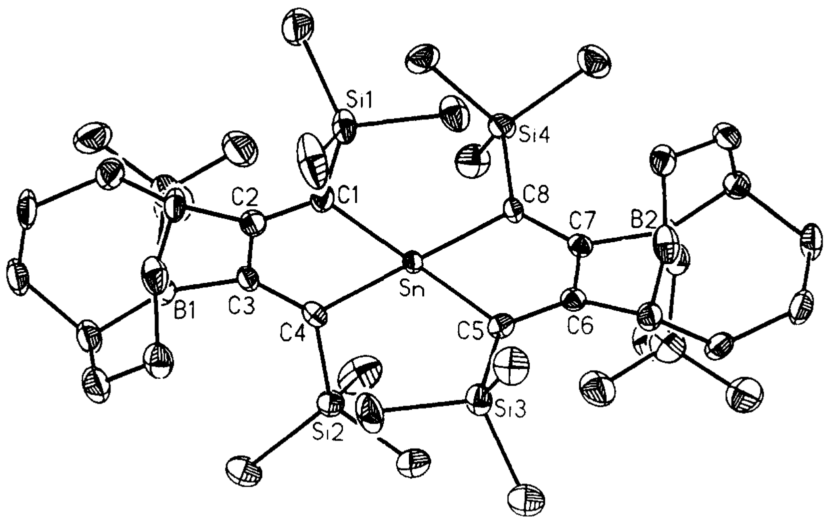
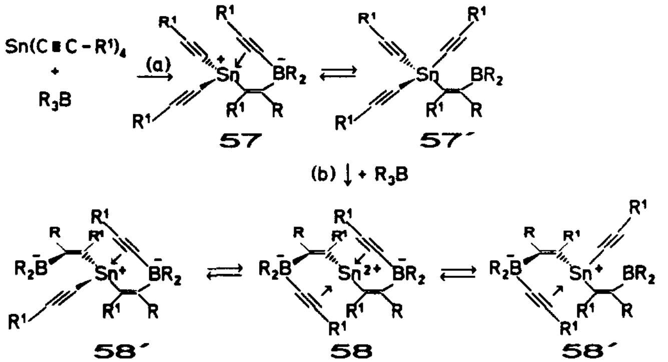


Fig. 3. Molecular structure of a *spiro*-tin compound obtained from the 1,1-organoboration reaction between two equivalents of 9-neopentyl-9-borabicyclo[3.3.1]nonane and one equivalent of $Sn(C{\equiv}CSiMe_3)_4$ [77]. Both bicyclic 9-BBN systems are extended by a C_2 unit, and the surroundings of the tin atom correspond to an extremely distorted tetrahedron. Selected bond lengths (picometres) and bond angles (degrees) are as follows: Sn—C(1), 215.0(4); Sn—C(4), 216.5(4); C(1)—C(2), 133.4(6); C(2)—C(3), 153.0(6); C(3)—C(4), 135.1(6); B(1)—C(3), 159.7(7); C(1)SnC(4), 84.2; C(5)SnC(8), 84.9(2).



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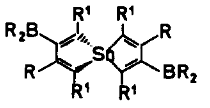
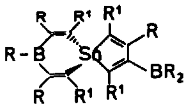


59

R¹ = alkyl

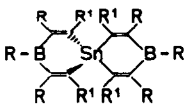
R = Et, ⁱPr



60

R¹ = alkyl

R = ⁱPr

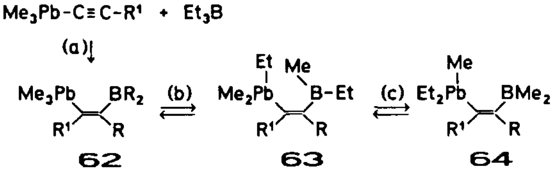


61

R¹ = Me

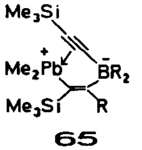
R = ⁱPr

−78 °C [78,79], and the products are thermally much less stable than the corresponding tin compounds. Even those triorganoboranes which did not react at all with 1-alkynyltin compounds because of steric hindrance can be used for 1,1-organoboration of 1-alkynyllead compounds. Examples for such boranes are $(Me_3SiCH_2)_3B$ [79] or triferrocenylborane (Fc = ferrocenyl) [80]. In many cases, the 1,1-organoboration products decompose at room temperature after some hours (in more favourable cases after some days) to give elemental lead, Me_4Pb and numerous other unidentified products. Interestingly, this decomposition is accompanied by exchange of Pb—alkyl and B—alkyl groups (**63**, **64**), and it is frequently observed (Eq. (30), paths b and c) if the alkene derivatives **62** are kept in solution at room temperature. This exchange takes place readily because of the preferred orthogonal position of the R_2B group with respect to the C=C—B plane (see Section 4.4 [80]) and because of the labile and polarized Pb—alkyl bond. Rather fast Me—Et exchange (after minutes at room temperature) is observed if the substituents R^1 are bulky (e.g. $R^1 = {}^tBu$). This type of exchange reaction takes place also in corresponding alkenyltin compounds, but only in the presence of special substuents R^1 which, by intramolecular N—Sn or O—Sn coordination (e.g. R^1 = 2-pyridyl or CH_2OSnMe_3 [81]), help to increase the polar character of the Sn—alkyl bond.

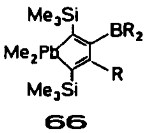


(30)

In principle, all products obtained from 1,1-organoboration reactions of mono- and di-1-alkynyltin compounds can also be observed using the corresponding 1-alkynyllead compounds. This also applies to the zwitterionic intermediates. Since the reaction conditions are extremely mild, it is also possible to observe intermediates which are not stable (see Section 7.2) under the conditions required for the organoboration of 1-alkynyltin compounds. An example is the intermediate **65** which is an immediate precursor of the plumboles **66**. In this reaction mixture, one can also identify the bis(alkenyl)lead derivative **67** in which 1,1-organoboration has taken place twice with the "wrong" (for plumbole formation) stereochemistry. However, finally all of these intermediates are converted to the plumbole [72], demonstrating again that the intermolecular 1,1-organoboration reactions are readily reversible.



65



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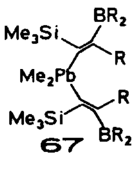
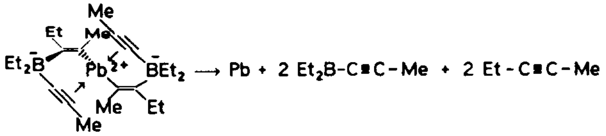


67

Tetra-1-alkynyllead compounds, $Pb(C{\equiv}CR^1)_4$, react readily with Et_3B, even at −78 °C [82]. However, it appears that already the first intermediates are too unstable for isolation and characterization. Thus, for R^1 = Me, one obtains quantitatively lead, $Et_2B{-}C{\equiv}CMe$ and $MeC{\equiv}CEt$ (Eq. (31)). Considering the structure of the potential intermediate **68** (see **58**), lead and the two alkynes are exactly the fragments to be expected for a "controlled", well-behaved decomposition of **68**.

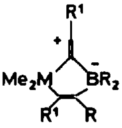


68

(31)

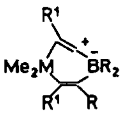
9. Zwitterionic intermediates: stabilized organotin- and organolead cations

The first experimental evidence for zwitterionic intermediates of the type **C**, **D**, **E** or **F** (see Section 1) was found by measuring ^{11}B NMR spectra of reaction solutions in order to monitor the 1,1-organoboration of $Me_2Sn(C{\equiv}C^tBu)_2$ [65]. An ^{11}B NMR signal at rather high field, typical of tetracoordinate boron atoms, suggested, in the absence of any other donor, the formation of an alkynylborate moiety together with the triorganotin fragment as the "counterion". This situation is shown in structure **D** and in **38** where the triorganoelement fragment with a positive charge coordinates to the $C{\equiv}C$ bond of the alkynylborate group. Until 1989 [78], there were no examples described in the literature where an alkynyl group was found to bridge a boron and a tin or a lead atom. Although the structures **C** to **F** can be understood as π complexes, there are alternative models such as β-metal-stabilized (hyperconjugation [83,84]) vinyl cations **H** and **I**, or bridged structures **J** and **K** in which the bonding can be described more generally by σ−π delocalization [83].

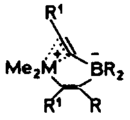


H

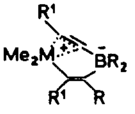
M = Sn, Pb



I



J



K

9.1. Zwitterionic intermediates with stabilized organolead cations

The search for firm structural evidence lasted then until 1989 when it proved possible to isolate a crystalline material from the 1,1-organoboration of dimethyldi-1-propynyllead [78]. X-ray analysis (Fig. 4) confirmed the proposed structure of intermediates of type **D**. The sum of bond angles at the lead atom, not counting the coordinative interaction with the $C{\equiv}C$ bond, is close to 360° (355.7(8)°), in accord with a trigonal planar surrounding of the lead atom expected for a "free" triorganolead cation. The slight pyramidal distortion shifts the lead atom towards the $C{\equiv}C$ bond. The coordination of the $C{\equiv}C$ bond is unsymmetrical with a shorter

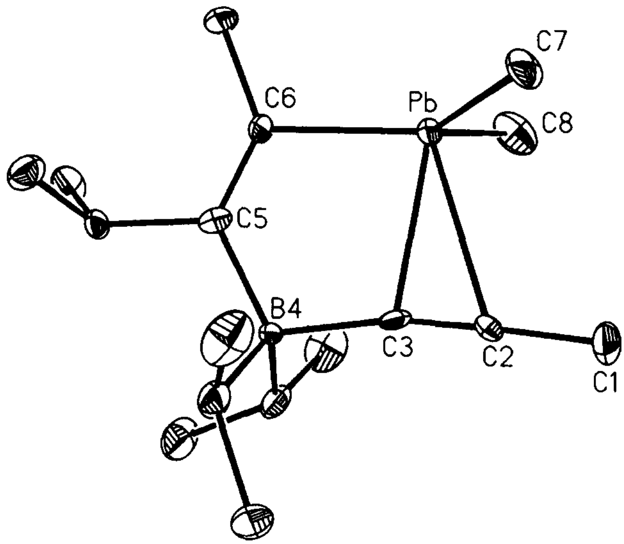


Fig. 4. Molecular structure of the zwitterionic intermediate obtained from the 1,1-organoboration reaction between $^{i}Pr_3B$ and $Me_2Pb(C{\equiv}CMe)_2$ [78]. Selected bond lengths (picometres) and bond angles (degrees) are as follows: Pb—C(2), 264.8(8); Pb—C(3), 246.7(6); Pb—C(6), 220.3(6); Pb—C(7), 222.2(7); Pb—C(8), 220.2(7); B—C(3), 164.0; B—C(5), 164.8(8); C(5)—C(6), 133.4(9); C(2)—C(3), 121.0(10); BC(3)C(2), 169.5(6); C(1)C(2)C(3), 177.3(7).

distance d[Pb—C(3)] = 246.7(6) pm for the boron-bonded alkynyl carbon atom [d[Pb—C(2)] = 264.8(8) pm]. The bond length d(C≡C) = 121.0(10) pm is hardly affected by the coordination and the bond angles B—C≡C [169.5(6)°] and C≡C—C [177.3(7)°] deviate little from 180°. This is typical for a weak coordinative interaction as is usually found if alkynyl groups function as a bridge between electron-deficient centres involving main group elements (e.g. in $[R_2Al{-}C{\equiv}C{-}R^1]_2$ [85], $R_2Ga{-}C{\equiv}C{-}R^1$ [86,87] or $R_2In{-}C{\equiv}C{-}R^1$ [87,88]). This differs considerably from structural features of bridging alkynyl groups in transition metal complexes [89–91]. The distance d(B—C≡) = 164.0(10) pm is rather long considering that the alkynyl carbon atom is sp hybridized (other d(B—C) values are 164.8(8), 165.2(9) and 165.6(9) pm). This, together with the $\delta(^{11}B)$ value ($\delta(^{11}B) = -2.6$), which differs by several parts per million from the range of $\delta(^{11}B)$ values for alkali metal alkynyltriorganoborates ($\delta(^{11}B) \approx -14$ to -20 [22]), indicates that there is a noticeable bonding interaction with the lead atom. The comparison of solid state ^{13}C and ^{207}Pb CP—MAS NMR data [92] with those for solutions ensures that the main features of the molecular structure in the solid are retained in solution. Coupling constants $J(^{207}Pb^{13}C)$ and $J(^{207}Pb^{1}H)$ are observed in solution for the bridging 1-propynyl group which could not be of comparable magnitude without a coordinative bond between the lead atom and the C≡C bond. The ^{207}Pb nuclear shielding is markedly reduced ($\delta(^{207}Pb) = +667.2$) when compared with the range of $\delta(^{207}Pb) \approx +300$ to -400 [25], valid for the majority of organolead compounds.

9.2. Zwitterionic intermediates with stabilized organotin cations

Unequivocal evidence for the existence of zwitterionic intermediates, obtained by the 1,1-organoboration of di-1-alkynyldimethyltin, was provided both by multinuclear NMR in solution and by a single-crystal X-ray analysis of **38** ($R = Et$, $R^1 = {}^iPr$, $R^2 = Me$) (Fig. 5) [63]. The molecular structure is analogous to that of the lead derivative (see Section 9.1), and the same is true for the relevant NMR parameters, including the $\delta(^{119}Sn)$ values. The distance $d(B{-}C{\equiv}) = 165.1(6)$ pm is markedly longer (see Section 9.1) than any other C—B bond length in **38**. The strong temperature dependence observed for many of the $\delta(^{119}Sn)$ values for compounds of type **38** indicates a dynamic process in which the alkynyl group is shifted backward and forward between the boron and the tin atom (**38**, **38′**; Eq. (26), path b).

It is expected that the nature of the coordination of the tin atom to the C≡C bond changes if another donor is present. Thus, if a donor function (e.g. an NMe_2 or an OMe group) can be included in R^1, the zwitterionic intermediates analogous to **38** should be more stable and the bonding situation may be rather different if a coordinative N—Sn or O—Sn bond is formed. This was indeed proved for numerous examples by multinuclear NMR and three of these intermediates were studied by single-crystal X-ray analyses [68] (Figs. 6–8). The surroundings of the tin atoms correspond now to a distorted trigonal bipyramid with the three organo groups in

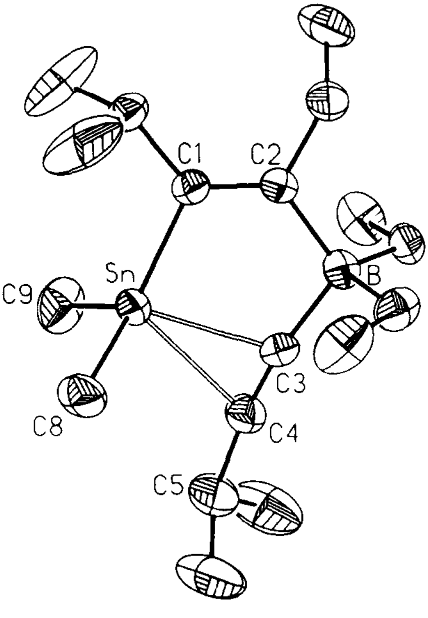


Fig. 5. Molecular structure of the zwitterionic intermediate **38** obtained from the 1,1-organoboration reaction between Et_3B and $Me_2Sn(C{\equiv}C^iPr)_2$ [63]. Selected bond lengths (picometres) and bond angles (degrees) are as follows: Sn—C(3), 233.9(4); Sn—C(4), 252.3(5); Sn—C(1), 211.6(4); Sn—C(8), 212.8(5); Sn—C(9), 213.6(5); B—C(3), 165.1(6); B—C(2), 161.6(6); C(1)—C(2), 133.4(6); C(3)—C(4), 121.3; BC(3)C(4), 170.1; C(3)C(4)C(5), 174.0.

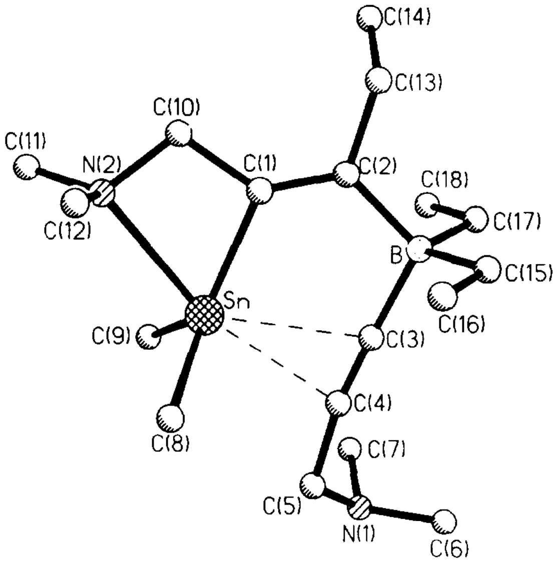


Fig. 6. Molecular structure of the zwitterionic intermediate obtained from the 1,1-organoboration reaction between Et_3B and $Me_2Sn(C{\equiv}C{-}CH_2NMe_2)_2$ [68]. Selected bond lengths (picometres) and bond angles (degrees) are as follows: Sn—C(3), 262.6(6); Sn—C(4), 260.4(5); Sn—C(1), 210.4(5); Sn—C(8), 214.2(8); Sn—C(9), 213.4(7); Sn—N(2), 252.1(4); B—C(3), 162.7; B—C(2), 162.9(8); C(1)—C(2), 134.2(8); C(3)—C(4), 122.0(7); BC(3)C(4), 177.8; C(3)C(4)C(5), 171.0.

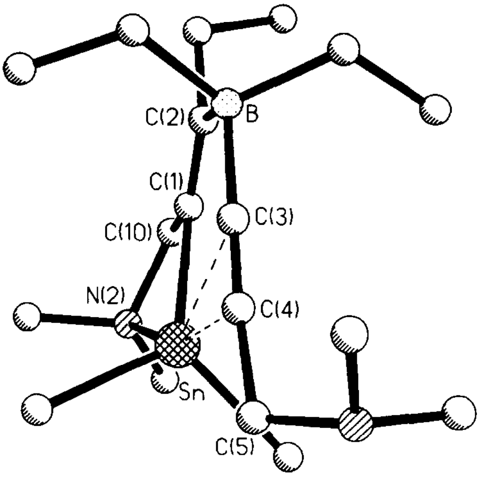


Fig. 7. Side view of the molecular structure shown in Fig. 6. The positions of the atoms B, C(2), C(1), Sn, N(2), C(3), C(4) differ very little from a common plane.

the equatorial plane, the C≡C bond in one of the axial positions and the nitrogen or oxygen atom in the other axial position. When the NMe_2 group is the donor, the tin atom is shifted out of the equatorial plane towards the nitrogen atom whereas,

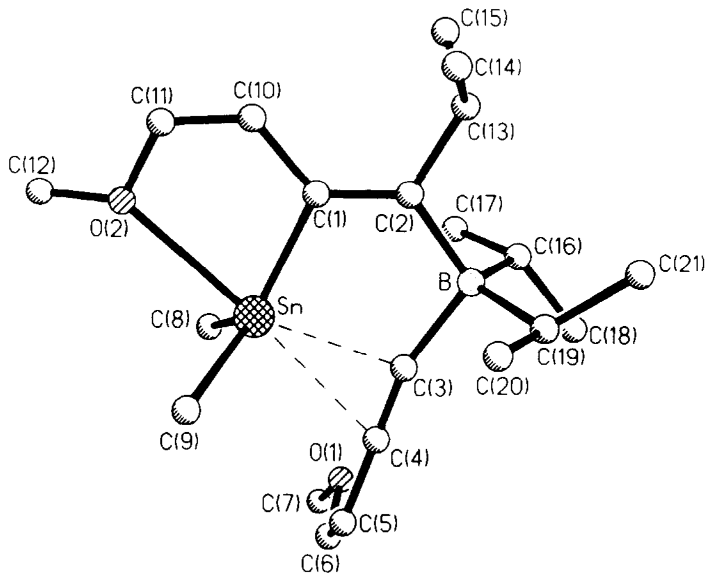


Fig. 8. Molecular structure of the zwitterionic intermediate obtained from the 1,1-organoboration reaction between $^{i}Pr_3B$ and $Me_2Sn(C{\equiv}C{-}CH{=}CH{-}OMe)_2$ [68]. Selected bond lengths (picometres) and bond angles (degrees) are as follows: Sn—C(3), 237.3(3); Sn—C(4), 266.1(3); Sn—C(1), 212.7(3); Sn—C(8), 211.3(5); Sn—C(9), 211.5(5); Sn—O(2), 259.2; B—C(3), 165.0(5); B—C(2), 164.3(4); C(1)—C(2), 135.3(4); C(3)—C(4), 122.1(5); BC(3)C(4), 163.5(3); C(3)C(4)C(5), 179.2(4).

in the case of the OMe group (Fig. 8), the opposite shift towards the C≡C bond is observed. This may be a function of both the ring size and the strength of the coordinative N—Sn bond as compared with the O—Sn bond. Although the distance between the tin atoms and the alkynyl carbon atoms is enlarged as compared with **38** in Fig. 5, there is still a coordinative interaction with the C≡C bond. This is evident from the molecular structure in the solid state showing the arrangement of all relevant atoms in one plane (see Fig. 7) and also in solution from the magnitude $|J(^{117/119}Sn^{13}C)|$ of coupling constants (range from 23 to 55 Hz) for the carbon atoms of the bridging alkynyl group.

The 1,1-organoboration of tetra-1-propynyltin proceeds stepwise via various zwitterionic intermediates. After twofold intermolecular 1,1-ethyloboration the reaction can be controlled to give **58** (Eq. (29), path b) ($R^1 = Me$, $R = Et$) as a crystalline solid which is stable up to −20 °C [74]. The result of the X-ray analysis (Fig. 9) shows that two bridging alkynyl groups are present and that there are only two Sn—C σ bonds forming a large CSnC bond angle of 140.9(1)°. Formally, this description corresponds to a diorganotin dication, stabilized by π coordination to the C≡C bonds of the two alkynylborate groups. Again, the main structural features in the solid state and in solution (at least below −40 °C) are comparable, as shown by ^{13}C and ^{119}Sn NMR data in both phases [76,78].

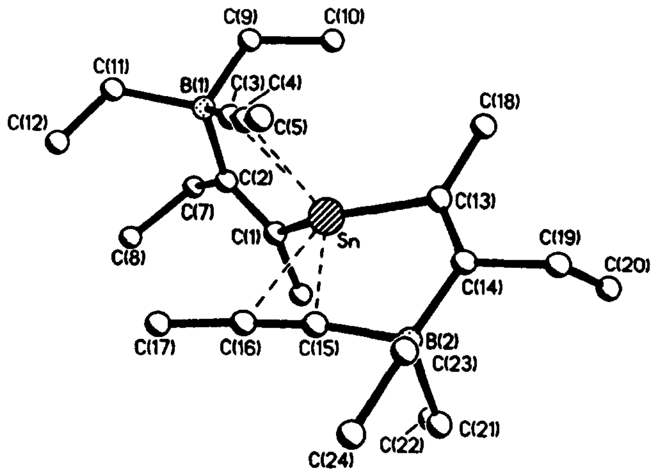


Fig. 9. Molecular structure of the zwitterionic intermediate **58** obtained from the 1,1-organoboration reaction between two equivalents of Et_3B and one equivalent of $Sn(C{\equiv}CMe)_4$ [74]. Selected bond lengths (picometres) and bond angles (degrees) are as follows: Sn—C(3), 235.5(3); Sn—C(4), 251.1(3); Sn—C(1), 211.7(3); Sn—C(13), 212.2(3); Sn—C(15), 235.1(3); Sn—C(16), 253.5(3); B(1)—C(3), 164.3(5); B(1)—C(2), 163.4(5); C(1)—C(2), 133.7(4); C(3)—C(4), 122.7(5); C(1)SnC(13), 140.9(1); B(1)C(3)C(4), 172.7(3); C(3)C(4)C(5), 175.8(3).

10. Conclusions

1,1-organoboration reactions of 1-alkynylmetal compounds make use of at least one B—C bond in order to form a new C—C bond in a highly stereospecific way, in most cases. Organometallic-substituted alkenes with a large variety of different substituents are accessible, in both high yield and high purity. These compounds allow application of numerous reactions which are typical of either $L_nM{-}C{=}$ or $R_2B{-}C{=}$ moieties. In addition, new synthetic aspects arise from reactions in which both the $L_nM{-}C{=}$ and the $R_2B{-}C{=}$ fragments are involved at the same time. Therefore, such alkenes must be considered as useful building blocks for further transformations.

The potential of 1,1-organoboration reactions increases further if there is another functional group or two or more alkynyl groups attached to the metal. The latter situation opens a novel, efficient and general route, via a sequence of intermolecular and intramolecular 1,1-organoborations, to new metallacycles, e.g. to metalloles or 1,1′-spirobimetalloles, which are not readily accessible by other methods. Metalloles possess an exciting chemistry and the new route to these compounds will give fresh impulses.

The mechanism of 1,1-organoboration has now been firmly established since it proved possible to isolate and characterize the first examples of intermediates in which an alkynyl group functions as a bridge between a boron and a tin or a lead atom. The chemical bonding of the bridging alkynyl group can be understood as a π complex, stabilizing a triorganotin or -lead cation, or a diorganotin dication by side-on coordination to the C≡C bond, or the widely used concept of $\sigma-\pi$ delocalization can be used to describe the bonding. The existence of "free" triorganosilicon, -germanium, -tin or -lead cations has been discussed in the literature; according to the geometrical surroundings of the tin or lead atom in some of the species reported here, the situation comes close to a "free" triorganoelement cation, stabilized by weak intramolecular interactions with the C≡C bond. Apart from the described rearrangement of the zwitterionic intermediates into the final 1,1-organoboration products, it can be expected that these reactive compounds will have an interesting chemistry of their own.

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References

[1] (a) F.E. Brinckman and F.G.A. Stone, J. Am. Chem. Soc., 82 (1960) 6218. (b) K. Niedenzu, Organomet. Chem. Rev., 1 (1966) 305. (c) H. Nöth and H. Vahrenkamp, J. Organomet. Chem., 11 (1968) 399. (d) K. Barlos and H. Nöth, Chem. Ber., 110 (1977) 3460. (e) P. Jutzi and A. Seufert, J. Organomet. Chem., 169 (1979) 327. (f) W. Haubold and J. Weidlein, Z. Anorg. Allg. Chem., 420 (1976) 251. (g) P.M. Treichel, J. Benedict and R.G. Haines, Inorg. Synth., 13 (1972) 32.

[2] (a) P.L. Timms, T.C. Ehlert, J.L. Margrave, F.E. Brinckman, T.C. Farrar and T.D. Coyle, J. Am. Chem. Soc., 87 (1965) 3819. (b) R.J. Wilcek, D.S. Matteson and J.D. Douglas, J. Chem. Soc., Chem. Commun., (1976) 401. (c) W. Biffar, H. Nöth and R. Schwerthöffer, Liebigs Ann. Chem., (1981) 2067. (d) J. Pfeiffer, W. Maringgele and A. Meller, Z. Anorg. Allg. Chem., 511 (1984) 185. (e) P. Paetzold, D. Hahnfeld, U. Englert, W. Wojnowski, B. Dreczewski, Z. Pawelec and L. Walz, Chem. Ber., 125 (1992) 1073. (f) E.P. Mayer, H. Nöth, W. Rattay and U. Wietelmann, Chem. Ber., 125 (1992) 401. (g) B. Frankhauser, H. Pritzkow and W. Siebert, Z. Naturforsch., Teil B, 49 (1994) 250. (h) J.D. Kennedy, W. McFarlane and B. Wrackmeyer, Inorg. Chem., 15 (1976) 1299.

[3] (a) W. Biffar, H. Nöth, H. Pommerening, R. Schwerthöffer, W. Storch and B. Wrackmeyer, Chem. Ber., 114 (1981) 49. (b) B. Wrackmeyer and K. Horchler, Z. Naturforsch., Teil B, 44 (1989) 1195.

[4] (a) B. Wrackmeyer and H. Nöth, Z. Naturforsch., Teil B, 29 (1974) 564. (b) H.-O. Berger, H. Nöth and B. Wrackmeyer, Chem. Ber., 112 (1979) 2866. (c) H.-O. Berger, H. Nöth, G. Rub and B. Wrackmeyer, Chem. Ber., 113 (1980) 1235.

[5] (a) K. Nozaki, K. Oshima and K. Utimoto, J. Am. Chem. Soc., 109 (1987) 2547. (b) K. Nozaki, K. Oshima and K. Utimoto, Tetrahedron, 45 (1989) 923.

[6] (a) K. Nozaki, Y. Ichinose, K. Watamatsu, K. Oshima and K. Utimoto, Bull. Chem. Soc. Jpn., 63 (1990) 2268. (b) M. Taniguchi, K. Oshima and K. Utimoto, Chem. Lett., (1993) 1751.

[7] (a) K. Uchida, K. Utimoto and H. Nozaki, J. Org. Chem., 41 (1976) 2941–2942. (b) J.A. Soderquist, J.C. Colberg and L. Del Valle, J. Am. Chem. Soc., 111 (1989) 4873–4878. (c) J.A. Soderquist and J.C. Colberg, Synlett, (1989) 25. (d) J.A. Soderquist and B. Santiago, Tetrahedron Lett., (1990) 51113. (e) M. Hoshi, Y. Masuda and A. Arase, J. Chem. Soc., Perkin Trans. I, (1990) 3237. (f) M. Hoshi, Y. Masuda and A. Arase, Bull. Chem. Soc. Jpn., 66 (1993) 914. (g) R. Köster, G. Seidel, F. Lutz, C. Krüger, G. Kehr and B. Wrackmeyer, Chem. Ber., 127 (1994) 813.

[8] (a) D. Seiferth, J. Am. Chem. Soc., 81 (1959) 1844. (b) P.R. Jones and T.F.O. Lim, J. Organomet.

Chem., 120 (1976) 27. (c) J.A. Soderquist and H.C. Brown, J. Org. Chem., 45 (1980) 3571. (d) K.K. Wang, Y.G. Gu and C. Liu, J. Am. Chem. Soc., 112 (1990) 4424.

[9] N.S. Hosmane, in G.A. Olah, K. Wade and R.E. Williams (eds.), Electron Deficient Boron and Carbon Clusters, Wiley, New York, 1991, pp. 215–235.

[10] (a) D.K. Srivastava, N.P. Rath and L. Barton, Organometallics, 11 (1992) 2263. (b) M.L. Thomson and R.N. Grimes, Inorg. Chem., 11 (1972) 1925. (c) A. Tabereux and R.N. Grimes, Inorg. Chem., 12 (1973) 792. (d) C.G. Savory and M.G.H. Wallbridge, J. Chem. Soc., Chem. Commun., (1971) 622. C.G. Savory and M.G.H. Wallbridge, J. Chem. Soc., Dalton Trans., (1972) 918.

[11] (a) D. Seiferth, K. Büchner, W.S. Rees, Jr., and W.M. Davis, Angew. Chem., 102 (1990) 912; Angew. Chem., Int. Edn. Engl., 29 (1990) 918. (b) L.J. Todd, A.R. Burke, H.T. Silverstein, J.L. Little and G.S. Wikholm, J. Am. Chem. Soc., 91 (1969) 3376. (c) R.W. Rudolph, R.L. Voorhee and R.E. Cochoy, J. Am. Chem. Soc., 92 (1970) 3351. (d) K.-S. Wong and R.N. Grimes, Inorg. Chem., 16 (1977) 2053. (e) P. Jutzi and P. Galow, J. Organomet. Chem., 319 (1987) 139. (f) N.S. Hosmane, U. Siriwardane, H. Zhu, G. Zhang and J.A. Maguire, Organometallics, 8 (1989) 566. (g) N.S. Hosmane and J.A. Maguire, J. Cluster Science, 4 (1993) 297.

[12] (a) P. Binger and R. Köster, Tetrahedron Lett., (1965) 1901. (b) R. Köster, Pure Appl. Chem., 49 (1977) 765. (c) P. Binger and R. Köster, Synthesis, (1973) 309. (d) R. Köster and A. Hagelee, Synthesis, (1976) 118. (e) A. Suzuki, Acc. Chem. Res., 15 (1982) 178.

[13] (a) J. Hooz and R. Mortimer, Tetrahedron Lett., (1976) 805. (b) K.K. Wang, K.-H. Chu, Y. Lin and J.-H. Chen, Tetrahedron, 45 (1989) 1105.

[14] (a) B. Wrackmeyer, Rev. Silicon, Germanium, Tin, Lead Compd., 6 (1982) 75. (b) B. Wrackmeyer, in S. Hermanek (ed.), Boron Chemistry — Proc. 6th Int. Meet. on Boron Chemistry (IMEBORON VI) World Scientific, Singapore, 1987, pp. 387–415.

[15] (a) W.E. Davidsohn and M.C. Henry, Chem. Rev., 67 (1967) 73. (b) L. Brandsma, Preparative Acetylenic Chemistry, Elsevier, Amsterdam, 2nd edn., 1988.

[16] V.S. Zavgorodnii and A.A. Petrov, Chem. Rev., 18 (1993) 1–91.

[17] B. Wrackmeyer, in J.J. Eisch and R.B. King (eds.), Organometallic Syntheses, Vol. 3, Elsevier, New York, 1986, pp. 446, 572.

[18] (a) K. Jones and M.F. Lappert, Proc. Chem. Soc., (1964) 22. (b) Yu.I. Derganow, T.F. Gerega and O.S. Dyachkovskaja, Russ. Chem. Rev., 46 (1977) 1132. (c) J. Lorberth, J. Organomet. Chem., 16 (1969) 327. (d) B. Wrackmeyer and C. Bihlmayer, J. Organomet. Chem., 266 (1984) 33.

[19] R. Köster, in R. Köster (ed.), Houben-Weyl-Methoden der Organischen Chemie, Vol. 13/3a, Thieme, Stuttgart, 1982, pp. 13–320.

[20] (a) H.C. Brown, Boranes in Organic Chemistry, Cornell University Press, Ithaca, NY, 1972. (b) H.C. Brown, Organic Synthesis via Boranes, Wiley, New York, 1975.

[21] (a) W.R. Croasmun and R.M.K. Carlson (eds.), Two-dimensional NMR Spectroscopy, VCH, Weinheim, 1987. (b) K. Nakanishi (ed.), One-dimensional and Two-dimensional NMR Spectra by Modern Pulse Techniques, Kodanasha, Tokyo, and University Science Books, Mill Valley, CA, 1990.

[22] (a) H. Nöth and B. Wrackmeyer, ^{11}B nuclear magnetic resonance spectroscopy of boron compounds, in P. Diehl, E. Fluck and R. Kosfield (eds.), NMR — Principles and Progress, Vol. 14, Springer, Berlin, 1978. (b) B. Wrackmeyer and R. Köster, in R. Köster (ed.), Houben-Weyl — Methoden der Organischen Chemie, Vol. 13/3c, Thieme, Stuttgart 1984, pp. 377–611. (c) B. Wrackmeyer, Annu. Rep. NMR Spectrosc., 20 (1988) 61.

[23] (a) H. Marsmann, ^{29}Si NMR spectroscopic results, in P. Diehl, E. Fluck and R. Kosfeld (eds.), NMR — Basic Principles and Progress, Vol. 17, Springer, Berlin, 1981, pp. 65–235. (b) E.A. Williams, Annu. Rep. NMR Spectrosc., 15 (1984) 235. (c) E. Kupce and E. Lukevics, in E. Buncel and J.R. Jones (eds.), Isotopes in the Physical and Biomedical Sciences, Vol. 2, Elsevier, Amsterdam, 1991, pp. 213–295.

[24] (a) B. Wrackmeyer, Annu. Rep. NMR Spectrosc., 16 (1985) 73. (b) J.D. Kennedy and W. McFarlane, in J. Mason (ed.), Multinuclear NMR, Plenum, New York, 1987, pp. 305–333.

[25] B. Wrackmeyer and K. Horchler, Annu. Rep. NMR Spectrosc., 22 (1990) 249.

[26] (a) R.K. Harris and A. Sebald, Organometallics, 7 (1988) 388. (b) B. Wrackmeyer, A. Sebald and L.H. Merwin, Magn. Reson. Chem., 29 (1991) 260. (c) B. Wrackmeyer, E. Kupce, G. Kehr and A. Sebald, Magn. Reson. Chem., 30 (1992) 964.

[27] (a) B. Wrackmeyer, E. Kupce and J. Kümmerlen, Magn. Reson. Chem., 30 (1992) 403. (b) B. Wrackmeyer, K. Wagner, A. Sebald, L.H. Merwin and R. Boese, Magn. Res. Chem., 29 (1991) S3. (c) B. Wrackmeyer, G. Kehr, D. Wettinger and W. Milius, Main Group Met. Chem., 16 (1993) 433.

[28] (a) L. Rosenblum, J. Am. Chem. Soc., 77 (1955) 5016. (b) R. Köster, Liebigs Ann. Chem., 618 (1958) 31. (c) R. Köster, Angew. Chem., 75 (1963) 1019; Angew. Chem., Int. Edn. Engl., 2 (1963) 174.

[29] R. Köster, G. Seidel and B. Wrackmeyer, Chem. Ber., 122 (1989) 1825.

[30] B. Wrackmeyer, J. Chem. Soc., Chem. Commun., (1988) 1624.

[31] R. Köster, G. Seidel, J. Süß and B. Wrackmeyer, Chem. Ber., 126 (1993) 1107.

[32] R. Köster, G. Seidel, I. Klopp, C. Krüger, G. Kehr, J. Süß and B. Wrackmeyer, Chem. Ber., 126 (1993) 1385.

[33] B. Wrackmeyer, G. Kehr and J. Süß, Chem. Ber., 126 (1993) 2221.

[34] B. Wrackmeyer and J. Süß, unpublished results, 1994.

[35] B. Wrackmeyer, D. Wettinger and W. Milius, J. Chem. Soc. Chem. Commun., (1995) 399.

[36] (a) B. Wrackmeyer, unpublished results, 1986.
(b) B. Wrackmeyer, S. Kundler and A. Ariza-Castolo, Phosporous Sulfur Silicon, 91 (1994) 229.

[37] A. Schmidt and B. Wrackmeyer, Z. Naturforsch., Teil B, 33 (1978) 855.

[38] C. Bihlmayer and B. Wrackmeyer, Z. Naturforsch., Teil B, 36 (1981) 1265.

[39] (a) B. Wrackmeyer, K. Wagner and S.T. Abu-Orabi, J. Organomet. Chem., 346 (1988) 333. (b) B. Wrackmeyer and S.T. Abu-Orabi, Chem. Ber., 120 (1987) 1603.

[40] C. Bihlmayer, S.T. Abu-Orabi and B. Wrackmeyer, J. Organomet. Chem., 322 (1987) 25.

[41] B. Wrackmeyer and U. Dörfler, manuscript in preparation.

[42] B. Wrackmeyer, Polyhedron, 5 (1986) 1709.

[43] (a) J. Dubac, A. Laporterie and G. Manuel, Chem. Rev., 90 (1990) 215. (b) E. Colomer, R.P.J. Corriou and M. Lheureux, Chem. Rev., 90 (1990) 265.

[44] B. Wrackmeyer, J. Organomet. Chem., 310 (1986) 151.

[45] A. Sebald and B. Wrackmeyer, J. Organomet. Chem., 304 (1986) 271.

[46] A. Sebald, P. Seiberlich and B. Wrackmeyer, J. Organomet. Chem., 303 (1986) 73.

[47] B. Wrackmeyer, in R.B. King and J.J. Eisch (eds.), Organometallic Syntheses, Vol. 4, Elsevier, New York, 1988, p. 457.

[48] S. Kerschl and B. Wrackmeyer, Z. Naturforsch., Teil B, 40 (1985) 845.

[49] S. Kerschl and B. Wrackmeyer, J. Chem. Soc., Chem. Commun., (1986) 403.

[50] S. Kerschl and B. Wrackmeyer, J. Chem. Soc., Chem. Commun., (1986) 1170.

[51] S. Kerschl and B. Wrackmeyer, J. Organomet. Chem., 338 (1988) 195.

[52] (a) B. Wrackmeyer, S.M. Frank, M. Herberhold, A. Simon and H. Borrmann, Chem. Ber., 124 (1991) 691. (b) B. Wrackmeyer, H.E. Maisel, S. Kerschl and W. Milius, J. Organomet. Chem., 490 (1995) 197.

[53] S. Kerschl and B. Wrackmeyer, Z. Naturforsch., Teil B, 41 (1986) 890.

[54] S. Kerschl and B. Wrackmeyer, J. Chem. Soc., Chem. Commun., (1985) 1199.

[55] S. Kerschl and B. Wrackmeyer, Chem. Ber., 121 (1988) 1451.

[56] C. Bihlmayer, S. Kerschl and B. Wrackmeyer, Z. Naturforsch., Teil B, 42 (1987) 715.

[57] (a) B. Wrackmeyer, Z. Naturforsch., Teil B, 33 (1978) 385. (b) B. Wrackmeyer and R. Zentgraf, J. Chem. Soc., Chem. Commun., (1978) 402.

[58] B. Wrackmeyer, J. Organomet. Chem., 205 (1981) 1.

[59] B. Wrackmeyer and C. Bihlmayer, J. Chem. Soc., Chem. Commun., (1981) 1093.

[60] B. Wrackmeyer, C. Bihlmayer and M. Schilling, Chem. Ber., 116 (1983) 3182.

[61] B. Wrackmeyer, G. Kehr and W. Milius, manuscript in preparation.

[62] B. Wrackmeyer, Organometallics, 3 (1984) 1.

[63] B. Wrackmeyer, S. Kundler and R. Boese, Chem. Ber., 126 (1993) 1361.

[64] L. Killian and B. Wrackmeyer, J. Organomet. Chem., 132 (1977) 213.

[65] L. Killian and B. Wrackmeyer, J. Organomet. Chem., 148 (1978) 137.

[66] L. Killian and B. Wrackmeyer, J. Organomet. Chem., 153 (1978) 152.

[67] S. Kerschl and B. Wrackmeyer, Z. Naturforsch., Teil B, 39 (1984) 1037.

[68] B. Wrackmeyer, S. Kundler, W. Milius and R. Boese, Chem. Ber., 127 (1994) 333.

[69] B. Wrackmeyer, G. Kehr and S. Ali, Inorg. Chim. Acta., 256 (1994) 51.
[70] B. Wrackmeyer and K. Horchler, Z. Naturforsch., Teil B, 45 (1990) 437.
[71] B. Wrackmeyer, J. Chem. Soc., Chem. Commun., (1986) 397.
[72] B. Wrackmeyer and K. Horchler, J. Organomet. Chem., 399 (1990) 1.
[73] B. Wrackmeyer, G. Kehr and D. Wettinger, Inorg. Chim. Acta, 220 (1994) 161.
[74] B. Wrackmeyer, G. Kehr and R. Boese, Angew. Chem., 103 (1991) 1374; Angew. Chem., Int. Edn. Engl., 30 (1991) 1370.
[75] B. Wrackmeyer and G. Kehr, Polyhedron, 10 (1991) 1497.
[76] B. Wrackmeyer, G. Kehr, A. Sebald and J. Kümmerlen, Chem. Ber., 125 (1992) 1597.
[77] B. Wrackmeyer, G. Kehr and R. Boese, Chem. Ber., 125 (1992) 643.
[78] B. Wrackmeyer, K. Horchler and R. Boese, Angew. Chem., 101 (1989) 1563; Angew. Chem., Int. Edn. Engl., 28 (1989) 1500.
[79] B. Wrackmeyer and K. Horchler von Locquenghien, Main Group Met. Chem., 13 (1990) 387.
[80] B. Wrackmeyer and K. Horchler, Organometallics, 9 (1990) 1881.
[81] B. Wrackmeyer, G. Guldner and S.T. Abu-Orabi, Tetrahedron, 45 (1989) 1119.
[82] B. Wrackmeyer and G. Kehr, unpublished results, 1990.
[83] A. Berndt, Angew. Chem., 105 (1993) 1034; Angew. Chem., Int. Edn. Engl., 32 (1993) 985, and references cited therein.
[84] (a) P.J. Stang, Z. Rappoport, M. Hannack and L.R. Subramanian, Vinyl Cations, Academic Press, New York, 1979. (b) H.-U. Siehl, F.-P. Kaufmann, Y. Apeloig, V. Braude, D. Danovich, A. Berndt and N. Stamatis, Angew. Chem., 103 (1991) 1546; Angew. Chem., Int. Edn. Engl., 30 (1991) 1479. (c) C. Dallaire and M.A. Brook, Organometallics, 12 (1993) 2332. (d) J.B. Lambert, Tetrahedron, 46 (1990) 2677. K.A. Nguyen, M.S. Gordon, G. Wang, J.B. Lambert, Organometallics, 10 (1991) 2798.
[85] G.D. Stucky, A.M. McPherson, W.E. Rhine, J.J. Eisch and J.L. Considine, J. Am. Chem. Soc., 96 (1974) 1941.
[86] B. Tecle, W.H. Ilsley and J.P. Oliver, Inorg. Chem., 20 (1981) 2335.
[87] T. Fjeldberg, A. Haaland, R. Seip and J. Weidlein, Acta Chem. Scand. A, 35 (1981) 437.
[88] W. Fries, W. Schwarz, H.-D. Hausen and J. Weidlein, J. Organomet. Chem., 159 (1978) 373.
[89] P.N.V. Kumar and E.D. Jemmis, J. Am. Chem. Soc., 110 (1988) 125.
[90] (a) T. Weidmann, V. Weinrich, B. Wagner, C. Robl and W. Beck, Chem. Ber., 124 (1991) 1363. (b) A.A. Cherkas, N. Hadj-Bagheri, A.J. Carty, E. Sappa, M.P. Pellinghelli and A. Tripicchio, Organometallics, 9 (1990) 1887.
[91] (a) K.E. Lee and K.T. Higa, J. Organomet. Chem., 449 (1993) 53. (b) J.R. Berenguer, L.R. Falvello, J. Fornies, E. Lalinde and M. Thomas, Organometallics, 12 (1993) 6.
[92] B. Wrackmeyer, K. Horchler, A. Sebald and L.H. Merwin, Magn. Reson. Chem., 28 (1990) 465.