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Metallacyclopentadienes and Related Heterocycles via 1,1-Organoboration of Alkyn-1-ylmetal Compounds

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ABSTRACT: *Metallacyclopentadienes (metalloles) containing M = Si, Ge, Sn, Pb, Ti, Pt can be prepared by 1,1-organoboration of alkyn-1-ylmetal compounds $L_nM{-}C{\equiv}C{-}R^1$ (R^1 = H, alkyl, aryl, silyl, etc; L depends on M, and can be hydrogen, alkyl, aryl, Cl, Br, amino groups, a chelating diphosphane, and one or more L can be again alkynyl groups). These reactions proceed via activation of the M–C≡ bond(s) by an electron-deficient triorganoborane BR_3 (R = alkyl, aryl; noncyclic, monocyclic, bicyclic, and tricyclic boranes), at first intermolecular and then intramolecular. In the course of these reactions, the M–C≡ bonds are cleaved, zwitterionic alkynylborate-like intermediates are formed, in which the metal-containing fragments are coordinated side-on to the C≡C bonds. In most cases, the 1,1-organoboration reactions tolerate various functional groups at the alkyne as well as at the metal. The characterization of intermediates and final products by X-ray structural analysis and by multinuclear magnetic resonance spectroscopy (NMR) is documented and described.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:188–208, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20222

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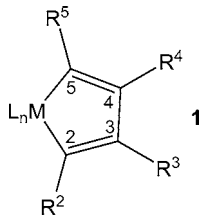
INTRODUCTION

In metallacyclopentadiene derivatives (metalloles) an L_nM fragment as in **1** induces interesting new properties of the diene system [1–4]. The tuning of these properties can be achieved by selecting an appropriate fragment L_nM, and also by a choice of different substituents at the carbon atoms in 2–5 positions. Although a number of routes are available [1,2], the straightforward synthesis of metalloles with the option to have a great variety of substituents both at M and in 2–5 positions is still a formidable problem.



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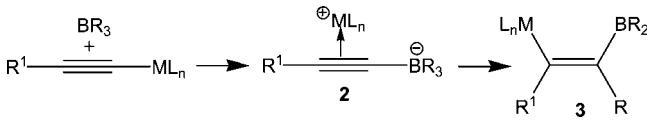
Formula **1**

Some time ago, we have proposed 1,1-organoboration of alkyn-1-ylmetal compounds as an alternative [5,6] to conventional metallole syntheses, and some of these results have been summarized [7]. The present report gives an overview on 1,1-organoboration reactions, focusing mainly on the synthesis of metalloles. It will be shown that 1,1-organoboration of alkyn-1-ylmetal compounds leads to metallacyclopentadienes with M = Si, Ge, Sn, Pb and some transition metals such as Ti and Pt.



SCHEME 1 1,1-Organoboration of a monoalkyn-1-ylmetal compound via a zwitterionic intermediate.

The advantage of this synthetic approach appears to be its simplicity and the wide variety of substituents for all ring positions.

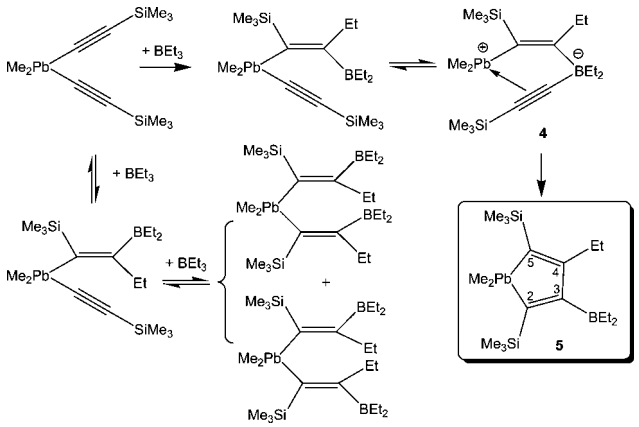
The mechanistic principle behind 1,1-organoboration is the activation of the M—C≡ bond by the electron-deficient boron atom in triorganoboranes, either intermolecular or intramolecular. As shown in Scheme 1 for an intermolecular 1,1-organoboration, this activation of the M—C≡ bond leads to cleavage of this bond, formation of an alknylborate-like zwitterionic intermediate **2**, followed by migration of one organyl group from boron to the neighbored alkynyl carbon atom. In most cases, this reaction is stereoselective, leading to alkenes **3**, in which the boryl group and the metal fragment are in cis-positions. If the metal fragment contains another alkynyl group linked to the metal, this stereochemistry will strongly favor an intramolecular activation of the next M—C≡ bond, and the way is free to the formation of heterocycles which could be metalloles. The intermediate **2** reminds of the reaction of alkali metal alkynyl borates with electrophiles [8–10] which also leads, sometimes stereo-specifically and in high yield, to alkenes of type 3.

The cleavage of the M—C≡ bond proceeds fast under rather mild reaction conditions (below −20°C) if this bond is strongly polarized (e.g., M = Sn, Pb), and it requires rather harsh reaction conditions (up to several days at 100°C) if it is less polar (e.g., M = Ge, Si). In any case, bulky groups L, R^1, or R, linked to the metal, the C≡C bond or to boron, respectively, expectedly slow down the progress of the 1,1-organoboration. In the case of M = Si, the presence of Si—Cl function(s) reduces the reactivity of the Si—C≡ bond toward triorganoboranes. If M is a transition metal (e.g., M = Ti, Pt), the whole situation becomes more complex, and general trends depending on L, R^1, and R are not readily apparent.

METALLACYCLOPENTADIENES WITH M = Si, Ge, Sn, Pb

Plumbacyclopentadienes

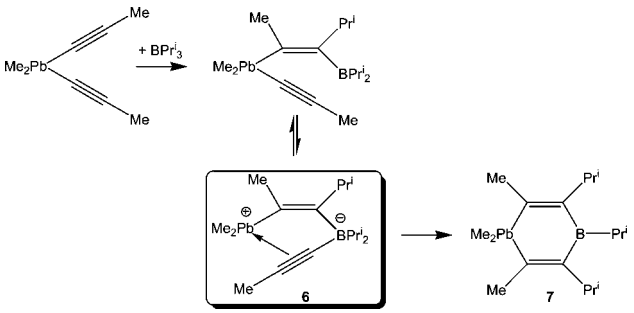
The Pb—C≡ bond in alkyn-1-yllead compounds is extremely reactive toward triorganoboranes



SCHEME 2 Formation of a plumbacyclopentadiene by 1,1-organoboration of bis(trimethylsilylethynyl)dimethylplunbane, proceeding through various intermediates including a zwitterionic species.

[7,11] and therefore, it is difficult to control the reactions. Furthermore, the synthesis of pure and stable dialkyn-1-yl(diorgano)lead compounds such as $Me_2Pb(C{\equiv}C{-}R^1)_2$ is not always straightforward (e.g., R^1 = H) [12]. The 1,1-organoboration proceeds somewhat more controlled by using bulky groups R and/or R^1. Thus, with $R^1 = SiMe_3$, the reaction of $Me_2Pb(C{\equiv}C{-}SiMe_3)_2$ with triethylborane leads to the plumbole **5** (Scheme 2) [13]. When the progress of this reaction was monitored by ^{29}Si and ^{207}Pb NMR spectroscopy, the formation of organometallic-substituted alkenes could be detected, for which the configuration at the C=C bonds is unfavorable for ring closure. Since the 1,1-organoboration is in equilibrium with 1,1-deorganoboration [7], in particular for rather labile M—C= bonds, the equilibrium is finally shifted toward the plumbole **5**, because the ring closure is not readily reversible. Evidence for the zwitterionic intermediate **4** is also available by NMR spectroscopy [13].

Zwitterionic intermediates of the type 4 are of prime importance to understand the formation of the final products [7]. They are also examples of the elusive triorganolead cations [14], in this case stabilized by coordinative interactions (side-on coordination) of the positively charged lead center with a C≡C bond. Therefore, numerous attempts have been made to prepare such intermediates for structural characterization by X-ray analysis. The search was successful, when the reaction of dimethyl-di(propyn-1-yl)lead with triisopropylborane was studied (Scheme 3). The intermediate **6** could be isolated at low temperature, and its molecular structure was confirmed by X-ray analysis in the solid state (Fig. 1) and multinuclear NMR in solution

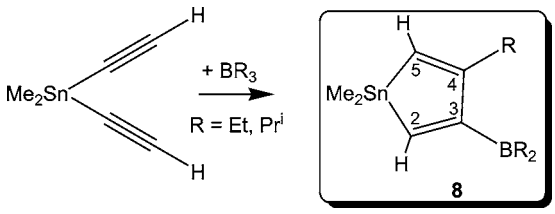


SCHEME 3 The reaction of dimethyl(dipropyn-1-yl)plumbane with triisopropylborane proceeds via a zwitterionic intermediate (see Fig. 1) to give a 1-pumba-4-bora-cyclohexa-2,5-diene.

[15]. A related derivative (R = cyclopentyl) was also studied by solid-state ^{207}Pb NMR [16]. However, the final rearrangement of **6** afforded selectively the 1-plumba-4-bora-cyclohexa-2,5-diene **7** [15] instead of a plumbole. In contrast to **4**, the rearrangement of the intermediate **6** takes place by 1,1-alkylboration (transfer of an isopropyl group from boron to carbon) instead of 1,1-vinylboration. The results summarized in the Schemes 2 and 3 show that there are at least two alternatives for the zwitterionic intermediate to rearrange into heterocyclic dienes.

Stannacyclopentadienes

1,1-Organoboration of diethynyl(diorgano)stannanes. In contrast to the corresponding lead compounds, numerous diethynyll(diorgano)stannanes $R^2_2Sn(C{\equiv}C{-}H)_2$ are readily accessible [12,16] and therefore, these alkyne derivatives became attractive targets for 1,1-organoboration reactions. The first stannacyclopentadienes (stannoles) prepared by 1,1-alkylboration were the compounds **8**, obtained in essentially quantitative yield (Scheme 4) [5]. Although the stannole **8** with R = Et can be distilled under reduced pressure, about 50% of the product is lost by decomposition in this process, and the pure liquid itself slowly changes already at room temperature into various other still unidentified compounds [17]. NMR spectra indicate that these rearranged products are not simply the result of [4+2]cycloadditions.



SCHEME 4 Stannacyclopentadienes are formed in high yield by 1,1-organoboration of diethynyltin compounds.

The proposed structure of **8** was based at that time entirely on NMR spectroscopy, mainly on ^{1}H and ^{13}C NMR, and there was no clear mechanistic evidence to explain its formation. In subsequent years, numerous other stannoles were prepared by this route starting from dialkyn-1-yltin compounds $R^2_2Sn(C{\equiv}C{-}R^1)_2$ with R^1 = alkyl, $SiMe_3$ [6,18], and also with different groups R^2 (e.g., Et, Pr^i, Bu, Bu^t, CH_2Ph, or Ph) [19,20]. However, in all these cases of noncyclic trialkylboranes BR_3 (R = Me, Et, Pr, Pr^i, Bu), the products were oily liquids. Although these could be clearly identified as stannoles by multinuclear NMR, direct structural evidence was still lacking. Then, first attempts were made to use 9-alkyl-9-borabicyclo[3.3.1]nonanes (R-9-BBN) for 1,1-organoboration reactions. It was found that ring expansion of the bicyclic system is the kinetically controlled reaction, whereas transfer of the group R is thermodynamically controlled [21,22]. If R = ethyl or a larger, branched alkyl group, the energy of activation for the rearrangement of the kinetically controlled into the thermodynamically controlled product appears to be quite high. Thus, 1,1-organoboration of diethynyltin compounds with an appropriate R-9-BBN should lead to twofold expansion of the bicyclic system [22]. This gave hope that a stannole ring integrated in a polycyclic system could give rise to crystalline materials. The approach is shown in Scheme 5, and the stannole **9** could be

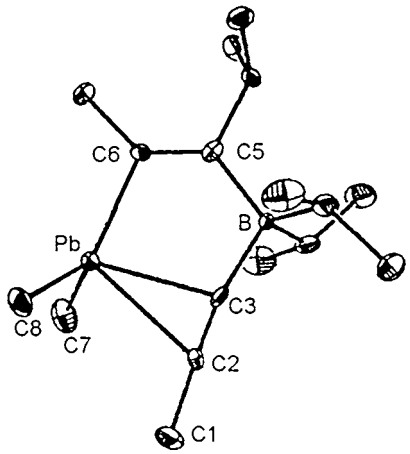
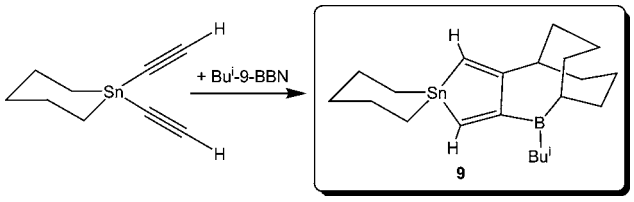


FIGURE 1 Molecular structure of the zwitterionic intermediate **6**, where a tri-coordinate lead atom is coordinated side-on to the C≡C bond of the alkynylborate unit. Selected bond lengths (pm) and angles (°): Pb–C(2) 264.8(6), Pb–C(3) 246.7(6), Pb–C(6) 220.3(3), Pb–C(7) 222.2(8), Pb–C(8) 220.6(7), C(1)–C(2) 148.1(10), C(2)–C(3) 121.0(10), B–C(3) 164.0(10), C(5)–C(6) 133.4(9); C(1)–C(2)–C(3) 177.3(7), C(2)–C(3)–B 169.5(6).



SCHEME 5 1,1-Diethynyl-1-stannacyclohexane reacts with 9-isobutyl-8-borabicyclo[3.3.1]nonane (Bu^i-9-BBN) to give a crystalline spirotin compound containing a stannacyclopentadiene unit (see Fig. 2).

isolated and fully characterized by NMR in solution, solid-state NMR, and also by X-ray structural analysis (Fig. 2) [23].

Stannacyclopentadienes: Search for Zwitterionic Intermediates Containing a Triorganotin Cation Stabilized by Side-On Coordination to a C≡C Bond. In the case of 1,1-organoboration of diethynyltin compounds, it proved impossible to isolate or even detect zwitterionic intermediates. However, for various groups R^1 other than hydrogen, zwitterionic intermediates could be detected by NMR spectroscopy [6], and in some cases they could be isolated as crystalline materials, and the molecular structures were determined by X-ray analysis [24,25]. These zwitterionic intermediates (examples, for which X-ray structures are available, are shown in Scheme 6) can be regarded as triorganotin cations [14a,26,27], stabilized by intramolecular side-on coordination of the positively charged tin center to the C≡C bond as in **10**. Since these species are fairly unstable toward rearrangement into stannoles or 1-stanna-4-bora-cyclohexa-2,5-dienes (e.g., $R^1 = Me$, $R = Pr^i$,

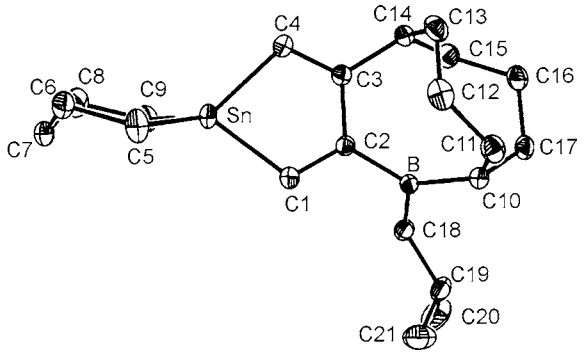
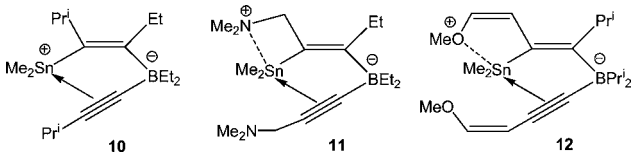


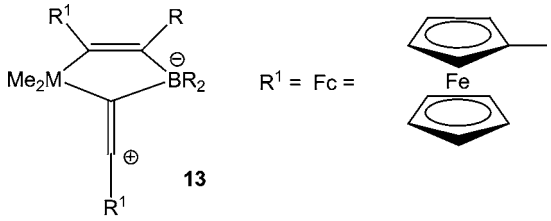
FIGURE 2 Molecular structure of the polycyclic tin compound **9** containing the stannacyclopentadiene unit. Selected bond lengths (pm) and angles (°): Sn–C(1) 213.3(2), Sn–C 212.7(2), Sn–C(5) 215.0(2), Sn–C(9) 214.8(2), C(1)–C(2) 135.5(3), C(2)–C(3) 150.6(3), C(3)–C(4) 134.7(3), C(2)–B 157.4(3); C(1)–Sn–C(4) 87.2(1), C(5)–Sn–C(9) 102.1(1), Sn–C(1)–C(2) 110.7(2), Sn–C(4)–C(3) 109.8(2), C(1)–C(2)–C(3) 117.4(2), C(2)–C(3)–C(4) 119.8(2).



SCHEME 6 Examples of zwitterionic compounds in which a triorganotin cation is coordinated side-on to the C≡C bond of an alkynylborate unit (all characterized by X-ray structural analysis).

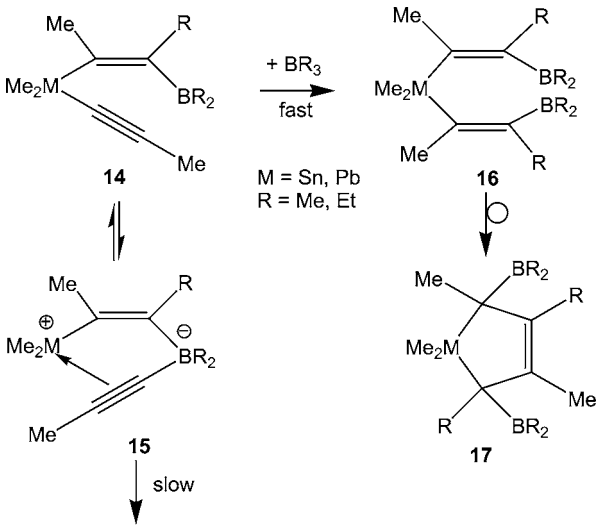
cyclopentyl), attempts were made to stabilize such intermediates further by coordination of the tin center to an amino-nitrogen or an ether-oxygen atom [25] as shown for **11** and **12**, respectively.

The structure of **10** [24] corresponds closely to that of the lead analogue **6** [15] (Scheme 3). The geometry of the alkynyl group is only slightly distorted in **6**, **10–12**, when compared with that of simple alkynes, and the distances between the metal and the alkynyl carbon atoms are different. However, the situation does not come close to the extreme case of bridging shown in the structure **13**. There is NMR spectroscopic evidence [28] that this structure is important for M = Sn, R = Et, and R^1 = Fc (where Fc is ferrocenyl). This would be consistent with the fact that the ferrocenyl group can help to stabilize the positive charge in vinyl cations [29], and organometallic groups in β-position relative to the positively charged carbon atom also exert a stabilizing effect [30].

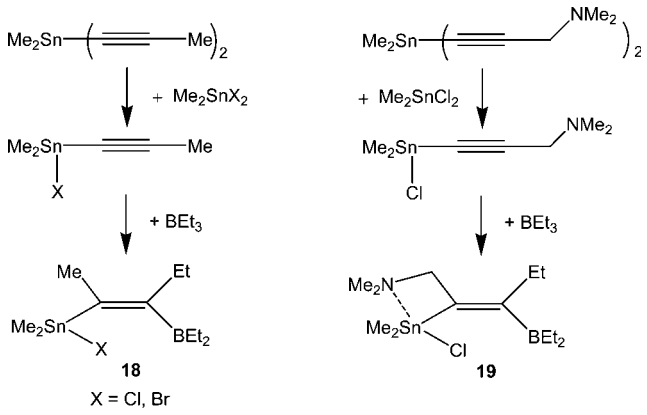


Formula **13**

As in the reaction of $Me_2Pb(C{\equiv}C{-}Me)_2$ with trialkylboranes [15], the tin analogue $Me_2Sn(C{\equiv}C{-}Me)_2$ also behaves differently [31], when compared with many other di(alkyny-1-yl)tin compounds [7]. There is no doubt about the intermediacy of the zwitterionic compound analogous to **10** [24]. The final product from the 1:1 reaction, however, is a 1-stanna-4-bora-cyclohexa-2,5-diene [31] along with traces of the respective stannole. Since in the case of di(propyn-1-yl)lead [15,32] and –tin compounds [31,32], in the presence of an excess of BR_3, the 1:1 reaction is not preferred for small trialkylboranes such as BMe_3 or BEt_3, the dynamic equilibrium indicated in Scheme 3, and shown again in Scheme 7, has to be considered more closely.



SCHEME 7 The unusual behavior of dialkyl(dipropyn-1-yl)tin and -lead compounds and their reaction with an excess of trimethyl- and triethylborane.



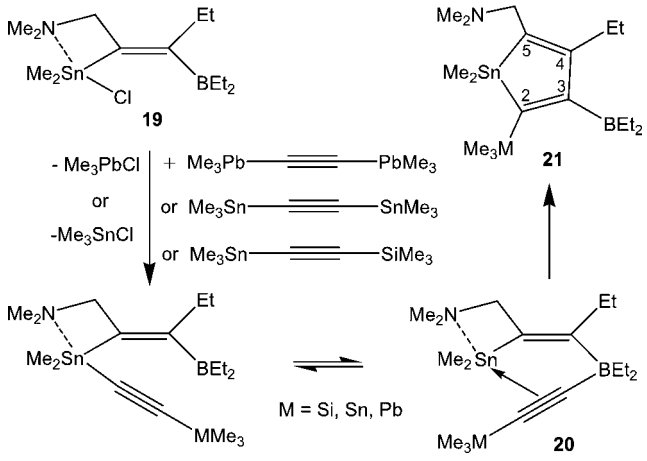
SCHEME 8 On the way to a stepwise synthesis of stannacyclopentadienes: Useful alkenes with halogeno(diemthyl)-stannyl and dialkylboryl groups in cis-positions.

Apparently, the rearrangement of the zwitterionic intermediates **15** into a metallole or 1-metalla-4-bora-cyclohexa-2,5-diene can become slow with respect to the intermolecular 1,1-organoboration reaction of the alkenyl(alkynyl)metal compounds **14**, leading to the di(alkenyl)metal compounds **16** which undergo further rearrangements. The final products are plumbol-3-enes [32] or stannol-3-enes **17** [31,32]. An explanation of the special role of the propyn-1-yl derivatives can be traced to the structure of **15**, where the methyl group adjacent to the olefinic carbon atom linked to M is not able to keep the MMe_2 group firmly in a favorable position for coordinative interactions with the C≡C bond. This destabilizes **15** relative to **14**, and the M–C≡ bond in **14** is available for the reaction with the excess of BR_3 to give **16**. The final rearrangement of **16** into **17** is a complex process [32] which will not be discussed in this review.

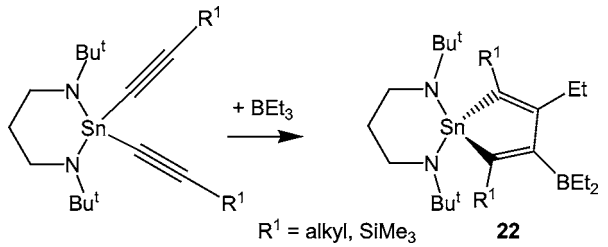
Stannacyclopentadienes: Stepwise Synthesis by 1,1-Organoboration. Starting from alkyn-1-yltin compounds, in which the Sn–C≡C–R^1 group and an Sn–X function (X = Cl or Br) are present, the 1,1-ethylboration leads to useful alkenyltin compounds of the type **18** [6,33] or **19** [34] (Scheme 8). The N–Sn coordination in **19** follows from a consistent set of multinuclear NMR data [34,35] in comparison with **18** (X = Cl). In particular, the increase in the ^{119}Sn nuclear magnetic shielding by almost 100 ppm shows that the tin atom is five-coordinate in **19**.

The Sn–X function invites for further transformations [34–36] including the reaction with lithium alkynides [6] or similar reagents [18,34,37] in order to introduce an alkyn-1-yl group. If this substitution is carried out under mild conditions, zwitterionic intermediates corresponding to **10** or **11** can be detected [34] prior to the formation of stannoles. Examples are the compounds **20**, in which it proved possible for the first time to obtain evidence for such a structure with an organometallic group linked to the C≡C bond [34] (Scheme 9). The rearrangement of **20** leads to the stannoles **21** which bear different substituents in the 2–5-positions [34]. NMR data, in particular coupling constants $^1J(^{119}Sn,^{13}C)$, suggest that there is also a weak coordinative N–Sn bond in the stannoles **21** [34].

Stannacyclopentadienes: 1,1-Organoboration of Dialkyn-1-yltin Compounds Bearing Amino Groups at the Tin Atom. Stannacyclopentadienes in which the tin atom bears additional functional groups are of



SCHEME 9 Examples for a stepwise synthesis of stannacyclopentadienes with organometallic groups in 2-position.

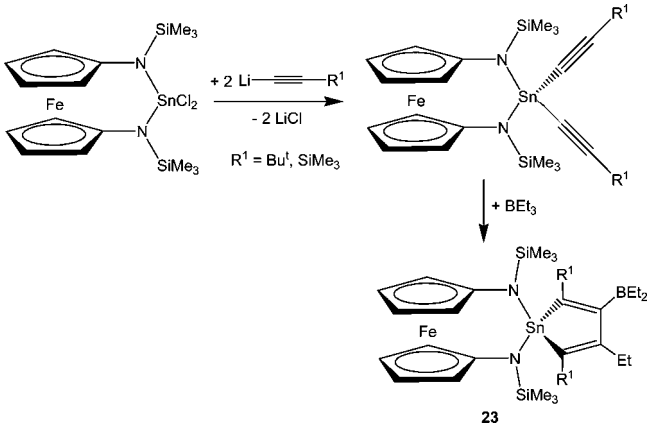


SCHEME 10 1,1-Organoboration of cyclic dialkyn-1-yltin amides.

interest for further transformations. Amino groups are particularly attractive since it is well known that the Sn—N bond is reactive [38,39], and that the amino functions can be easily modified by the introduction of various substituents. Since alkyn-1-yltin compounds of the type $(R^2_2N)_2Sn(C{\equiv}C{-}R^1)_2$ bearing simple dialkylamino groups with $R^2 = Me$ or Et undergo fast exchange reactions [40], cyclic derivatives with bulky substituents at the nitrogen atoms [41] appeared to be more attractive for 1,1-organoboration [42] (Scheme 10). The mechanism is analogous to that established for the dialkyn-1-yl(diorgano)tin compounds, with zwitterionic intermediates [42].

The concept of using cyclic tin amides in organoboration reaction could also be exploited in the chemistry of 1,3,2-diazastanna[3]-ferrocenophanes [43], where the 1,1-organoboration afforded the spirotin compounds **23** with a stannol unit [44] (Scheme 11). Here it proved possible to confirm the stannole structure by X-ray analysis for $R^1 = SiMe_3$ (Fig. 3) and an extensive set of liquid and solid-state NMR data [44].

Noncyclic dialkyn-1-yl-bis(amino)tin compounds can be used for 1,1-ethylboration if the two groups at each nitrogen atom are fairly bulky that means *tert*-butyl groups, trialkylsilyl groups, and



SCHEME 11 Formation and 1,1-organoboration of 2,2-dialkyn-1-yl-1,3,2-diazastanna-[3]ferrocenophanes.

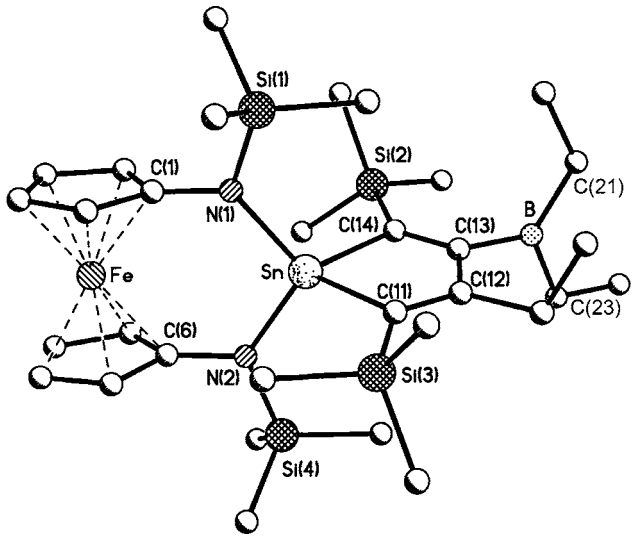
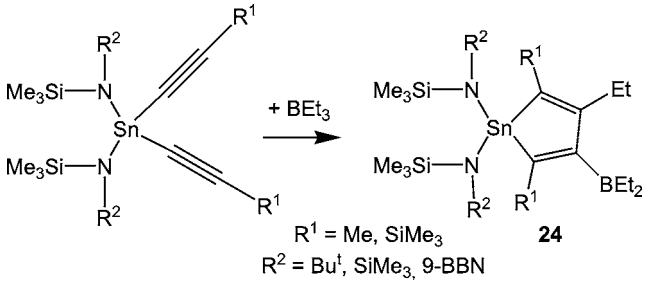


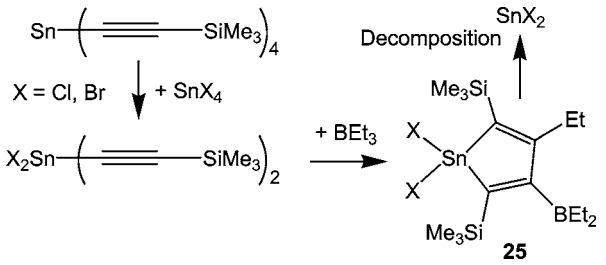
FIGURE 3 Molecular structure of the spirotin compound **23** containing the 1,3,2-diazastanna-[3]ferrocenophane ring and a stannacyclopentadiene ring. Selected bond lengths (pm) and angles (°):Sn–N(1) 204.6(4), Sn–N(2) 204.2(4), Sn–C(11) 214.8(5), Sn–C(14) 216.7(5), C(11)–C(12) 133.0(7), C(12)–C(13) 155.8(8), C(13)–C(14) 133.7(7), B–C(13) 157.5(9), Fe-ring centroid 163.3 and 163.7, Fe–Sn 384.5; N(1)–Sn–N(2) 109.03(17), C(11)–Sn–C(14) 85.5(2), C(12)–C(11)–Sn 106.2(4), C(11)–C(12)–C(13) 121,7(5).

dialkylboryl groups are suitable [45]. Examples are shown in Scheme 12, and the solid-state structure of **24** ($R^1 = SiMe_3$; $R^2 = 9$-BBN) was confirmed by X-ray analysis [45]. These 1,1-ethylboration reactions require prolonged heating up to 100°C in order to induce the intermolecular 1,1-ethylboration in the first step. Therefore, zwitterionic intermediates could not be detected, since these rearrange fast, under the reaction conditions, into the stannoles **24**. The substituent pattern for the 2-5-positions strongly suggests that the same mechanism as for other dialkyn-1-yltin compounds is responsible.

Stannacyclopentadienes: 1,1-Organoboration of Dialkyn-1-yltin Dihalides. Stannolcyclopentadienes



SCHEME 12 1,1-Ethylboration of noncyclic dialkyn-1-yltin diamides.

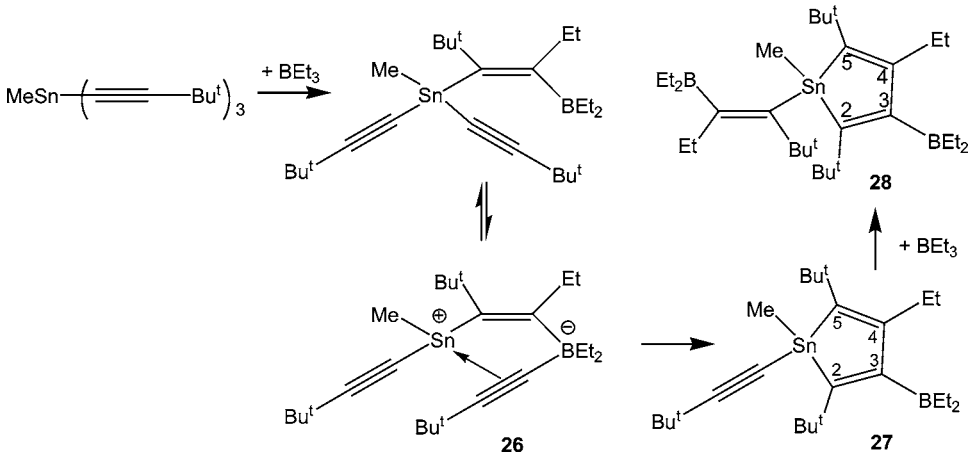


SCHEME 13 1,1-Ethylboration of dialkyn-1-yltin dichlorides and –bromides.

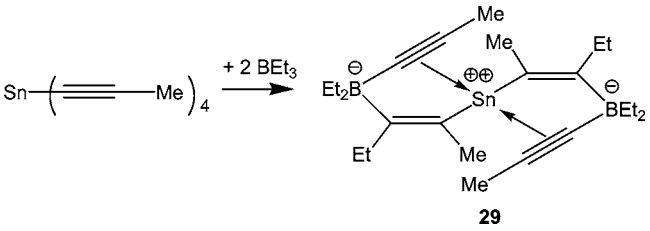
(stannoles) with two Sn—X functions (X = Cl, Br) would be ideal starting materials for almost unlimited functionalization at the tin atoms, including reduction toward tin(II) compounds. Therefore, attempts have been made to obtain dialkyn-1-yltin dihalides from exchange reactions of tetra(alkyn-1-yl)tin, $Sn(C{\equiv}C{-}R^1)_4$, with tin tetrahalides, SnX_4 [46]. This works reasonably well for $R^1 = Bu^t$, $SiMe_3$. However, 1,1-ethylboration of $X_2Sn(C{\equiv}C{-}Bu^t)_2$ is slow, and numerous unidentified side products are formed. In contrast, $X_2Sn(C{\equiv}C{-}SiMe_3)_2$ reacts smoothly with triethylborane to give the desired stannoles **25** (Scheme 13) which could be clearly identified by NMR spectroscopy in solution [47]. Unfortunately, the stannoles **25** are fairly unstable at room temperature, since insoluble SnX_2 is formed together with numerous products, some of which could be identified as siloles by their ^{29}Si NMR signals [47].

Stannacyclopentadienes: 1,1-Organoboration of Trialkyn-1-y(organo)stannanes. Trialkyn-1-yl(organo)-stannanes $R^2Sn(C{\equiv}C{-}R^1)_3$ react with trialkylboranes in the same way as other alkyn-1-yltin compounds [7,48]. Following the initial intermolecular 1,1-alkylboration, highly dynamic zwitterionic intermediates such as **26** are formed. These can rearrange by intramolecular 1,1-organoboration either to stannoles **27** or to 1-stanna-4-boracyclohexa-2,5-dienes, depending on R^1 and R. It is also possible that further intermolecular 1,1-alkyboration takes place which leads to bis(alkenyl)- or even tris(alkenyl)tin compounds which rearrange finally to stannol-3-enes. If stannoles of the type **27** are formed, there is one exocyclic alkynyl group left which can undergo 1,1-organoboration to give a stannole of the type **28** with an exocyclic alkenyl group linked to tin. A typical reaction sequence is shown in Scheme 14 for R = Et, $R^1 = Bu^t$, and R^2 = Me [48].

Stannacyclopentadienes: 1,1-Organoboration of Tetraalkyn-1-ylstannanes. Tetraethynyltin, $Sn(C{\equiv}CH)_4$, reacts readily with BEt_3 to give a complex mixture of compounds which could not be analyzed [49]. In contrast, the reaction of tetrapropyn-1-yltin with BEt_3 in a 1:2 ratio can be controlled to give a zwitterionic intermediate **29** with an unprecedented structure, in which the tin atom is side-on coordinated to two C≡C bonds (Scheme 15). The molecular structure of **29** was confirmed by X-ray analysis [50]. The surroundings of the tin atom correspond to a strongly distorted tetrahedron (centers of the C≡C bonds and the two olefinc carbon atoms), the Sn—C σ bonds form an angle of 140.9(1)°, the C≡C bonds are slightly elongated (122.2(5) and 122.7(5) pm), when compared with alkynes, and the deviation from linearity of the B—C≡C—Me units are small (BCC:172.7(3)°, CCC: 175.8(3)°). The compound **29** decomposes above −20°C to give a complex mixture of products



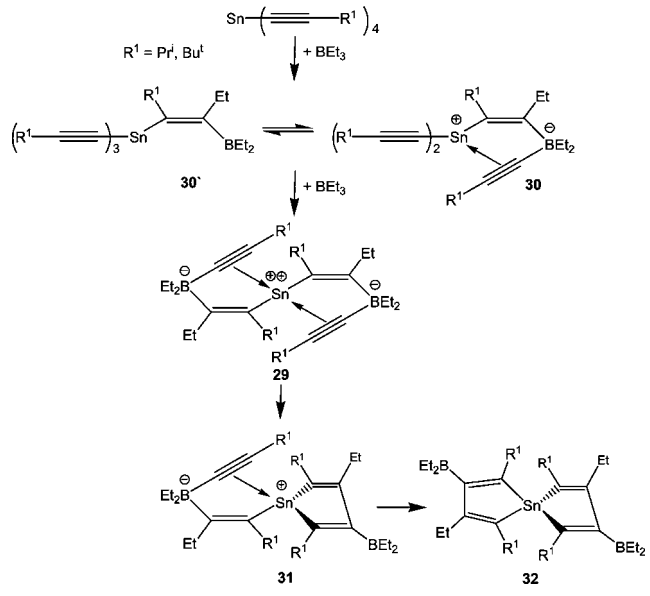
SCHEME 14 An example for 1,1-ethylboration of trialkyn-1-yltin compounds.



SCHEME 15 1,1-Organoboration of tetraalkyn-1-ylstannanes: Formation of a zwitterionic intermediate with two alkynyl groups coordinated side-on to tin.

which has been partly analyzed [51]. Although stannoles are present in this mixture, they could not be isolated in pure state. If triisopropylborane is used instead of BEt_3, clean formation of a spirotin compound is observed with two six-membered rings [52].

With other substituents R^1 in $Sn(C{\equiv}C{-}R^1)_4$ such as $R^1 = Et$, Pr^i, Bu, Bu^t, or $SiMe_3$, the results were excellent with respect to stannole formation in the reactions with BEt_3 [53]. In these cases, spirotin compounds (1,1′-spirobistannoles) were obtained in essentially quantitative yield. For $R^1 = Pr^i$ or Bu^t, a number of intermediates (**29** ($R^1 = Pr^i$, Bu^t), **30**, **31**) could be identified [53], and the final products were the spirotin compounds of type **32** (Scheme 16). The intermediates of type **30**, the first products of 1,1-organoboration of $Sn(C{\equiv}C{-}R^1)_4$, are highly fluxional with respect to the bridging alkynyl group. In solution, there is also a fluxional behavior of the intermediates **29**, whereas the intermediates **31** are less fluxional.



SCHEME 16 From tetraalkyn-1-ylstannanes to "1,1-spirobistannoles" by 1,1-organoboration reactions.

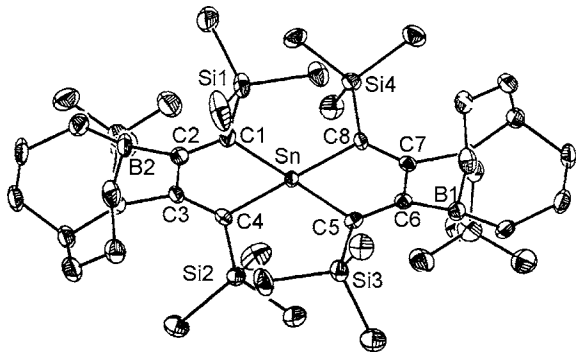


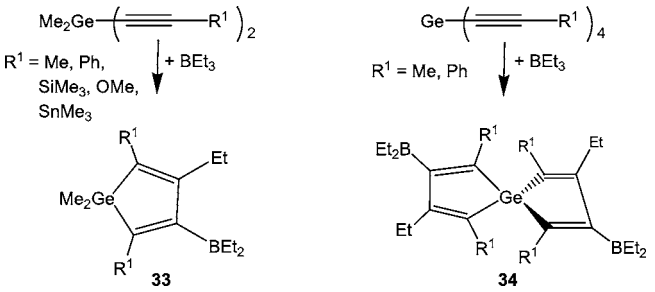
FIGURE 4 Molecular structure of the "1,1′-spiro-bistannole" **32.** Selected bond lengths (pm) and angles (°): Sn–C(1) 215.0/4), Sn–C(4) 216.5(4), C(1)–C(2) 133.4(5), C(2)–C(3) 143.0(5), C(3)–C(4) 135.1(6); C(1)–Sn–C(4) 84.2(2), C(1)–Sn–C(5) 117.4(2), C(1)–Sn–C(8) 126.3(2), Sn–C(1)–C(2) 106.9(3), C(1)–C(2)–C(3) 121.9(4), C(2)–C(3)–C(4) 118.7(4).

When $Sn(C{\equiv}C{-}SiMe_3)_4$ was treated with an excess of neopentyl-9-BBN, the molecular structure of the resulting spirotin compound could be determined by X-ray analysis [54] (Fig. 4). As in the case of **9** [23], the 9-BBN system is expanded by two carbon atoms. The surroundings of the tin atom can be described as an extremely distorted tetrahedron, since the endocyclic bond angles at the tin atom are only 84.2(2)°. Because of the bulkiness of the groups present, the stannole rings deviate slightly from planarity.

Germacyclopentadienes

Alkyn-1-ylgermanes react with triorganoboranes in the same way as their tin and lead congeners [7]. Since the reactions require heating from 60 to 80°C for several hours, the isolation or detection of zwitterionic intermediates was not possible so far. Both dialkyn-1-yl(diorgano)germanium, $Me_2Ge(C{\equiv}C\text{-}R^1)_2$, and tetraalkyn-1-ylgermanium compounds, $Ge(C{\equiv}C{-}R^1)_4$, have been studied in their reactivity toward triethylborane [51]. This has led to the germoles **33** [7,55] and spirogermanium compounds (1,1′-spirobigermoles) **34** [51] (Scheme 17). In the case of $Me_2Ge(C{\equiv}C{-}R^1)_2$ the germole **33** was also obtained for $R^1 = OMe$ [56]. This is noteworthy, since the 1,1-ethylboration of the analogous tin compound $Me_2Sn(C{\equiv}C\text{-}OMe)_2$ was accompanied by extensive decomposition [56].

Starting from $Me_2Ge(C{\equiv}C{-}SnMe_3)_2$ [57], the 1,1-ethylboration proceeds primarily by cleavage of the more reactive $Sn{-}C{\equiv}$ bond(s). Consecutive 1,1-ethylboration and 1,1-deethylboration take place until the stereochemistry is favorable for irreversible ring closure to the germole ring.

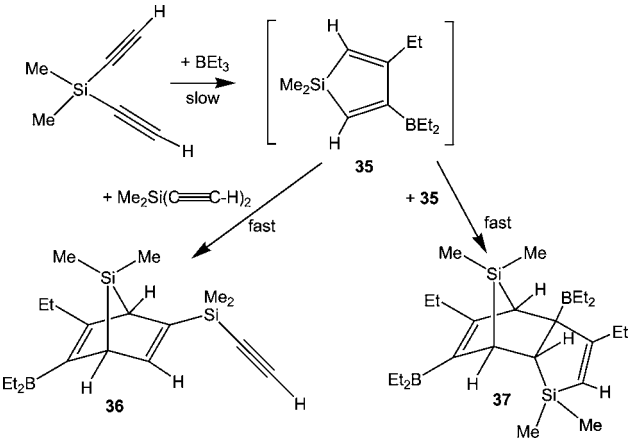


SCHEME 17 Germacyclopentadienes by 1,1-organoboration of dialkyny-1-ylgermanium and tetraalkyn-1-ylgermanium compounds.

Silacyclopentadienes

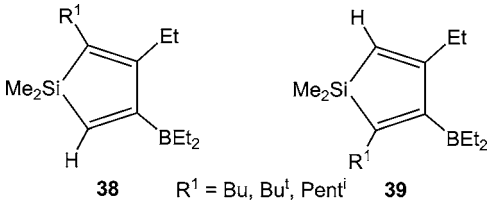
General Remarks. The reactivity of the Si—C≡ bonds toward triorganoboranes is relatively low [7]. That means most of the 1,1-organoboration reactions of alkyn-1-ylsilanes require rather harsh reaction conditions such as heating of the reaction mixtures at 100–110°C for several days or even weeks. Therefore, the starting materials as well as the desired products have to be stable under these conditions. This is not a problem with most alkyn-1-ylsilanes. However, numerous triorganoboranes decompose at elevated temperatures by 1,2-dehydroboration forming boron hydrides [58]. Then, 1,2-hydroboration of the alkyn-1-ylslianes may compete with 1,1-organoboration, and this can give rise to complex mixtures of products. Triethylborane is well suited for these 1,1-orgaboborations, since 1,1-dehydroboration does not take place below 200°C. Furthermore, the desired products of 1,1-organoboration, in the present case, silacyclopentadienes (siloles) possess limited stability, since it is well known that siloles can readily undergo [4+2]cycloadditions to give dimers or even more complex systems [1]. This can happen if the substituents at the silole ring in 2–5-positions are not bulky. If the substituents are bulky, other rearrangements are conceivable, leading to decomposition accompanying the formation of the siloles. However, siloles are an important class of compounds [1–4], and it is worthwhile to find and optimize conditions which allow the synthesis of a variety of siloles with a choice of different substituents at the silicon and also in 2–5-positions.

Silacyclopentadienes: 1,1-Ethylboration of Dialkyn-1-yl(dimethyl)silanes. Diethynyl (dimethyl)-silane, $Me_2Si(C{\equiv}C{-}H)_2$, reacts slowly at 80–90°C with triethylborane to give the silole **35** which however, reacts fast with the starting alkyne by [4+2]cycloaddition to **36**, and, if the concentration of the starting alkyne is decreasing, it dimerizes to



SCHEME 18 1,1-Ethylboration of diethynyl(dimethyl)silane, followed by [4+2]cycloadditions.

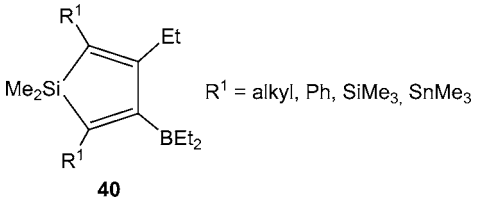
37 [59] (Scheme 18). NMR spectra indicate that isomers of **36** and **37** may also be present, and that there are numerous other compounds formed in small amounts, in particular if the reaction time increases. Apparently, at least one substituent other than hydrogen in 2,5-positions is needed to stabilize the silole. This was shown by the 1,1-ethylboration of $Me_2Si(C{\equiv}C{-}H)C{\equiv}C{-}R^1$ ($R^1 = Bu$, $Pent^i$, Bu^t), where the siloles **38** and **39** (as mixtures of isomers) can be detected prior to [4+2]cycloadditions with the starting alkyne. This [4+2]cycloaddition plays a minor role for $R^1 = Bu^t$, and in this case the isomer **39** is formed almost exclusively, since the reactivity of the Si—C≡C—Bu^t unit toward the initial intermolecular 1,1-ethylboration is much lower than that of the Si—C≡C—H unit [59].



Formulae **38** and **39**

The 1,1-ethylboration of dialkyn-1-yl(dimethyl)-silanes of the type $Me_2Si(C{\equiv}C{-}R^1)_2$ with R^1 = alkyl, Ph, $SiMe_3$ [60], $SnMe_3$ [57] leads selectively to the siloles **40**. Since prolonged heating at about 100°C is required (excerpt of $R^1 = SnMe_3$), intermediates cannot be detected. The substituent pattern for the 2–5-positions is exactly analogous to that of stannoles, for which the mechanistic details have been elucidated [7,24,25]. In the case of $R^1 = SiMe_3$, it is not clear which Si—C≡ bond is attacked first. In any case, 1,1-ethylboration and 1,1-deethylboration take

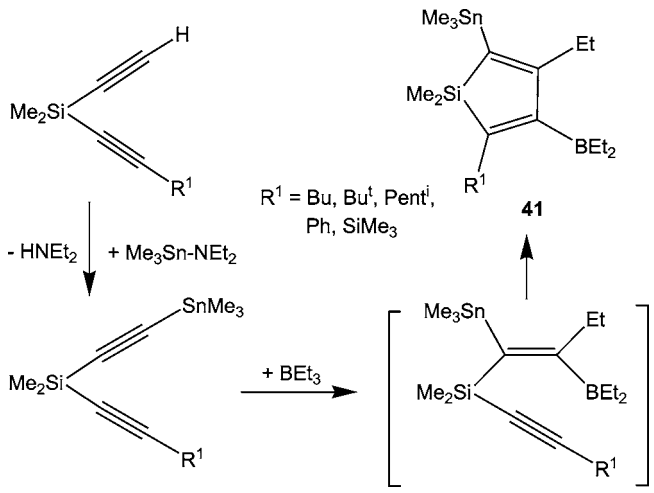
place until the stereochemistry is favorable for irreversible ring closure. In the case of $R^1 = SnMe_3$, there is no doubt that the Sn—C≡ bond(s) are cleaved at the beginning of 1,1-ethylboration [57]. Again, 1,1-ethylboration and 1,1-deethylboration occur until a configuration at the C=C bond is reached in order to close the ring.



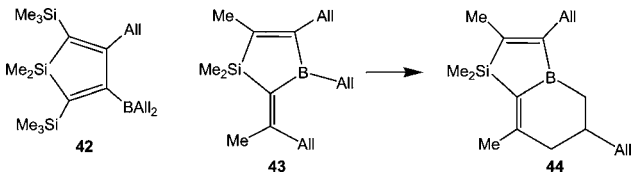
40

Formula **40**

Dialkyn-1-yl(dimethyl)silanes bearing different alkyn-1-yl groups are kinetically stable, and can be prepared in good yields by stepwise synthesis [61]. The availability of $Me_2Si(C{\equiv}C{-}R^1)C{\equiv}C{-}H$ opens a convenient access to $Me_2Si(C{\equiv}C{-}R^1)C{\equiv}C{-}SnMe_3$. In the latter, the high reactivity of the Sn—C≡ bond toward triorganoboranes, when compared to the Si—C≡ bond, allows to carry out the 1,1-organoboration under mild conditions (–78°C to room temperature), since the energy of activation for the final intramolecular 1,1-vinylboration involving the Si—C≡ is also not too high. These reactions afford selectively the siloles **41** in essentially quantitative yield [61] (Scheme 19).



SCHEME 19 Formation of dialkyn-1-yl(dimethyl)silanes with alkynyl groups of greatly different reactivity toward triorganoboranes: generation of silacyclopentadienes under mild reaction conditions.

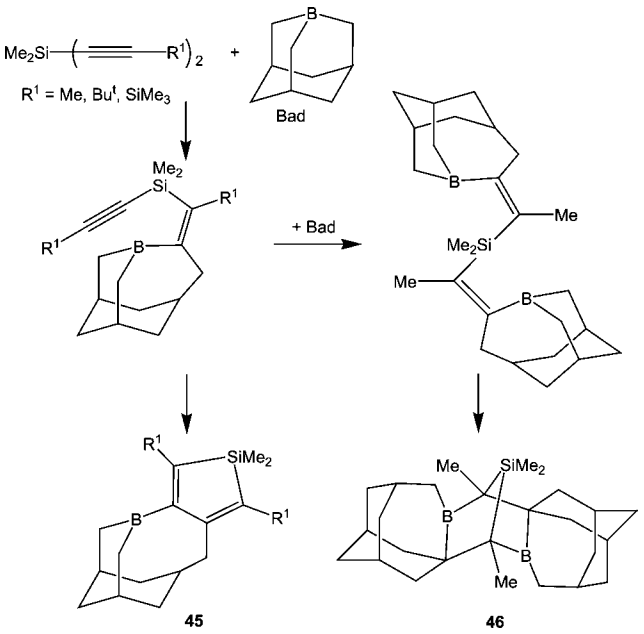


SCHEME 20 1,1-Allylboration versus 1,2-allylboration: competition may lead to heterocycles other than siloles.

Silacyclopentadienes: 1,1-Organoboration of Di(alkyn-1-yl)dimethylsilanes Using More Reactive Triorganoboranes, Such as Triallylborane, 1-Boraadamantane and Trivinylboranei. Triallylborane ($BAll_3$) [62] and in particular 1-boraadamantane (Bad) [63] are known to be much more reactive than triethylborane. This is also true for organoboration reactions which take place for Bad already at room temperature [64,65] and for $BAll_3$ after gentle heating at 50–60°C [65,66]. In the case of $BAll_3$ (Scheme 20), the 1,2-allylboration [62] can compete with 1,1-allylboration [66,67]. Thus, the reaction of $Me_2Si(C{\equiv}C{-}SiMe_3)_2$ with $BAll_3$ affords selectively the silole **42**, the expected result of consecutive 1,1-organoborations [68]. In contrast, the reaction of $Me_2Si(C{\equiv}C{-}Me)_2$ with $BAll_3$ leads first to the heterocycle **43** which then undergoes an intramolecular 1,2-allylboration [62] to give the bicyclic **44** [68]. The formation of **43** can be explained assuming a 1,1,allylboration to take place for the first Si—C≡C—Me unit, followed by an intramolecular 1,2-allylboration of the second Si—C≡C—Me unit [68].

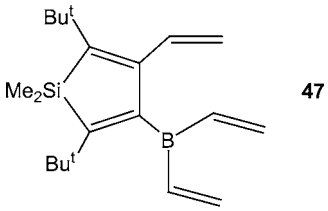
In the case of 1-boraadamantane, the reaction with dialkyn-1-yl(dimethyl)silanes $Me_2Si(C{\equiv}C{-}R^1)_2$ ($R^1 = Me$, Bu^t, $SiMe_3$) is finished at room temperature after several hours to give the tetracyclic siloles **45** [69] (Scheme 21). Solely for $R^1 = Me$, this 1,1-organoboration is nonselective, since a 7-sila-2,5-diboranorbornane derivative **46** is also obtained [69]. The compound **46** is the result of twofold 1,1-organoboration of the alkyne, followed by rearrangement; its molecular structure is analogous to that of a related tin derivative which has been studied by X-ray analysis [69]. Considering the enormous reactivity of the 1-boraadamantane, a second intermolecular 1,1-organoboration can easily compete with the intramolecular 1,1-organoboration. Indeed, the reaction of Bad with di(alkyn-1-yl)tin derivatives, where the Sn—C≡ bonds are much more labile than the Si—C≡ bonds, leads mainly to the 7-stanna-2,5-diboranorbornanes [69].

Trivinylborane appears to be slightly more reactive than triethylborane in 1,1-organoboration reactions [70]. However, its complete reaction with $Me_2Si(C{\equiv}C{-}Bu^t)_2$ still requires heating at 100–110°C for 2 h. This organoboration is accompanied by



SCHEME 21 1-Boraadamantane reacts with alkyn-1-ylsulanes already at room temperature, and a second intermolecular 1,1-organoboration may well compete with intramolecular 1,1-vinylboration.

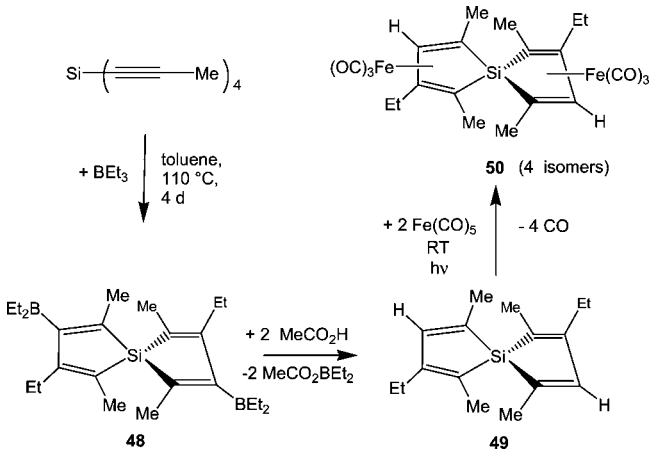
partial decomposition of trivinylborane. The fairly insoluble decomposition products can be separated by filtration to leave the pure silole **47** [70].



Formula **47**

Silacyclopentadienes: 1,1-Organoboration of Tetraalkyn-1-ylsilanesi. The reaction of tetraalkyn-1-ylsilanes $Si(C{\equiv}C{-}R^1)_4$ in boiling toluene in the presence of a large excess of triethylborane leads to spirosilanes (1,1′-spirobisoles) **48** in the cases of $R^1 = Me$, Ph [51] (Scheme 22). Intermediates were proposed, in which only one, two, or three alkyn-1-yl groups had reacted. Treatment of **48** ($R^1 = Me$) with acetic acid affords the spirosilane **49**, of which the $Fe(CO)_3$ complexes **50** were prepared. One of the four diastereomers could be separated, and this meso-isomer was characterized by an X-ray structural analysis [51] (Fig. 5).

For $R^1 = Bu^t$, the 1,1-ethylboration with BEt_3 can be carried out to give almost (>90%) selectively the



SCHEME 22 1,1-Organoboration of tetrapropyn-1-ylsilane with BEt_3 affords "1,1-spiro-bisiloles" which can be readily converted into various derivatives.

silole **51** [71] (Scheme 23). The analogous silole **52** can be obtained for $R^1 = SiMe_3$ and 9-ethyl-9-borabicyclo[3.3.1]nonane (Et-9-BBN) [71]. This borane is stable at 110°C for prolonged periods, and therefore, it can be used in 1,1-organoboration reactions of alkyn-1-ylsilanes.

Silacyclopentadienes: 1,1-Organoboration of Dialkyn-1-ylsilanes Containing Si—H Functions. The scope of silole chemistry is greatly enhanced if by introducing reactive functions at the silicon atom. It proved straightforward so far to use 1,1-organoboration of dialkyn-1-yl(methyl)silanes $Me(H)Si(C{\equiv}C{-}R^1)_2$ in the same way as the dimethylsilanes. The reactions with triethylborane proceed

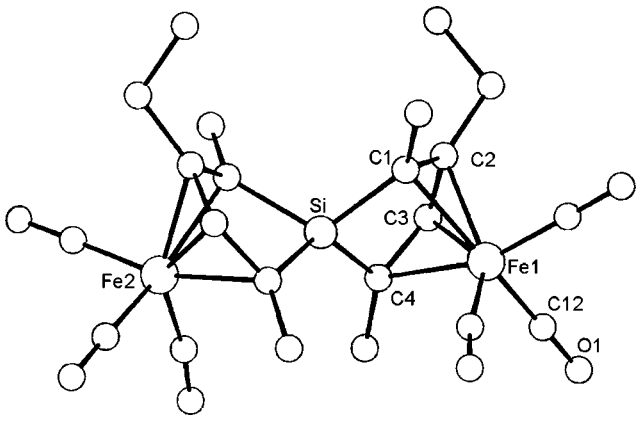
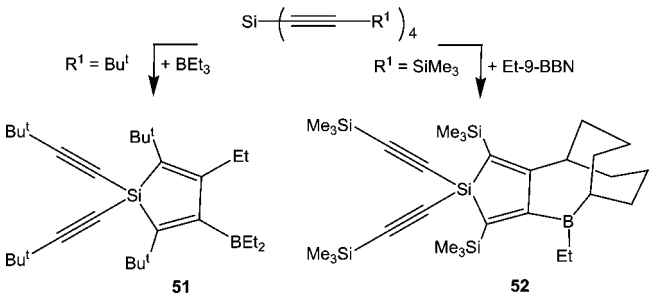


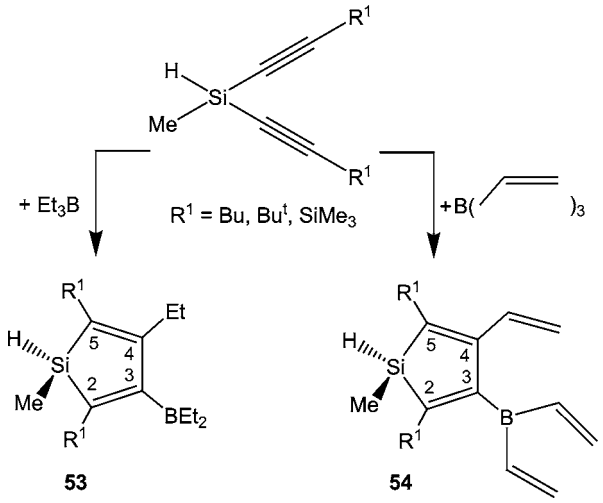
FIGURE 5 Molecular structure of **50**, the bis(tricarbonyliron) complex of a "1,1-spiro-bisilole". Selected bond lengths (pm) and angles (°): Si–C(1) 182.8(6), Si–C(4) 186.0(5), C(1)–C(2) 143.7(8), C(2)–C(3) 141.3(8), C(3)–C(4) 141.7(8), Fe(1)–C(1) 214.6(5), Fe(1)–C(3) 205.6(5), C(1)–Si–C(9) 114.0(2).



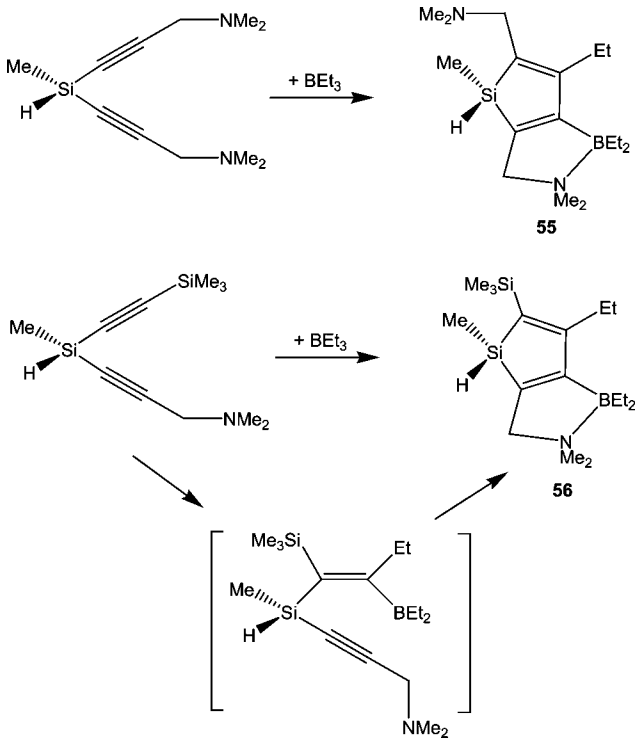
SCHEME 23 The 1,1-organoboration of tetraalkyn-1-ylsilanes with bulky groups R^1 into siloles bearing two alkyn-1-yl groups at silicon.

somewhat faster which can be explained by the reduced steric hindrance for the initial attack of the borane at the Si—C≡ bond. Examples are given in Scheme 24 for the siloles **53**, using BEt_3, and **54**, using trivinylborane [70]. The boryl group in **53** ($R^1 = Bu$) could be removed by the reaction with ethanolamine, leaving the Si—H function untouched [70].

It was also shown that siloles can be prepared by 1,1-ethylboration if there are the Si—H function and an amino functions in R^1 ($R^1 = CH_2NMe_2$) (Scheme 25). In this case, a coordinative N—B bond is present in the silole **55** [72]. The kinetic stability of the Si—C≡ bond allows us to prepare numerous dialkyn-1-ylsilanes bearing different alkyn-1-yl groups. As shown in Scheme 25, almost selective (>85%) formation of the silole **56** was found, when $Me(H)Si(C{\equiv}C{-}CH_2NMe_2)C{\equiv}C{-}SiMe_3$ was heated



SCHEME 24 Examples of 1,1-organoboration using triethylborane or trivinylborane, leading to siloles bearing an Si–H function.

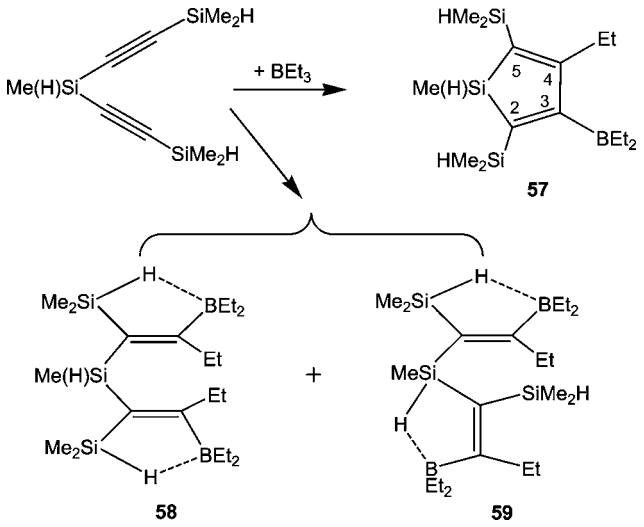


SCHEME 25 Examples of 1,1-organoboration, using triethylborane, leading to siloles bearing an Si–H function in 1-position and the CH_2-NMe_2 group in 2,5-positions.

with an excess of BEt_3. This indicates that preferably the Si—C≡ bonds in the Si—C≡C—Si unit react first with BEt_3, and then the intramolecular vinylboration takes place to give the silole. The analogous reaction of $Me(H)Si(C{\equiv}C{-}CH_2NMe_2)C{\equiv}C{-}Bu$ afforded a 1:1 mixture of silole isomers, because the reactivity of both Si—C≡ bonds toward BEt_3 is comparable [72].

In the presence of Si—H functions in three silyl groups, 1,1-ethylboration also leads to a silole **57** along with bis(alkenyl)silanes **58** and **59**, in which the stereochemistry is unfavorable for ring closure [73] (Scheme 26). It appears that in these bis(alkenyl)silanes, electron-deficient Si—H—B bridges stabilize the configurations at the C=C bonds and prevent 1,1-deethylboration under the experimental conditions (15 h at 100°C). The existence of such Si—H—B bridge has been firmly established in particular by ^{29}Si NMR spectroscopy [67,74,75] in solution and, in one case, also by X-ray structural analysis [76].

1,6-Dihydro-1,6-disilapentalenes and Other Fused Heterocycles: 1,1-Organoboration of Triynes and Tetraynes. The kinetic stability of Si—C≡ bonds invites for the synthesis of triynes [77] or tetraynes [78], where the C≡C bonds are separated by two or more $SiMe_2$ units (or $SiMe_2$ and $SnMe_2$ units),

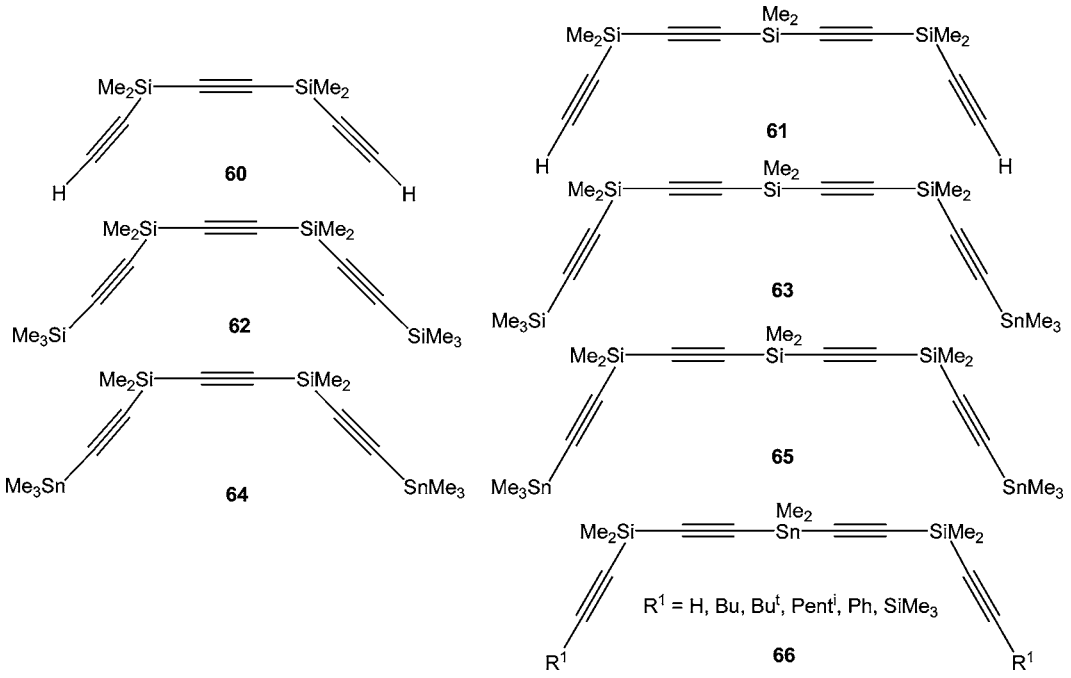


SCHEME 26 A silacyclopentadiene with three Si–H functions; loss of stereoselectivity as a result of electron-deficient Si–H–B bridges.

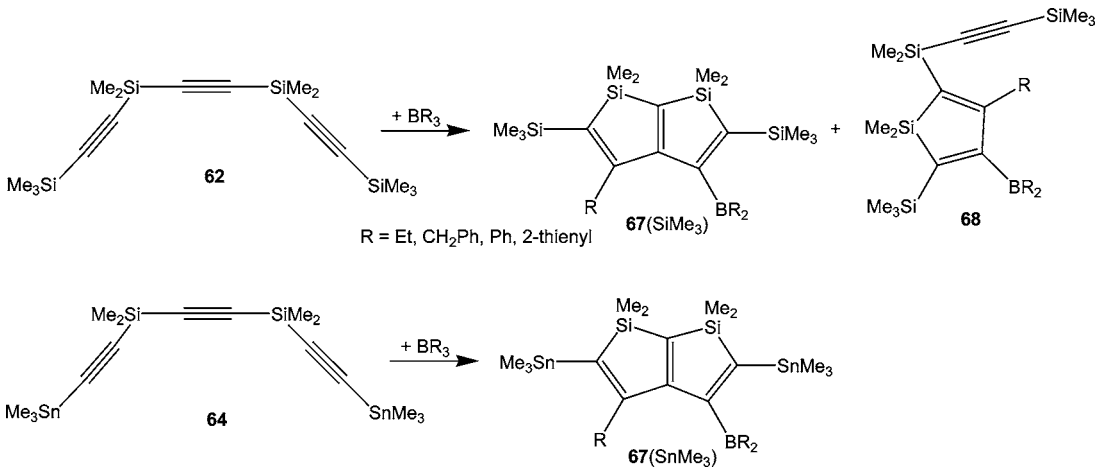
and the terminal positions in the molecule can be hydrogen (**60**,**61**), $SiMe_3$ (**62**,**63**,**66**) or $SnMe_3$ (**63–65**), or organyl groups (**66**) (Scheme 27). 1,1-Organoboration of such triynes or tetraynes can lead to novel siloles and fused heterocycles. Considering the mechanism of 1,1-organoboration, the structure of the respective products will depend on the site, where 1,1-organoboration starts, and whether intermolecular 1,1-organoboration is followed immediately by intramolecular 1,1-organoboration. The polyynes with terminal hydrogen (**60**,**61**) react with triethylborane in boiling toluene. However, complex mixtures are formed in both cases [77,78]; this can be understood considering the results of the 1,1-ethylboration of diethynyl(dimethyl)silane [59].

In contrast, the reaction of the triyne **62** with triorganoboranes is almost selective, leading to 1,6-dihydro-1,6-disilapentalene derivatives **67** ($SiMe_3$) together with small amounts of the silole **68** which is the result of the initial attack at the central Si—C≡C—Si unit [77]. The formation of 1,6-dihydro-1,6-disilapentalene derivatives **67** ($SnMe_3$) is highly selective, since the Sn—C≡ are much more reactive than Si—C≡ bonds toward triorganoboranes [77] (Scheme 28).

These results for the triynes were encouraging with regard to the 1,1-organoboration of tetraynes [78]. The asymmetrically substituted tetrayne **65** should react with BEt_3 by an intermolecular 1,1-ethylboration at the reactive Sn—C≡ bond, followed by a series of intramolecular 1,1-organoboration reactions (Scheme 29). Monitoring of the progress of the reaction by NMR spectroscopy allowed to detect the intermediates **69** and **70**. In the final step, which required heating at 110°C in toluene for 72 h, a mixture of the fused heterocycles **71** and **72** (ratio 3:2) is formed. Apparently, because of steric repulsion these harsh reaction conditions are needed, and the result is the alternative reaction to a six-membered



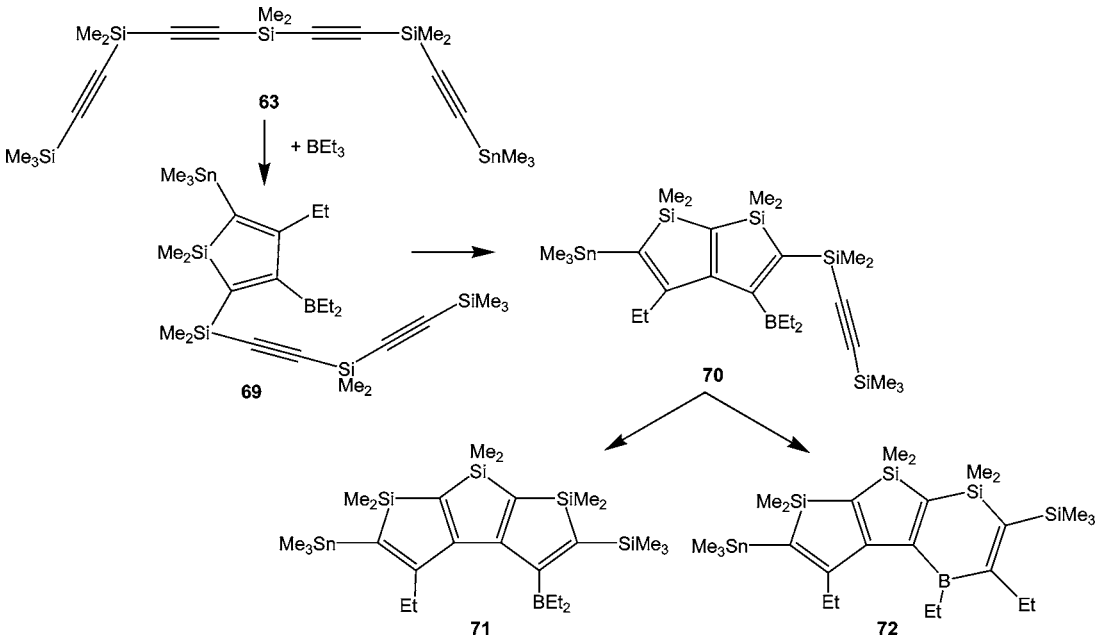
SCHEME 27 Examples of triynes and tetraynes with Si–C≡ and Sn–C≡ bonds.



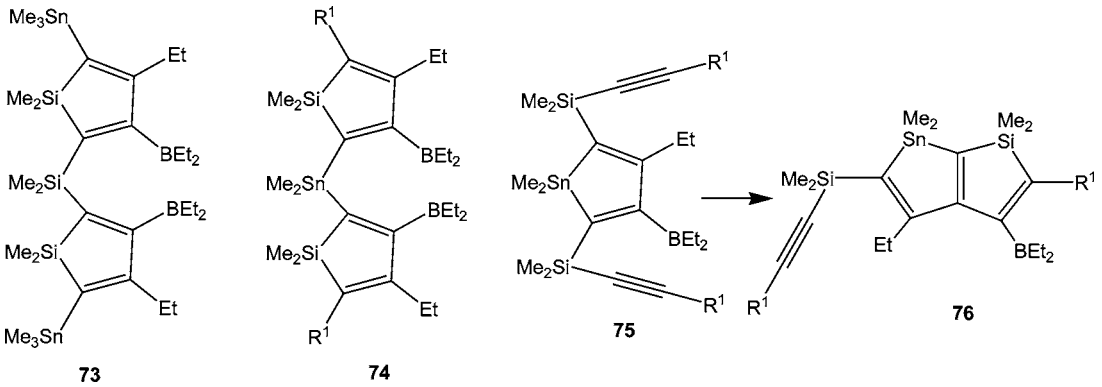
SCHEME 28 1,1-Organoboration of triynes: a route to 1,6-dihydro-1,6-disilapentalenes.

heterocycle in **72** [78]. In principle, one could expect similar products from the reaction of the tetrayne **65** with BEt_3. However, in this case it was not possible to prevent the simultaneous attack of BEt_3 at both Sn—C≡ bonds, and this resulted in the selective formation of the "bis(silolyl)silane" 73 [78]. If there is an $SnMe_2$ group in the center of the tetrayne as in **66**, the 1,1-organoboration leads to mixtures of compounds such as **74** (analogous to **73**), and a stannole of type **75** which can rearrange into 1,6-dihydro-1-stanna-6-silapentalene derivatives **76** [78] (Scheme 30).

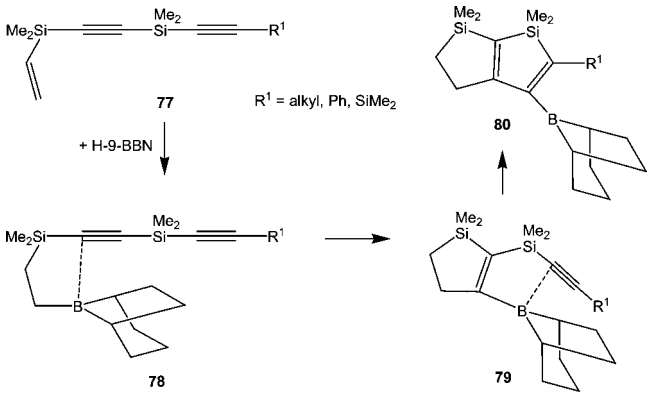
Silacyclopentadienes: Combination of 1,2-Hydroboration and 1,1-Organoboration. It is well known that olefinic double bonds are more reactive with respect to 1,2-hydroboration when compared with C≡C triple bonds [79]. This fact can be exploited for compounds of the type **77** to generate a triorganoborane such as **78** first by selective 1,2-hydroboration of the vinyl group. In **78**, suitable Si—C≡C units are available for intramolecular 1,1-organoboration reactions to give first **79** followed by the final formation of a bicyclic silacyclopentadiene **80** (Scheme 31) [80].



SCHEME 29 1,1-Otganoboration of trimethylstannyl-substituted tetrayne: a route to 1,6-dihydro-1,6-disilapentalenes and other fused heterocycles.



SCHEME 30 Some products formed by 1,1-prganoboration of tetraynes.



SCHEME 31 Siloles via combination of 1,2-hydroboration, followed by consecutive intramolecular 1,1-organoboration reactions.

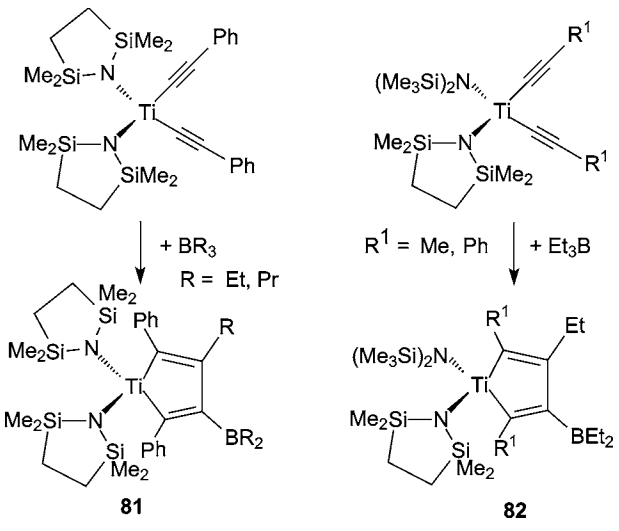
METALLACYCLOPENTADIENES WITH M = Ti, Pt

Titanacyclopentadienes: 1,1-Organoboration of Dialkyn-1-yl-bis(amino)titanium Compounds

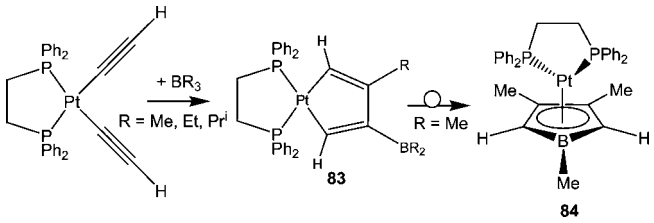
There are numerous reports about titana- and zirconacyclopentadienes, in which the titanium bears two η^5-cyclopentadienyl ligands [81–83]. We have set out to prepare titanacyclopentadienes with amido ligands at titanium. First, a convenient synthesis of bis(amido)titanium dichlorides was developed [84,85], and these dichlorides were converted into dialkyn-1-yltitanium compounds which were then treated with trialkylboranes for 1,1-organoboration [86]. The titanacyclopentadienes **81** and **82** (Scheme 32) cannot be isolated in pure state. However, their ^{13}C NMR spectra are typical and prove the proposed pattern of substituents. The analogy to the metalloles of group 14 elements is obvious, and therefore, the mechanism of the titanacyclopentadiene formation should be comparable.

Platinacyclopentadienes: 1,1-Organoboration of cis-Diethynyl-bis(phosphane)-platinum(II)

Various di(alkyn-1-yl)bis(phosphane)platinum(II) complexes [87,88] have been studied in 1,1-organoboration reactions. Although, at a first glance, transition metal fragments containing platinum should be ideal candidates for side-on coordination to C≡C bonds, giving rise to the formation of zwitterionic intermediates as found for tin and lead, such species have not been detected so far. In the case of the diethynyl derivatives, the 1,1-alkylboration leads selectively to platinacyclopentadienes **83** [89,90] (Scheme 32) which have the same pattern of substituents in 2–5-positions as the corresponding siloles and stannoles. Therefore, it is suggested that the analogous mechanism is



SCHEME 32 Formation of dialkyn-1-yltitanium diamides, followed by 1,1-organoboration to give titanacyclopentadienes.



SCHEME 33 Formation of platinacyclopentadienes by 1,1-organoboration, followed by intramolecular rearrangement into a borole complex.

in operation. This means that the intermolecular 1,1-organoboration proceeds by cleavage of the Pt—C≡ bond, formation of an unstable zwitterionic intermediate which rearranges fast into the platinacyclopentadiene ring. The complex **83** (R = Me) slowly rearranges further into a borole complex **84** [90], where the bis(phosphane)platinum fragment is centered above the BC_4 ring. Borole complexes are well known for many transition metal fragments [91].

All attempts to use other alkyn-1-yl groups —C≡C—R^1 (R^1 = Me, Bu^t, C(Me)=CH_2, Ph, $SiMe_3$) also together with a chelating diphosphane other than dppe (e.g., dmpe, depe) in 1,1-organoboration reactions with BEt_3 did not lead to platinacyclopentadienes so far [92]. Other combinations of ligands at platinum such as two ethynyl groups together with the chelating phosphane Ph_2P—C_7H_7 (C_7H_7 = 1-cyclohepta-2,4,6-trienyl) also did not give a platinacycloentadiene when the reaction with BEt_3 was carried out [93].

CHARACTERIZATION OF METALLACYCLOPENTADIENES BY MULTINUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

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

^{1}H and ^{13}C NMR measurements of metallacyclopentadienes provide important information on structure and molecular dynamics as usual for organometallic compounds [94]. ^{1}H NMR spectra are particularly useful for metallacyclopentadienes prepared by 1,1-organoboration of ethynylmetal compounds, since the signals of the olefinic ^{1}H nuclei in the products are useful for structural assignments, as shown for the platinacyclopentadiene **79** (R = Et) (Fig. 6).

In the case of the metallacyclopentadienes reported here, there is a typical pattern of ^{13}C NMR signals in the region for olefinic carbon atoms (Fig. 7): three sharp ^{13}C NMR signals and one broad. The latter belongs to the carbon atom linked to boron,

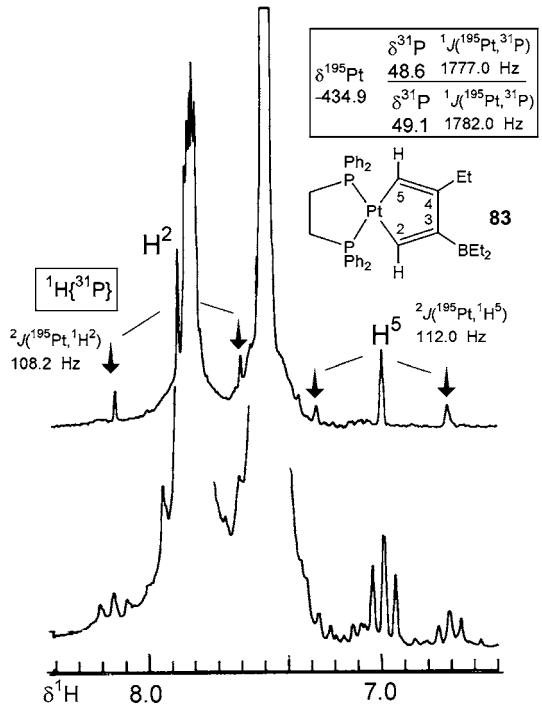


FIGURE 6 200 MHz ^{1}H NMR spectra of the platinacyclopentadiene **83**, showing the range for aromatic and olefinic protons. It is shown that ^{31}P decoupling is extremely useful for the interpretation of the spectra. In addition, relevant ^{31}P and ^{195}Pt NMR data are given in the insert.

and the increase in line width is the typical result of partially relaxed ^{13}C—^{11}B spin–spin coupling owing to the efficient quadrupole-induced spin relaxation of ^{11}B nuclei (I = 3/2) [95].

If the metals possess magnetically active isotopes of appreciable natural abundance with I = 1/2, such as ^{29}Si (4.7%), $^{117/119}$Sn (7.61 and 8.58%), ^{207}Pb (22.6%), and ^{195}Pt (33.8%), the sharp ^{13}C NMR signals are accompanied by satellites (Fig. 7) with the respective intensities owing to the coupling constants ^1J(M,^{13}C) and ^2J(M,^{13}C), all of which are useful for assignment purposes. The chemical shifts δ^{13}C for the olefinic carbon atoms in metallacyclopentadienes are in the usual range [96,97], governed by known substituent effects. Noteworthy in this context is the extreme deshielding effect exerted by titanium [98] adjacent to the olefinic carbon atoms in 2,5-positions which serves conveniently for the structural assignment in the compounds **81** and **82** [86].

^{11}B NMR Spectroscopy

Although the ^{11}B nucleus has a sizeable quadrupole moment (I = 3/2), NMR measurements are straightforward and provide meaningful results [99]. The

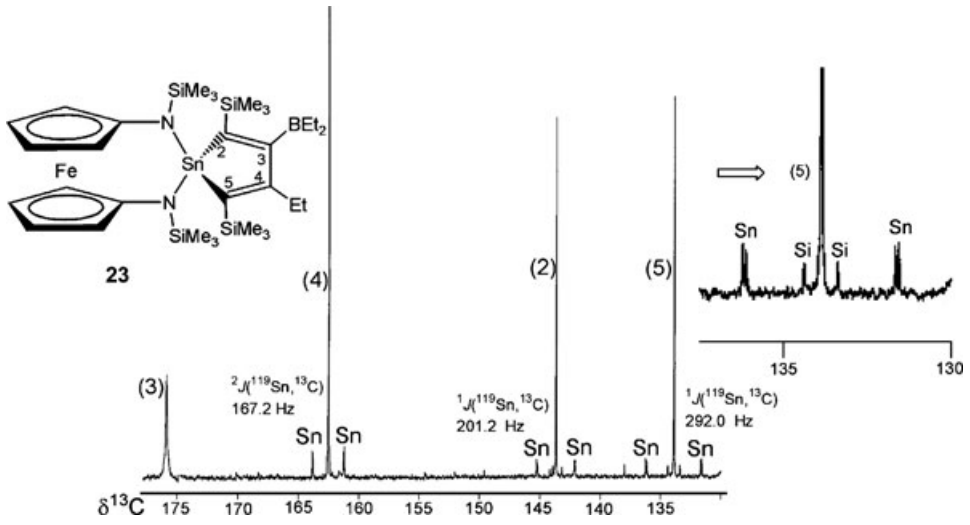


FIGURE 7 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the spirotin compound **23**, showing the range for the olefinic carbon atoms. There are four ^{13}C NMR signals, three sharp and one broad (C(3), bonded to boron). The sharp signals are accompanied by satellite signals due to the presence of the ^{29}Si and $^{117/110}Sn$ isotopes. The relative magnitudes of the coupling constants $^nJ(^{117/119}Sn,^{13}C)$ and $^nJ(^{29}Si,^{13}C)$ helps for the assignment.

^{11}B NMR signals of the metallacyclopentadienes bearing the diorganoboryl group on 3-postion are rather broad ($h_{1/2} > 400$ Hz), and the $\delta^{11}B$ values ($\delta^{11}B(Et_2O{-}BF_3) = 0$) are in the region typical for three-coordinate boron atoms linked to three carbon atoms ($\delta^{11}B$ from +70 to +88 ppm) [99]. If the boron atoms become tetra-coordinate (e.g., in **56**), this is indicated by a marked increase in ^{11}B nuclear magnetic shielding [72,99]. Since in most cases the $\delta^{11}B$ values of the starting triorganoboranes and the metallacyclopentadienes are similar, the change in the line widths of the ^{11}B NMR signals has to be considered. Both the increase in the molecular weight and the lower local symmetry around the boron atoms cause a significant increase in the line widths of the ^{11}B NMR signals for the products when compared to that for the respective triorganoborane. Moreover, when the progress of the 1,1-organoboration reactions is monitored by ^{11}B NMR, the presence of unstable zwitterionic intermediates becomes readily apparent, since these give rise to fairly narrow ^{11}B NMR signals with $\delta^{11}B$ values from −5 to −10 ppm in the typical range (at low frequencies) for tetra-coordinate boron atoms, close to the range for tetraorganoborates [6,13,24,25,99].

^{29}Si NMR Spectroscopy

The presence of SiMe or SiH groups in relevant compounds studied makes it possible to use polarization transfer techniques [100] (e.g., INEPT, HSQC) for studying reaction solutions and final products even for diluted solutions. The ^{29}Si NMR signals ($\delta^{29}Si(SiMe_4) = 0$) of alkyn-1-ylsilanes are always at low frequencies when compared to those of the products. In general, the ^{29}Si resonances of silacyclopentadienes are shifted toward high frequencies relative to noncyclic alkenylsilanes or six-membered rings such as 1-sila-4-bora-cyclohexa-2,5-dienes. This trend is further amplified if there are organometallic substituents such as $SiMe_3$ or $SnMe_3$ groups in 2,5-positions. Since $SiMe_3$ groups serve frequently as substituents for metallacyclopentadienes, their ^{29}Si NMR signals are particularly helpful to establish the formation of intermediates and their conversion into the final products. This is shown in Fig. 8 for the progress in the formation of plumbole **5** [13] (Scheme 2). The ^{29}Si NMR signals are accompanied by ^{207}Pb satellites due to $^2J(^{207}Pb, ^{29}Si)$ and $^3J(^{207}Pb, ^{29}Si)$ across the C≡C bond in the zwitterionic intermediate **4**. The information from the ^{29}Si NMR spectra, in this case, is further complemented by data from ^{207}Pb NMR spectra (vide infra).

The characterization of silacyclopentadienes by ^{29}Si NMR spectra cannot always be based on the $\delta^{29}Si$ values, since these data are frequently in a range typical of many organosilanes. However, the observation of satellite signals due to $^{29}Si{-}^{13}C$, or in some cases $^{29}Si{-}^{29}Si$, and/or $^{117/119}Sn{-}^{29}Si$ spin–spin coupling is indicative. This is shown for the silole **41** ($R^1 = SiMe_3$) in Fig. 9.

^{119}Sn NMR Spectroscopy

The NMR sensitivity of the ^{119}Sn nucleus (factor 25.7 relative to ^{13}C!) and the large range of chemical shifts

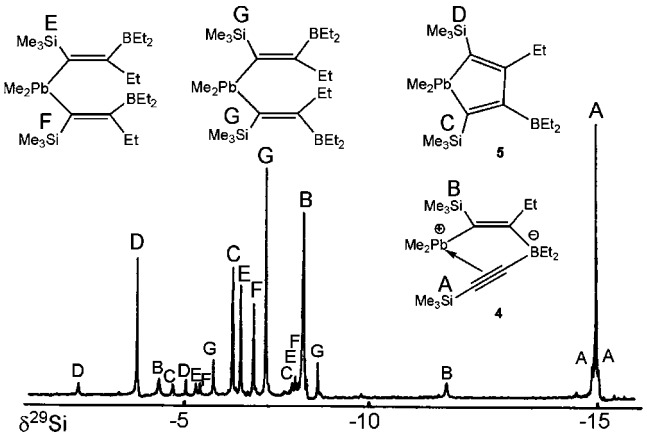


FIGURE 8 59.6 MHz ^{9}Si{^{1}H} NMR spectrum (refocused INEPT [100]) of a reaction mixture typical of partially equilibrated 1,1-organoboration reactions. The ^{29}Si NMR signals of intermediates, including the zwitterionic intermediate **4**, prior to final irreversible rearrangement into the plumbacyclopentadiene **5**, are visible. The assignment is confirmed by the ^{207}Pb satellites due to ^{207}Pb–^{29}Si spin–spin coupling, the respective ^{207}Pb NMR signals (not shown), and by the time-dependent changes in the relative signal intensities.

δ^{119}Sn (>4000 ppm; δ^{119}Sn(SnMe$_4$) = 0) make ^{119}Sn NMR an ideal tool for monitoring of reactions and for structural assignments [101]. Thus, changes in the coordination number of the tin atom are indicated, even if the coordinative interactions are weak. Moreover, the line widths of the ^{119}Sn NMR signals are markedly affected by vicinal ^{119}Sn—^{11}B spin–spin coupling [102] (Fig. 10) [77]. The zwitterionic intermediates, in which a triorganotin cation is coordinated side-on to the C≡C bond (e.g., in **10–12**, **20**, **26**, **29–31**), are readily identified in solution by their ^{119}Sn NMR signals at unusually (for organotin compounds) high frequencies (e.g., **10**: δ^{119}Sn 215.4 or **29**: δ^{119}Sn 165.6). In stannacyclopentadienes with SiMe$_3$ substituents in 2,5-positions, the ^{119}Sn resonances are shifted markedly to high frequencies. This is the same trend as found for δ^{29}Si of corresponding siloles. In contrast to stannoles, the ^{119}Sn resonances of the 1-stanna-4-bora-cyclohexa-2,5-dienes are at much lower frequencies and therefore, in mixtures these products can be easily distinguished from stannoles.

^{207}Pb NMR Spectroscopy

^{207}Pb NMR spectra can be readily obtained for the products as well as for intermediates in the course of the 1,1-organoboration reactions. Chemical shifts δ^{207}Pb cover a large range of >10,000 ppm [103], with δ^{207}Pb(PbMe$_4$) = 0. The zwitterionic intermediates such as **4** (δ^{207}Pb + 767.0) or **6** (δ^{207}Pb + 667.2) show ^{207}Pb NMR signals at high frequency. As for the corresponding siloles (δ^{29}Si) and stannoles (δ^{119}Sn), the ^{207}Pb NMR signal of the plumbole **5** (δ^{207}Pb + 543.2) with SiMe$_3$ groups in 2,5-positions is at rather high frequency [13]. This is particularly striking if one compares this δ^{207}Pb value with that for the 1-plumba-4-bora-cyclohexa-2,5-diene **7** (δ^{207}Pb –195).

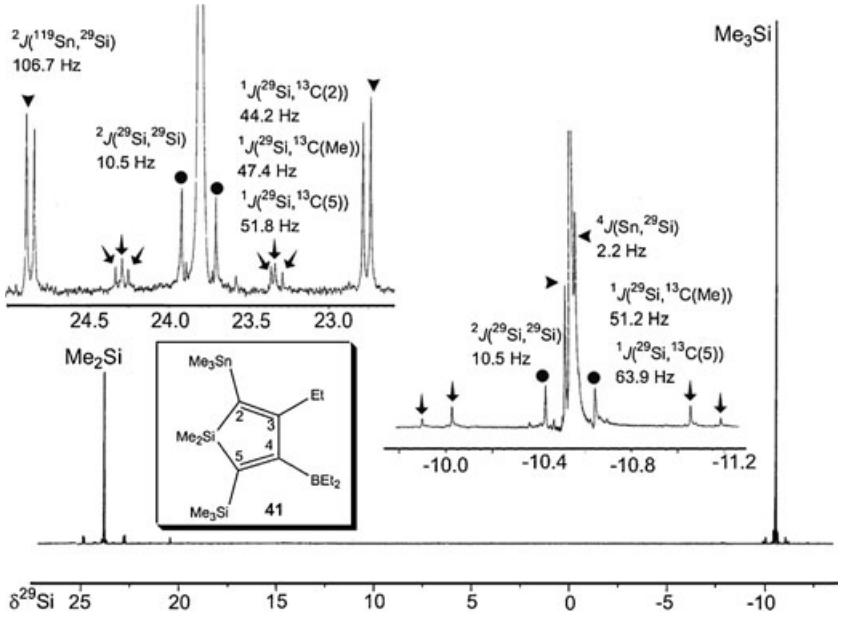


FIGURE 9 49.7 MHz ^{29}Si{^{1}H} NMR spectrum (refocused INEPT [100]) of the silacyclopentadiene derivative **41**, showing satellite signals for the isotopomers containing ^{29}Si,^{13}C, two ^{29}Si nuclei, and ^{29}Si,$^{117/119}$Sn. Note the marked magnetic deshielding of ^{29}Si as part of the five-membered ring relative to the exocyclic SiMe$_3$ group.

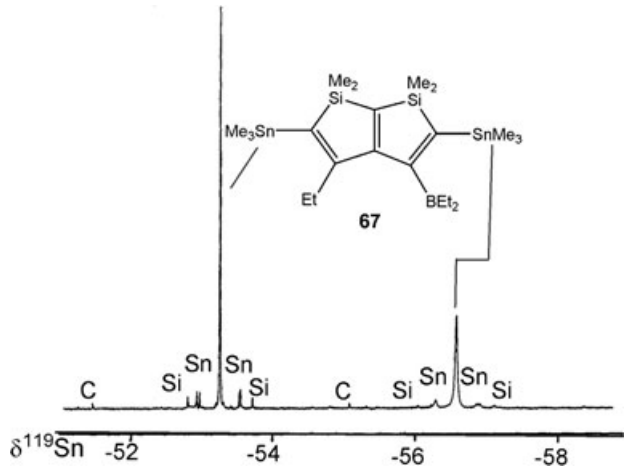


FIGURE 10 93.5 MHz $^{119}Sn\{^1H\}$ NMR spectrum (refocused INEPT) of the 1,6-dihydro-1,6-disilapentalene derivative **67**. Note the increase in the line width of one of the ^{119}Sn NMR signals as the result of partially relaxed scalar ^{119}Sn–^{11}B spin–spin coupling across three bonds. Satellite signals due to the presence of ^{13}C, ^{29}Si, and $^{117/119}Sn$ are marked.

^{31}P NMR and ^{195}Pt NMR Spectroscopy

^{31}P NMR spectroscopy [104] is an extremely sensitive analytical technique if modern NMR equipment is used ($\delta^{31}P(H_3PO_4;\ 85\%\ aq.) = 0$). Thus, the formation of the platinacyclopentadienes is readily monitored by ^{31}P NMR, since the ^{31}P NMR signals of the starting materials are accompanied by ^{195}Pt satellite signals with characteristic values for $^1J(^{195}Pt,^{31}P)$ [104,105]. New signals with other $\delta^{31}P$ values and in particular with other coupling constants $^1J(^{105}Pt,^{31}P)$ appear as soon as new products are formed. In the case of the platinacyclopentadienes **79**, the magnitude of $^1J(^{105}Pt,^{31}P)$ becomes much smaller (see Fig. 6 for data) than for the starting complexes, and the ^{31}P nuclei become inequivalent, giving rise to the typical appearance of an AB spin system with a small coupling constant $^2J(^{31}P,^{31}P)$. Clearly, ^{31}P NMR is also of great value if further rearrangements are in progress. Thus, the first hint on the formation of the borole complex **80** came from ^{31}P NMR, when new ^{31}P NMR signals appeared at $\delta^{31}P$ 42.5, 33.7, accompanied by ^{105}Pt satellites with $^1J(^{195}Pt,^{31}P) = 4535$ and 4922 Hz, respectively, values more typical for Pt(0) than for Pt(II) phosphane complexes.

Although, ^{195}Pt NMR spectra can be readily measured [106], there are rather few NMR data available for platinacyclopentadienes. The interpretation of $\delta^{195}Pt$ data is difficult, since the various influences on ^{195}Pt nuclear magnetic shielding are much less easy to separate than for main group nuclei. However, owing to the large range of chemical shifts $\delta^{195}Pt$ (>10,000 ppm), any change in the structure of the respective platinum complex will have a marked effect on the $\delta^{195}Pt$ value (the absolute frequency $\Xi(^{195}Pt) = 21.4$ MHz serves as the reference). Thus, it is not surprising that the $\delta^{195}Pt$ value for **83** (R = Me) changes from –436.4 to $\delta^{195}Pt$ –1832.0 upon rearrangement into the borole complex **84**. In any case, the values $^1J(^{195}Pt,^{31}P)$, measured in the ^{31}P NMR spectra are found again in the splitting of the ^{195}Pt NMR signals, giving unequivocal evidence for the connectivity of these nuclei.

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