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# Reactions of zwitterionic $\eta^2$-(alkyn-1-yl-borate)alkenyltin compounds with Lewis bases

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**Abstract**

The different Lewis-acidic centres in the zwitterionic $\eta^2$-(alkyn-1-yl-borate)alkenyltin compounds **1** and **2** react with Lewis bases (pyridine, N-Me-imidazole, trialkylphosphanes, fluoride). Depending on sterical and electronic conditions and on the nature of the Lewis base, either the boron, tin or carbon atom is involved in these reactions. Formation of borane adducts (**3**, **4**, **7**, **8**, **17**) is accompanied by migration of a boron-bonded alkynyl group to the tin atom. Coordination at the tin atom is weak (**5**, **6**) except in the case of fluoride (**10**–**12**) and 2,2-bipyridyl (**18**). Phosphanes coordinate either to boron, to tin or to carbon. In the latter case, vinyl cationic fragments are stabilised (**9**, **19**–**22**), which are believed to be important potential intermediates in the reversible rearrangement of 1-alkynyl-stannyl(boryl)alkenes **1′**, **2′** into the zwitterionic $\eta^2$-(alkyn-1-yl-borate)alkenyltin compounds **1** and **2**, respectively. All new compounds were characterised by $^1$H-, $^{11}$B-, $^{13}$C-, $^{31}$P- and $^{119}$Sn-NMR. 

*Keywords:* Alkynes; Boron; Tin; Zwitterionic compounds; Adducts; NMR

## 1. Introduction

Side-on coordinated alkynes are well known in transition metal complexes [1], and there is a great structural variety [1,2]. In the case of Main Group metals, such types of complexes are rare [2g], and until recently, examples have been known mainly for beryllium [3a], aluminium [3b] or gallium compounds [3c]. In the course of 1,1-organoboration reactions [4] of 1-alkynyltin or -lead compounds, zwitterionic intermediates have been proposed which were finally isolated and fully characterised, including X-ray structural analysis [5–7]. In these compounds an alkynylborate fragment is present in which there is an intramolecular side-on coordination of the C≡C bond to a formally positively charged metal (lead [5] or tin [6,7]) centre. These compounds are labile with respect to migration of the alkynyl group from the boron back to the metal atom as well as to rearrangement to metalloles, 1,4-metallabora-cyclohexa-2,5-dienes and other heterocycles [4–7]. Thus, there are numerous reactive sites in these molecules, and their reactivity in particular towards Lewis bases is of interest considering the competition between boron, tin or carbon atoms as potential electrophilic centres. In this study, we have focused on the tin compounds **1** [7] and **2** [6], and on Lewis bases such as pyridine, 1-methyl-imidazole, trimethylphosphane and the fluoride anion. The compounds **1** were selected in order to check on sterical effects (**1a**,**b** [7a]), on the influence of intramolecular N–Sn coordination (**1c** [7b]), and on the effects exerted by a reasonably stable zwitterionic structure (**1d** had turned out to be a particularly stable intermediate [7a]: most likely the $^i$Pr group at the C=C bond keeps the $Me_2Sn$ moiety in a favourable position for the side-on coordination to the C≡C bond). The compound **2** is unique since the tin atom possesses a formally twofold positive charge. However, its basic structural features are similar to those of **1a**, **b** or **d**. The reactions of **1** and **2** with the Lewis bases were monitored by multinuclear magnetic resonance spectroscopy ($^1$H-, $^{11}$B-, $^{13}$C-, $^{119}$Sn-NMR).

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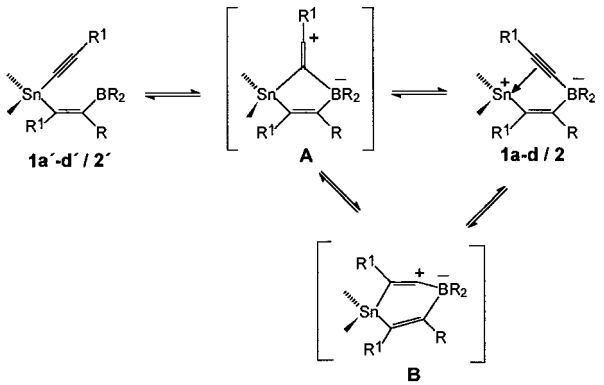
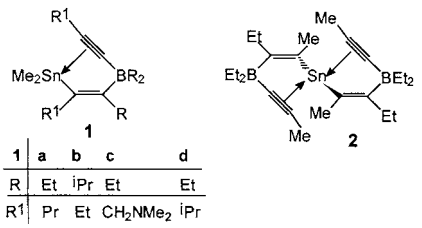



Scheme 1.

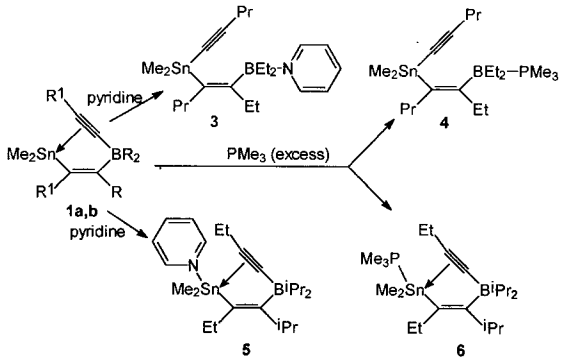



The dynamic NMR spectra of the compounds **1** and **2** are in accordance with an equilibrium in which the alkynyl group migrates between the boron and the tin atoms [4,6–8]. This is shown in Scheme 1 by **1** and **1′**, **2** and **2′**, and by the vinyl cations **A** and **B**, which are potential intermediates (most likely unstable without a Lewis base) representing the extreme cases of bridging alkynyl groups [9]. A major goal of this study is the identification of the structures **1**, **1′**, **2**, **2′**, and **A** and/or **B** in the presence of Lewis bases.

## 2. Results and discussion

### 2.1. Reactions of *1a* with pyridine and trimethylphosphane

The zwitterionic compound **1a** reacts with both pyridine and $PMe_3$ to give the borane adducts **3** and **4**, in which the alkynyl group has migrated from the boron back to the tin atom (Scheme 2). No other products could be detected by NMR, starting from $-78$°C. It appears that the Lewis-acidic character of the tin atom in **1a** is low, and that the three-coordinate boron atom in the $Et_2B$ group of the isomer **1a′**, which is in a dynamic equilibrium with **1a** (even at $-78$°C), can be readily attacked by a nucleophile (c.f. Section 2.6, reaction of **2** with pyridine). The $^{119}$Sn chemical shifts of the adducts **3** and **4** do not change significantly with temperature; this indicates that there is no further exchange of the alkynyl group. In the case of **4**, the




Scheme 2.

broad $^{31}$P-NMR signal of the excess of $PMe_3$ shows that free phosphane is in fast exchange with **4**, and this is also evident from the $^{119}$Sn-NMR signal which becomes significantly broader at 0°C when compared with the sharp signal observed at $-60$°C.

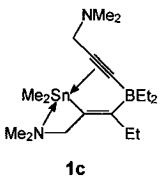
### 2.2. Reactions of *1b* with pyridine and trimethylphosphane

In the case of **1b**, both pyridine and $PMe_3$ are anchored at the tin atom to give the compounds **5** and **6** (Scheme 2). With increasing temperature the $^{119}$Sn-NMR signals of **5** and **6** are shifted markedly to higher frequencies; this is indicative of dissociation into **1b** and the respective Lewis base. It is likely that the bulky isopropyl groups at the boron atom prevent the formation of a reasonably stable borane adduct even if **1b′** is in equilibrium with **1b**. Then the tin atom is the next best site for nucleophilic attack. The lifetime of the vinyl cationic species **A** or **B** may be too short or repulsive interactions of the Lewis base with other substituents at the boron and/or carbon atoms are too strong for trapping these species.The compounds **3**–**6** are formed quantitatively and can be isolated ($<0$°C) as colourless solids. They are unstable at room temperature with respect to rearrangement to stannoles and 1,4-stannabora-cyclohexa-2,5-dienes, as has been observed for **1a** and **1b** themselves [7a]. The borane adducts **3** and **4** are more stable than the tin adducts **5** and **6**, and the pyridine adducts **3**, **5** are more stable than the $PMe_3$ adducts **4** and **6**.

### 2.3. Treatment of *1c* with pyridine and trimethylphosphane

The zwitterionic compound **1c** does not react with pyridine or $PMe_3$. This can be explained, considering the structure of **1c** in which the tin atom is coordinated not only side-on to the C≡C bond but also to the nitrogen atom of the $Me_2N$ group in $R^1$ at the olefinic carbon atom [7b]. Although it must be assumed that

this intramolecular N–Sn coordination weakens the side-on coordination to the C≡C bond, at the same time it hinders migration of the alkynyl group from boron back to the tin atom. Therefore, a nucleophilic attack at the boron atom, as in the case of **1a**, is not preferred, and the tin atom is protected against nucleophilic attack because of the presence of the coordinative N–Sn bond.

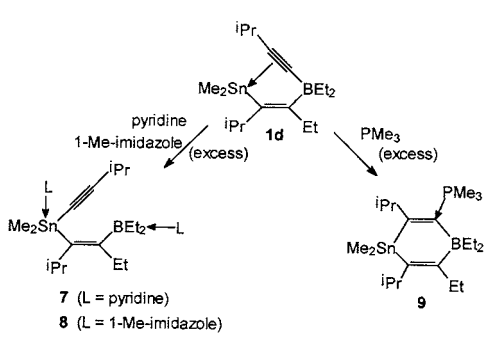



**1c**

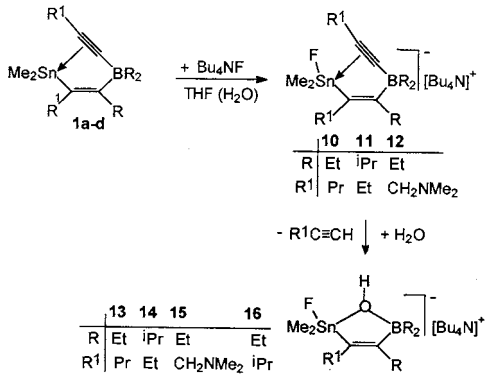
### 2.4. Reactions of *1d* with pyridine, 1-methyl-imidazole and trimethylphosphane

The compound **1d** reacts with the Lewis bases in different ways (Scheme 3). At low temperature, pyridine and 1-methyl-imidazole are coordinated to both tin and boron to give the products **7** and **8**, in which the alkynyl group is linked to the tin atom. According to NMR spectra, there is fast intramolecular exchange of the Lewis bases. Above −30°C, intermolecular exchange with an excess of the Lewis base becomes fast. Since the equilibrium between **1d** and **1d′** lies mainly on the side of **1d** [7a], even if solutions are warmed to 0°C, it can be assumed that the first step of the reaction (c.f. Section 2.6, the reaction of **2** with pyridine) at −60°C leads to a coordinative N–Sn bond, followed by transfer of the alkynyl group from the boron to the tin atom, and formation of the borane adduct.

The reaction of **1d** with $PMe_3$ leads to an equilibrium with slow exchange (as compared to the NMR time scale) at temperatures below −30°C. NMR spectra show that there is a novel compound **9** (Scheme 3) present in addition to **1d** (ratio 1:4), which can be identified by its NMR data as a derivative of **B** containing a vinyl cationic fragment (Scheme 1) stabilised by P–C coordination. The formation of **9** is reversible. The




Scheme 3.




Scheme 4.

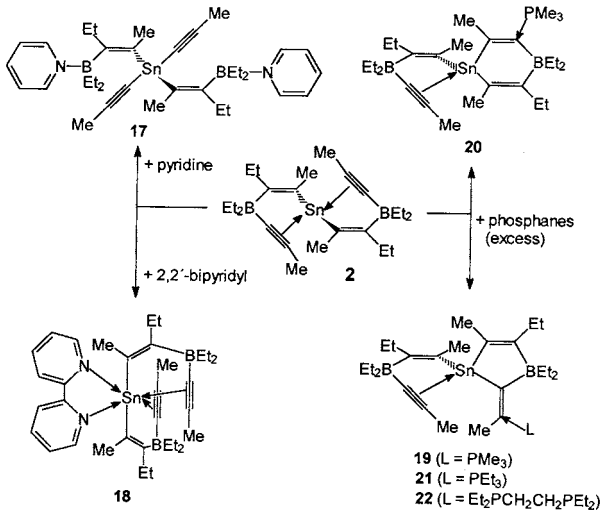
$^{31}$P-NMR signal of free $PMe_3$ is broadened, and the $^{119}$Sn-NMR signal is shifted by 6 ppm to lower frequency upon cooling from −60 to −90°C, indicating weak P–Sn coordinative interactions in addition to the P–C bond. As in the reaction of **1d** with nitrogen bases, coordination of $PMe_3$ to the tin atom is likely to be the first step. This induces destabilisation of the alkyne-tin coordination, and in the course of rearrangements, which may be much slower than in the cases of the reactions of **1a** or **1b** with $PMe_3$, one of the potential intermediate species (**B**) is trapped by $PMe_3$.

### 2.5. Reactions of *1a–d* with fluoride anions ($Bu_4NF$ in THF)

All four compounds **1a–d** react already at −65°C with $Bu_4NF$ (Scheme 4) to give compounds with Sn–F bonds. In the cases of **1a–c**, it proved possible to identify the first intermediates **10–12** that then react with water (present in the reagent $Bu_4NF$ in THF) to give the 2,5-dihydro-1,2,5-oxoniastannaboratole derivatives **13–15**. In the case of **1d**, the analogous reaction leads rapidly to **16** and no intermediate analogous to **10–12** was observed. The final formation of the heterocycles **13–16** is in agreement with the results obtained for the reaction of compounds of type **1** with methanol [10].

### 2.6. Reactions of *2* with pyridine, 2,2′-bipyridyl, trimethyl-, triethylphosphane, and 1,2-bis(diethylphosphanyl)ethane (depe)

The reaction of **2** with pyridine affords the compound **17** (Scheme 5), in which both alkynyl groups are linked to the tin atom and both boryl groups are coordinated by pyridine. This finding corresponds to that for the reaction of **1a** with pyridine (c.f. Section 2.1). In contrast, the reaction of **2** with 2,2′-bipyridyl leads to the complex **18**, in which two coordinative N–Sn bonds are present and the alkynyl groups stay at the boron atoms. It appears that **18** is stabilised by the




Scheme 5.

chelate effect which would be lost in the case of coordinative N–B interactions. Thus, it is conceivable that also in the reaction of **2** with pyridine one or two coordinative N–Sn bonds are present at first in an unstable complex (not detected) which then rearranges to **17**. Both compounds **17** and **18** are yellow solids that decompose already at 0°C to give a large number of unidentified products. Pyridine can be removed from **17** in a vacuum ($<10^{-3}$ Torr) for a prolonged time just below 0°C, and **2** is recovered unchanged.

Compound **2** reacts readily with phosphanes. The reaction with $PMe_3$ affords a 1:1 mixture of the isomers **19** and **20**, in which the intermediate species of type **A** and **B**, respectively, are stabilised. Only one of the two zwitterionic fragments in **2** reacts; the second one remains unaffected even in the presence of a large excess of $PMe_3$. The reaction of **2** with $PEt_3$ or depe leads to the compounds **21** or **22** for which a structure analogous to that of **19** (type **A**) can be assigned. The mixture **19**/**20** is a colourless solid and **21**, **22** are viscous oils; all compounds **19**–**22** decompose on warming to room temperature in an uncontrolled way.

### 2.7. NMR spectroscopic results

The proposed structures of the new compounds follow from consistent sets of NMR data given in Tables 1–7 ($^{11}$B-, $^{13}$C-, $^{31}$P- and $^{119}$Sn-NMR) and in Section 4 ($^{1}$H-NMR). In addition to routine 1D and 2D NMR techniques, INEPT experiments [11], based on long-range coupling constants, were used for assignments. In $^{13}$C-NMR spectra, the most useful criterions for assignments, apart from the usual patterns of chemical shifts, are $^{117/119}$Sn satellite signals corresponding to $^{n}J(^{110}\mathrm{Sn},^{13}\mathrm{C})$ ($n = 1, 2, 3, 4$) [12], and the broadening of the signals owing o partially relaxed scalar $^{13}$C–$^{11}$B coupling [13]. Most NMR spectra had to be recorded at low temperatures as a result of the inherent instability of the compounds studied. This is often inconvenient for $^{11}$B-NMR spectra, which then exhibit very broad lines because of very fast $^{11}$B quadrupolar relaxation.

The $^{13}$C-NMR spectra of the adducts **3**, **4**, **7**, **8** (Tables 1 and 3), **17** (Table 6) show that the alkynyl group is linked to tin, since the respective signals are sharp and the magnitude of $^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C}_{\equiv})$ is in the expected order of magnitude. At low temperature, NMR spectra show separate signals for the coordinated

Table 1
$^{13}$C-, $^{119}$Sn-, $^{11}$B- and $^{31}$P-NMR data [a] of **1a**, **23** and the adducts **3**, **4**, **23(py)**

| Number | $\delta^{13}$C | | | | | | | $\delta^{119}$Sn | $\delta^{11}$B |
|---|---|---|---|---|---|---|---|---|---|
| | $Me_2Sn$ | SnC= | BC= | SnC≡ | PrC≡ | $BEt_2$ | EtC= | | |
| **1a** [b] | −0.1 [248.0] | 137.7 [648.0] | 181.3 (br) | 108.2 (br) | 117.0 [45.2] | 18.3, 12.8 (br) | 25.8, 14.6 [139.5] [17.4] | +199.6 | −3.1 |
| **3** [c] | −2.6 [382.6] | 140.9 [674.6] | 165.7 [106.3] | 107.7 [59.4] | 87.4 [320.4] | 12.6, 9.1 (br) | 25.3, 15.1 [116.6] [15.3] | −127.9 | +4.6 |
| **23** [d] | −7.9 [316.1] | 139.3 [526.3] | 162.0 (br) | – | – | 21.7, 9.1 (br) | 22.9, 14.5 [83.9] [10.4] | −48.5 | +84.2 |
| **23(py)** [e] | −5.4 [308.4] | 141.7 [588.6] | 165.0 (br)[76.8] | – | – | 12.8, 9.2 (br) | 24.9, 15.3 [97.6] [13.1] | −59.0 | +5.6 |
| **4** [f] | −0.7 [376.6] | 140.2 [686.6] | 167.3 (br) | 110.2 [42.5] | 93.0 (br) | 11.5, 11.0 (br) | 27.4, 15.6 [122.6] [16.3] | −128.2 | −9.7 |

[a] In $CDCl_3$, at 243 K; coupling constants $^{n}J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ in brackets (±1 Hz); n.m. means not measured, and (br) denotes broad $^{13}$C-NMR signals owing to partially relaxed scalar $^{13}$C–$^{11}$B coupling. **23**: (*E*)-3-diethylboryl-4-trimethylstannyl-hept-3-ene; **23(py)**: borane–pyridine adduct of **23**.

[b] $\delta^{13}\mathrm{C} = 34.9$ [135.7], 26.7 [43.1], 13.9 (Pr–C=); 22.3, 22.2, 13.1 (Pr–C≡).

[c] $\delta^{13}\mathrm{C} = 37.5$ [73.0], 24.0 [n.m.], 13.4 (Pr–C=); 21.7, 21.2, 12.7 (Pr–C≡); 144.5, 138.3, 123.9, (B-py).

[d] $\delta^{13}\mathrm{C} = 35.5$ [58.9], 23.8 [12.0], 14.1 (Pr–C=).

[e] $\delta^{13}\mathrm{C} = 37.0$ [73.0], 23.7 [n.m.], 13.4 (Pr–C=); 144.5, 138.0, 123.4 (py).

[f] $\delta^{13}\mathrm{C} = 38.3$ [86.7], 25.1 [13.6], 14.0 (Pr–C=); 22.3, 22.1, 13.5 (Pr–C≡); 14.6 $^{1}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 3.6$ Hz ($PMe_3$); $\delta^{31}$P at 213 K: −13.8.

Table 2
$^{13}C$-, $^{119}Sn$-, and $^{11}B$-NMR data [a] of **1b** and the tin adducts **5** and **6**

| Number | $\delta^{13}C$ | | | | | | | $\delta^{119}Sn$ | $\delta^{11}B$ |
|---|---|---|---|---|---|---|---|---|---|
| | $Me_2Sn$ | SnC= | BC= | BC≡ | EtC≡ | $B^iPr_2$ | $^iPrC$= | | |
| **1b** [b] | 3.0 [238.3] | 141.0 [649.6] | 181.6 (br) | 104.2 (br) | 119.3 [46.9] | 20.3, 21.3, 21.4 (br) | 32.7, 21.6 [153.1] [n.m.] | +188.0 | +4.5 |
| **5** [c] | 0.4 [315.0] | 139.9 [707.4] | 181.7 (br) | 105.7 (br) | 119.7 [26.2] | 20.2, 21.7 (br) | 32.7, 21.8 [160.2] [13.6] | +78.4 | −2.6 |
| **6** [d] | 1.6 [288.8] | 140.3 [685.3] | 181.5 (br) | 105.1 (br) | 119.6 [33.2] | 20.4, 21.7 (br) (br) | 32.7, 21.9 [159.1] [13.6] | −86.6 | −2.0 |

[a] In $CDCl_3$, at 243 K; coupling constants $^nJ(^{119}Sn,^{13}C)$ in brackets [ ± 1 Hz]; n.m. means not measured, and (br) denotes broad $^{13}C$-NMR signals owing to partially relaxed scalar $^{13}C$–$^{11}B$ coupling.
[b] $\delta^{13}C = 28.0$ [130.8], 18.0 [50.7] (Et–C=); 14.4, 13.9 (Et–C≡).
[c] $\delta^{13}C = 28.2$ [123.7], 17.2 [n.m.] (Et–C=); 14.6, 14.0(Et–C≡).
[d] $\delta^{13}C = 29.0$ [125.3], 17.7 [n.m.], (Et–C=); 14.5, 13.9 (Et–C≡).

Table 3
$^{13}C$-, $^{119}Sn$-, $^{11}B$- and $^{31}P$-NMR data [a] of **1d** and the adducts **7**, **8**

| Number | $\delta^{13}C$ | | | | | | | $\delta^{119}Sn$ | $\delta^{11}B$ |
|---|---|---|---|---|---|---|---|---|---|
| | $Me_2Sn$ | SnC= | BC= | SnC≡ | $^iPrC$≡ | $BEt_2$ | EtC= | | |
| **1d** [b] | 2.1 [240.9] | 146.8 [625.6] | 177.4 (br) | 106.1 (br, 79.6) | 123.3 [48.0] | 17.9, 12.7 (br) | 25.4, 15.6 [136.5] [16.3] | +215.4 | −2.6 |
| **7** [c] | −1.4 [380.9] | 151.2 [644.7] | 163.7 [103.0] | 115.1 [54.5] | 88.9 [299.7] | 14.0, 9.7 (br) | 26.3, 15.4 [117.7] [n.m.] | −167.9 | −4.1 |
| **8** [d] | −2.3 [376.6] | 148.6 [662.7] | 164.6 [100.0] | 114.8 [51.2] | 89.1 [270.8] | 13.6, 9.5 (br) | 25.6, 15.2 [118.8] [n.m.] | −169.1 | −1.5 |

[a] In $CDCl_3$, at 243 K; coupling constants $^nJ(^{119}Sn,^{13}C)$ in brackets [ ± 1 Hz]; n.m. means not measured, and (br) denotes broad $^{13}C$-NMR signals owing to partially relaxed scalar $^{13}C$–$^{11}B$ coupling; **1d**, **11** at 213 K; $^nJ(^{31}P,^{13}C)$ in parentheses( ± 1 Hz), $^nJ(^{119}Sn,^{31}P)$ in braces { ± 2 Hz}.
[b] $\delta^{13}C = 31.5$ [128.6], 26.0 [26.2], ($^iPr$–C=); 23.2, 22.6 ($^iPr$–C≡).
[c] $\delta^{13}C = 33.0$ [58.3], 25.4 [n.m.], ($^iPr$–C=); 21.1, 22.6 ($^iPr$–C≡); 144.9, 138.6, 123.6 (coordinated pyridine).
[d] $\delta^{13}C = 34.1$ [61.0], 22.3 [n.m.], ($^iPr$–C=); 20.8, 21.9 ($^iPr$–C≡); 134.3, 124.4, 119.5, 32.5 (coordinated 1-Me-imidazole).

Table 4
$^{13}C$-, $^{119}Sn$-, $^{11}B$-, and $^{19}F$-NMR data [a] of the products **10**–**12** from the reactions of **1a**, **1b**, **1c** with $Bu_4NF$

| Number | $\delta^{13}C$ | | | | | $\delta^{119}Sn$ | $\delta^{11}B$ | $\delta^{19}F$ |
|---|---|---|---|---|---|---|---|---|
| | $Me_2Sn$ | SnC= | BC= | BC≡ | $R^1C$≡ | | | |
| **10** [b] | 4.6 [n.m.] (19.5) | 139.0 [n.m.] (11.4) | 176.3 (br) | 112.5 (br) | 107.5 | −41.0 {1760.4} | −8.7 | −163.2 {1757.8} |
| **11** [c] | 4.8 [439.1] (20.8) | 143.7 [824.0] (11.4) | 177.2 (br) | 110.4 (br) | 111.0 | −63.3 {1770.0} | −7.4 | −158.7 {1770.0} |
| **12** [d] | 3.3 [512.3] (19.6) | 134.7 [997.3] (18.0) | 182.4 (br) | 120.6 (br) | 99.9 | −30.9 {1851.7} | −9.2 | −169.9 {1851.7} |

[a] In THF-$d_8$ at 243 K; coupling constants: $^nJ(^{119}Sn,^{13}C)$ in brackets [ ± 1 Hz], $^nJ(^{19}F,^{13}C)$ in parentheses ( ± 1 Hz), $^nJ(^{119}Sn,^{19}F)$ in braces { ± 3 Hz}, n.m. means not measured, and (br) denotes broad $^{13}C$-NMR signals owing to partially relaxed scalar $^{13}C$–$^{11}B$ coupling.
[b] Further signals were not assigned owing to overlap of resonances.
[c] $\delta^{13}C = 21.4$ (br), 23.1, 23.2 ($B^iPr_2$); 33.6 [159.1], 23.4 [n.m.], ($^iPrC$=); 28.6 (br) [95.4], 17.9 (EtC=); 15.8, 15.6(Et–C≡), 58.3, 24.3, 20.5, 14.3 ($Bu_4N$).
[d] $\delta^{13}C = 19.2$ (br), 11.6 ($BEt_2$); 25.0 [n.m.], 17.1 [19.1], (Et–C=); 59.7 (br) [105.7], 45.1 ($Me_2NCH_2$–C = =); 47.7, 43.8($Me_2NCH_2$–C≡); 58.3, 24.3, 20.5, 14.3 ($Bu_4N$).

and the free Lewis base (Fig. 1). The presence of two donor molecules each (pyridine or 1-methyl-imidazole) in **7** and **8** is indicated by the relative integral intensities of the $^{13}C$-NMR signals recorded under conditions for quantitative assessment (Fig. 1). For comparison with the data for **3**, the NMR data of (*E*)-3-diethylboryl-4-trimethylstannyl-3-heptene **23** and its pyridine adduct **23(py)** were recorded (Table 1). In the latter, pyridine has no choice but to coordinate to the boron atom.

The $^{119}Sn$ nuclear shielding in **7** and **8** is increased by about 40 ppm with respect to **3** and **4**, as a result of the increased coordination number of the tin atoms in the

former compounds. Interestingly, $^{119}$Sn-NMR spectra of mixtures of 1-alkynyltin compounds and pyridine do not reflect any significant adduct formation. Therefore, the presence of the triorganotin cationic fragment in **1d** is indeed responsible for the primary N–Sn coordination. The $\delta^{119}$Sn value (−277.4) of **17** could be interpreted also in terms of a structure analogous to **18** ($\delta^{118}$Sn −190.0). However, the completely different line widths of the $^{11}$B-NMR signals (**17** (243 K): $h_{1/2}$ = 1700 ± 100 Hz, and **18** (298 K): 180 ± 10 Hz) and the pattern of the $^{13}$C-NMR data (Table 6; see in particular the coupling constants $^{n}J(^{119}Sn,^{13}C)$), rule out this possibility. The comparison of $^{13}$C-NMR data of **17** with those of **3** and **23** shows trends that are consistent with the presence of analogous structural fragments.

The NMR data of the complexes **5** and **6** (Table 2) indicate that these complexes are much more labile than **3** and **4**. In **5** and **6**, rapid exchange between coordinated and free Lewis basis takes place, even at low temperature. The $^{13}$C-NMR data of the alkynyl group prove that this group is still linked to boron, and coordination of the respective Lewis base to the tin atom is evident from the change in the $\delta^{119}$Sn value by more than 100 ppm with respect to that of **1b** ($\delta^{119}$Sn + 188.0). In contrast with **5**, the 2,2′-bipyridyl complex **18** (Table 6) is fairly stable with respect to dissociation. Similar to **2** [5], various dynamic processes connected with the two side-on coordinated alkyne groups take place in solution. However, below −30°C the structure of **18** appears to be rigid when compared to the NMR time scale, as indicated by the appearance of the appropriate number of signals for prochiral groups ($^{1}$H(=C–CH$_2$–) and $^{1}$H,$^{13}$C(B(CH$_2$CH$_3$)$_2$) signals).

The formation of the Sn–F bond in **10**–**12** follows straightforwardly from the $^{19}$F-NMR signals (sharp, absence of $^{19}$F–$^{11}$B coupling) and the magnitude of $^{1}J(^{119}Sn,^{19}F)$. There are only a few of such data of monomeric triorganotin fluorides in the literature [14b], most of which have $|^{1}J(^{119}Sn,^{19}F)| > 2200$ Hz. In the case of penta-coordinate organotin anions with Sn–F

Table 5
$^{13}$C-, $^{119}$Sn-, $^{11}$B- and $^{19}$F-NMR data [a] of the 2,5-dihydro-1,2,5-oxonia-stannaboratole derivatives **13**, **14**, **15**, **16**

| Number | $\delta^{13}$C | | | | $\delta^{119}$Sn | $\delta^{11}$B | $\delta^{19}$F |
|---|---|---|---|---|---|---|---|
| | $Me_2Sn$ | SnC= | BC= | $BR_2$ | | | |
| **13** [b] | 1.9 [476.3] | 137.0 [912.3] | 173.7 (br) | 18.8, 11.1 (br) | −104.1 {1814} | +4.1 | −141.5 {1819} |
| **14** [c] | 1.7 [453.4] | 140.1 [898.7] | 174.5 (br) | 19.4, 22.5, 22.8 (br) | −110.1 {1929} | +0.5 | −131.0 {br} |
| **15** [d] | 1.4 [507.4] | 133.3 [949.9] | 180.6 (br) | 18.9, 11.2 (br) | −92.0 {br} | +4.6 | −135.7 [n.m.] |
| **16** [e] | 3.2 [501.4] | 145.9 [862.1] | 169.4 (br) | 18.8, 11.4 (br) | −97.9 {1801} | −8.2 | −140.0 [n.m.] |

[a] In THF-$d_8$ at 243 K; coupling constants: $^{n}J(^{119}Sn^{13}C)$ in brackets [± 1 Hz], $^{n}J(^{19}F^{13}C)$ in parentheses (± 1 Hz), $^{n}J(^{119}Sn^{19}F)$ in braces {± 3 Hz}, n.m. means not measured; (br) denotes broad $^{13}$C-NMR signals owing to partially relaxed scalar $^{13}$C–$^{11}$B coupling; {br} means a broad signal because of dynamic processes.

[b] $\delta^{13}$C = 24.6 [144.4], 15.6 [19.1] (EtC=); 35.0 [114.4], 25.8 [13.6], 14.6 (PrC=); 59.1, 24.5, 20.5, 13.9 ($Bu_4N$).

[c] $\delta^{13}$C = 31.8 [163.4], 22.9 [15.3] ($^{i}$PrC=); 27.7 [110.2], 17.1 [16.7], (EtC=); 58.8, 23.3, 19.7, 13.5 ($Bu_4N$).

[d] $\delta^{13}$C = 24.9 [140.6], 15.7 [15.7] (EtC=); 60.8 [101.4], 45.0 [n.m.], ($Me_2NCH_2C$=); 59.1, 24.5, 20.5, 14.0 ($Bu_4N$).

[e] $\delta^{13}$C = 25.3 [134.0], 16.0 [18.5] (EtC=); 32.3 [103.5], 24.3 [17.4], ($^{i}$PrC=); 58.1, 26.1, 20.1, 14.0 ($Bu_4N$).

Table 6
$^{13}$C-, $^{119}$Sn- and $^{11}$B-NMR data [a] of **2** and the adducts with pyridine (**17**) and 2,2′-dipyridyl (**18**)

| Number | $\delta^{13}$C | | | | | | | $\delta^{119}$Sn | $\delta^{11}$B |
|---|---|---|---|---|---|---|---|---|---|
| | SnC= | BC= | BC≡C | BC≡C | MeC= | MeC≡ | EtC= | | |
| **2** [b] | 130.8 [522.6] | 190.0 (br) | 109.1 (br)[134.1] | 124.9 [66.7] | 19.5 [174.0] | 6.8 | 25.7, 14.0 [154.0] [14.1] | +165.6 | −5.6 |
| **17** [c] | 138.0 [795.6] | 165.9 (br) | 91.7 [382.6] | 104.2 [64.3] | 22.8 [86.7] | 5.3 [7.6] | 26.6, 13.8 [137.3] [16.4] | −277.4 | −8.0 |
| **18** [d] | 138.2 [1060.0] | 176.9 (br) | 104.9 (br)[n.m.] | 125.5 [n.m.] | 20.1 [164.0] | 7.9 | 25.1, 13.8 [204.0] [n.m.] | −190.0 | −4.8 |

[a] In $CDCl_3$, at 243 K; coupling constants $^{n}J(^{119}Sn,^{13}C)$ in brackets [± 1 Hz]; n.m. means not measured, and (br) denotes broad $^{13}$C-NMR signals owing to partially relaxed scalar $^{13}$C–$^{11}$B coupling.

[b] $\delta^{13}$C = 16.8 (br), 13.0 ($BEt_2$) $h^{1/2}$ ($^{11}$B{$^{1}$H}, 263K, $CD_2Cl_2$) ≈ 280 ± 10 Hz.

[c] $\delta^{13}$C = 13.2 (br), 9.9{br}($BEt_2$); 146.1 (C2), 124.7 (C3), 139.3 (C4) (pyridine); $\delta^{13}$C(213K) = 165.6 (br) (=CB); 137.4 (SnC=); 26.4 [133], 13.6 [17.9] (=CEt); 22.5 [85.0] (=CMe); 13.1 (br), 10.2 {br}, 9.4 {br} ($BEt_2$); 5.2 (≡CMe); $h^{1/2}$ ($^{11}$B{$^{1}$H}, 243K, $CD_2Cl_2$) ≈ 1700 ± 100 Hz.

[d] $\delta^{13}$C (243K, $C_7D_8$) = 18.8 (br), 18.2, 13.5, 13.9 ($BEt_2$); 148.5 (C2), 121.6 (C3), 139.8 (C4), 126.0 (C5), 149.7 (C6) (2,2′-bipyridyl); $h^{1/2}$ ($^{11}$B{$^{1}$H}, 298K, $C_7D_8$) ≈ 180 ± 10 Hz.

Table 7
$^{13}C$-, $^{119}Sn$-, $^{11}B$- and $^{31}P$-NMR data [a] of the stabilised intermediates containing a vinyl cationic fragment **9**, **19**, **20**, **21**, **22**

| Number | $\delta^{13}C$ | | | | | | | | $\delta^{119}Sn$ | $\delta^{31}P$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | SnC(1′)= | BC(1″)= | BC≡C | BC≡C | SnC= | BC= | SnC(2)= | =CP | | |
| **2** [b] | 130.8 [522.6] | 190.0 (br) | 109.1 (br) [134.1] | 124.9 [66.7] | | | | | +165.6 | |
| **19** [c,e] | 135.2 [513.4] (5.1) | 180.7 (br) | 110.3 (br) | 108.5 [55.9] | 132.9 [492.5] (5.1) | 187.1 (br) | 217.7 (br) | 117.0 [28.0] (46.7) | +172.6 (457.8) | +3.1 [457.8] |
| **20** [d,e] | 130.8 [517.1] | 184.2 (br) | 108.2 (br) | 110.0 [59.3] | 126.8 [584.1] (3.4) | 184.2 (br) | 165.7 [325.9] (13.7) | 156.2 (br) | +45.8 (327.5) | −1.5 [327.5] |
| **9** [f] | −2.2 (MeSn) [273.2] (1.4) | | | | 143.5 [589.6] | 170.0 (br) | 179.1 [398.9] (14.3) | 169.5 (br) (48.5) | −144.6 (317.4) | −4.8 [317.4] |
| **21** [g] | 135.5 [508.6] (5.1) | 181.5 (br) | 111.2 (br) | 109.5 [56.7] | 133.1 [482.5] (5.1) | 187.2 (br) | 220.8 (br) | 114.1 [24.7] (40.7) | +170.0 (437.8) | +22.7 [437.8] |
| **22** [h] | 135.5 [503.0] (5.5) | 180.6 (br) | 110.8 (br) | 109.6 [55.6] | 133.1 [472.5] (4.9) | 186.7 (br) | 219.8 (br) | 113.5 [26.2] (39.4) | +169.1 (436.6) | 23.0 [437.8] (31.7) −16.9 (31.7) |

[a] In $CH_2Cl_2$–$CD_2Cl_2$ at 243 K; coupling constants $^nJ(^{119}Sn,^{13}C)$ and $^nJ(^{119}Sn,^{31}P)$ in brackets [ ± 1, ± 3 Hz], $^nJ(^{31}P,^{13}C)$ in parentheses ( ± 1 Hz); n.m. means not measured, and (br) denotes broad $^{13}C$-NMR signals owing to partially relaxed scalar $^{13}C$–$^{11}B$ coupling.

[b] $\delta^{13}C = 19.5$ [174.0] ($R^1C=$ ); 6.8 ($R^1C\equiv$); 25.7 [154.0], 14.0 [14.1] (=CEt);16.8 (br), 13.0 ($BEt_2$).

[c] 243 K; $PMe_3$ in excess; in a 1:1 mixture with **20** (1:1). $\delta^{13}C = 33.6$ [99.2] (39.0) (d) (C(3)Me); 25.0[123.8], 24.2[117.0] ( = CEt); 20.1[149.2], 19.3[115.3] (< 1) (d) (=CMe); 6.3 (≡CMe); (see footnote f); from 2D $^{13}C/^1H$ HETCOR experiments: $^2K(^{31}P,^{13}C(C(3)Me))/^3K(^{31}P,^1H(C(3)Me)) > 0$; $^3K(^{119}Sn,^{31}P)/^4K(^{119}Sn,^1H(C(3)Me)) > 0$; $^1K(^{31}P,^{13}C(C(3))/^3K(^{31}P,^1H(C(3)Me)) > 0$; $^1K(^{31}P,^{13}C(PMe_3))/^2K(^{31}P,^1H(PMe_3)) < 0$; $h^{1/2}$ ($^{119}Sn$) = 180 Hz; $h^{1/2}$ ($^{31}P\{^1H\}$) = 4 Hz.

[d] 243 K; $PMe_3$ in excess. $\delta^{13}C = 27.0$ [124.0] (32.2) (d) (C(2)Me); 26.1 [50.9] (3.9) (d) (C(5)Et); 24.8 [111.9] (C(2′)Et); 20.7, 19.0 (C(1′, 6)Me); 6.2 (≡CMe); (see footnote f); from 2D $^{13}C/^1H$ HETCOR experiments: $^3K(^{31}P,^{13}C(C(3)Me))/^4K(^{31}P,^1H(Me)) < 0$; $^1K(^{31}P,^{13}C(PMe_3))/(^2K\ (^{31}P,^1H(PMe_3)) < 0$; $h^{1/2}$ ($^{119}Sn\{$inverse gated $^1H$ decoupled$\}) > 250$ Hz; $h^{1/2}$ ($^{31}P$) = 13 Hz.

[e] $^{13}C$ resonance signals (not assigned): $\delta^{13}C = 16.7(46.7)$ (d), 13.2 (50.6) ($PMe_3$); 14.4, 14.4, 14.1, 13.9 (=CEt); 18.0(br), 14.1, 13.9, 13.6, 13.0, 12.6, 12.5, 12.4, 12.1 ($BEt_2$).

[f] $\delta^{11}B$ −4.1; further $^{13}C$-NMR signals were not assigned because of overlap of signals for **9** with those of **1d** and a stannole, the final rearrangement product [7a].

[g] 263 K; $PEt_3$ in excess. $\delta^{13}C = 35.1$ [100.2] (32.7) (d) (C(3)Me); 25.0 [116.3], 24.3 [117.7], 14.6, 14.0 (=CEt); 20.2 [148.2], 19.4 [202.0] (1.5) (d) (=CMe); 18.0 (br), 17.3 (br), 14.0, 13.4, 12.7, 12.6 ($BEt_2$); 14.1 (44.9) (d), 6.5(4.6) (d) ($PEt_3$); 6.3 (≡CMe); from 2D $^{13}C/^1H$ HETCOR experiments: $^2K(^{31}P,^{13}C(C(5)Me))/^3K(^{31}P,^1H(C(5)Me)) > 0$; $^1K(^{31}P,^{13}C(PEt_3))/^2K(^{31}P,^1H(PEt_3)) < 0$; $^2K(^{31}P,^{13}C(PEt_3))/^3K(^{31}P,^1H(PEt_3)) < 0$; $h^{1/2}$ ($^{119}Sn$) = 180 Hz; $h^{1/2}$ ($^{31}P$) = 4 Hz.

[h] 263 K; less than one equivalent of depe; $\delta^{13}C = 34.6$ [99.2] (32.7) (d) (C(3)Me); 24.7 [111.2], 24.0 [116.6], 14.3, 13.9 (=CEt); 20.0 [149.6], 19.2 [113.9] (=CMe) 18.2 (br), 17.3 (br), 13.8, 13.6, 12.5, 12.3 ($BEt_2$); 13.6 (38.7) (d), 6.4 (4.2) (d) ($PEt_2$); 9.2 $^2J(^{31}P^{13}C) = 12.0$ Hz, $^5J(^{31}P^{13}C) = 4.2$ Hz (dd) ($PEt_2$) 6.5 (≡CMe).

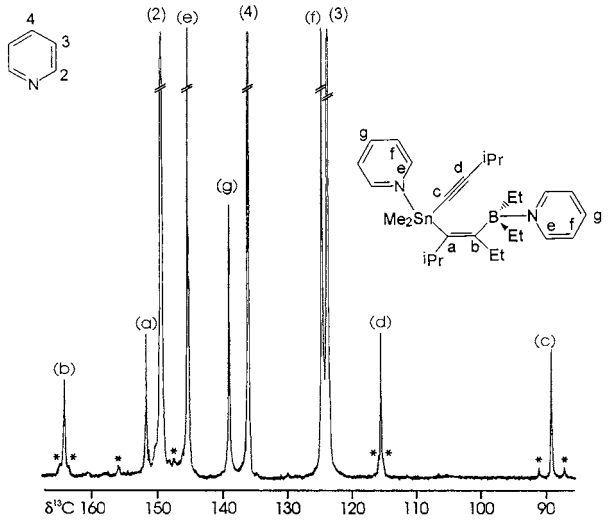



Fig. 1. 75.5 MHz $^{13}C\{^1H\}$-NMR spectrum of the bis(pyridine) adduct **7** (in $CDCl_3$ at $-60°C$), showing the range of the alkynyl, olefinic and aromatic $^{13}C$ nuclei (recorded by inverse gated $^1H$ decoupling for suppression of the NOE and quantitative comparison of integrated signal intensities). The signals for free pyridine (marked 2, 3, 4) are clearly distinguished from those for coordinated pyridine (marked e, f, g). The integrated intensity of (g) is twice as compared to that of (a), (b), (c), or (d). The signal (b) is broader owing to partially relaxed scalar $^{13}C$–$^{11}B$ coupling. $^{117/119}Sn$ satellites (for data see Table 3) are marked by asterisks.

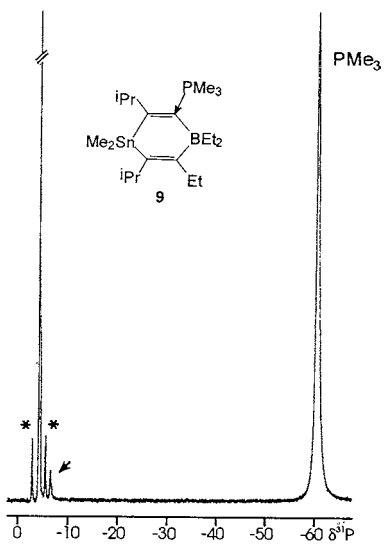



Fig. 2. 121.3 MHz $^{31}P\{^1H\}$-NMR spectrum of the reaction solution (in $CDCl_3$ at $-30°C$) containing **1d**, $PMe_3$ and the zwitterionic 1-stanna-4-borata-cyclohexa-2,5-diene derivative **9**. The $^{117/119}Sn$ satellites ($^3J(^{119}Sn,^{31}P) = 317.4$ Hz) are marked by asterisks (an arrow marks an impurity). The signal of $PMe_3$ is significantly broadened (see text).

bonds (fluorine occupies the axial position(s)), the magnitude of $|\,^1J(^{119}Sn,^{19}F)\,|$ has been reported to be in the order of 2000 Hz or somewhat less [14b], close to the values observed for **10**–**12** ($|\,^1J(^{119}Sn,^{19}F)| = 1806 \pm 46$ Hz) and also for **13**–**16** ($|\,^1J(^{119}Sn,^{19}F)| = 1865 \pm 65$ Hz). This suggests that the surroundings of the tin atoms in **10**–**12** can be described as a distorted trigonal bipyramid, where the two methyl groups and the olefinic carbon atom are in the equatorial plane, and the fluorine and the side-on coordinated alkyne group are in axial positions. This type of geometry has been found by X-ray structural analysis for donor atoms other than fluorine [7b]. In the cases of **13**–**16**, the analogous structure can be proposed where the oxygen atom occupies the axial position, as was shown for the molecular structure of an organo-substituted 2,5-dihydro-1,2,5-oxoniaboratole-THF adduct [15].

The structures of the $PMe_3$-stabilised intermediates containing a vinyl cationic fragment (Scheme 1(**A** and **B**)) are proposed for the compounds **9** and **19**–**22** on the basis of the NMR data given in Table 7. The $^{31}P$-NMR spectra (Fig. 2) show the free phosphane and signal(s) for the carbon-bonded phosphane; the latter are accompanied by $^{117/119}Sn$ satellites due to $^3J(^{117/119}Sn,^{31}P)$. In the case of **22**, there are two doublets due to $^3J(^{31}P,^{31}P) = 31.7$ Hz. The $^{119}Sn$-NMR spectra show doublets with the coupling constant $^1J(^{119}Sn,^{31}P)$. The well-documented difference in $^{119}Sn$ nuclear shielding [14] between five- (**19**) and six-membered rings (**20**) is also found ($\Delta^{119}Sn = 126.8$ ppm). The highly shielded $^{119}Sn$ nucleus in **9** ($\delta^{119}Sn$ $-144.6$) fits into the pattern known for 1-stanna-4-borata-cyclohexa-3,5-dienes [14,16]. The $^{13}C$-NMR spectra reveal patterns (broad and sharp doublets due to $^nJ(^{31}P,^{13}C)$ with $^{117/119}Sn$ satellites) in the olefinic region, typical of the cyclic structures of **A** and/or **B**, in which $PMe_3$ is linked to the formally positively charged carbon atom. This is also shown by the magnitude of $^1J(^{31}P,^{13}C)$ of about 48 Hz which is typical of tetraorganophosphonium salts [17].

## 3. Conclusions

The zwitterionic compounds **1a**–**d** and **2** show a multifaceted behaviour towards various Lewis bases. It appears that adduct formation at the tin atom takes place in all cases at low temperature, although this product could not always be detected. In the case of the fluoride anion, the Sn–F interaction is most stable. Pyridine prefers the boron atom if sterical conditions allow for the coordinative B–N bond. However, 2,2′-bipyridyl stays linked to the tin atom in **18** as a chelate ligand. Phosphanes can stabilise fragment containing a vinyl cationic fragment. The present data do not help to predict whether the formation of the five- or the six-membered ring is preferred. In any case, it proved possible to trap all reactive intermediates containing Lewis acidic centres at the tin, boron or carbon atom by selecting the correct Lewis base.

## 4. Experimental

### 4.1. General and starting materials

All preparative work and the handling of compounds was carried out in an Ar or $N_2$ atmosphere, using carefully dried solvents and dry glassware, and observing all precautions to exclude oxygen and moisture. Starting materials were prepared following literature procedures: **1a**,**b**,**d** [7a], **1c** [7b], **2** [6] The Lewis bases were commercially available and used without further purification. NMR spectra were measured from samples in 5 mm tubes: Jeol FX90Q ($^{11}$B, $^{119}$Sn); Bruker AC 300 ($^{1}$H, $^{11}$B, $^{13}$C, $^{119}$Sn); Bruker AM 500 and DRX 500 ($^{1}$H, $^{13}$C, $^{119}$Sn), all equipped with multinuclear facilities and variable-temperature units; chemical shifts are given with respect to the residual signal of the respective deuterated solvent ($CHCl_3$–$CDCl_3$; $CHDCl_2$; THF-$d_7$; toluene-$d_7$) [$\delta\,^{1}H(Me_4Si) = 0$], to the signal of the deuterated solvent [$\delta\,^{13}C(Me_4Si) = 0$], to external $Et_2O$–$BF_3$ [$\delta\,^{11}B = 0$ for $\Xi(^{11}B) = 32.083971$ MHz], external $H_3PO_4$, 85% aq, [$\delta\,^{31}P = 0$ for $\Xi(^{31}P) = 40.480747$ MHz], and to external $Me_4Sn$ [$\delta\ ^{119}Sn = 0$ for $\Xi(^{119}Sn) = 37.290665$ MHz].

### 4.2. Syntheses

#### 4.2.1. Reactions of the compounds **1** with pyridine, 1-methyl-imidazole, or trimethylphosphane (NMR scale; pyridine complexes **3**, **5**, **7**, 1-methyl-imidazole complex **8**, $PMe_3$ complexes **4**, **6**, **9**)

A solution of **1** (0.5 mmol) in $CDCl_3$ (0.5 ml) in an NMR tube is cooled to − 78°C and pyridine, 1-methylimidazole, or $PMe_3$ is added in one portion. The mixture is studied by NMR, and the compounds **3**, **4**, **7** and **8** can be isolated, after removing of all volatile materials at − 30°C in a vacuum ($5 \times 10^{-2}$ Torr) as colourless solids. These compounds decompose when stored above 0°C.

*4.2.1.1. Complex* ***3***. $^{1}$H-NMR ($CDCl_3$/243 K): $\delta$ [$^{n}J(^{119}Sn,^{1}H)$] = 0.34 [56.3] (s, 6H, $SnMe_2$); 0.26 (br), 0.27 (br) (10H, $BEt_2$); 1.57 (br), 0.56 (t) (5H, Et); 2.35 (t), 1.17 (br), 0.74 (t) (7H, =CPr); 1.98 (t), 1.28 (m), 0.71 (t) (7H, ≡CPr).

*4.2.1.2. Complex* ***4***. $^{1}$H-NMR ($CDCl_3$/243 K): $\delta$ [$^{n}J(^{119}Sn,^{1}H)$] = 0.38 [54.4] (s, 6H, $SnMe_2$); 0.66 (t), (6H, $B(CH_2CH_3)_2$, $^{1}H(BCH_2)$ signals overlap with other signals); 1.96(q), 0.88(t) (5H, Et); 2.35 (t), 1.22 (m), 0.85 (t) (7H, =CPr); 2.15 (t), 1.47 (m), 0.91 (t) (7H, ≡CPr).

*4.2.1.3. Complex* ***5***. $^{1}$H-NMR ($CDCl_3$/243 K): $\delta$ [$^{n}J(^{119}Sn,^{1}H)$] = 0.65 [n.m.] (s, 6H, $SnMe_2$); 1.05 (m), 0.72 (d) (14H, B$^{i}Pr_2$); 2.48 (m), 0.96 (d) (7H, $^{i}$Pr); 2.14 (q), 0.73 (t) (5H, =CEt); 2.12 (q), 1.04 (t) (5H, ≡CEt).

*4.2.1.4. Complex* ***6***. $^{1}$H-NMR ($CDCl_3$/243 K): $\delta$ [$^{n}J(^{119}Sn,^{1}H)$] = 0.63 [49.1] (s, 6H, $SnMe_2$); 0.38 (br), 0.73 (d) (14H, B$^{i}Pr_2$); 2.45 (m), 0.75 (d) (7H, $^{i}$Pr); 2.43 (q), 0.93 (t) (5H, =CEt); 2.89 (q), 1.15 (t) (5H, ≡CEt).

*4.2.1.5. Complex* ***7***. $^{1}$H-NMR ($CDCl_3$/213 K): $\delta$ [$^{n}J(^{119}Sn^{1}H)$] = 0.26 (br) (s, 6H, $SnMe_2$); 0.35 (br), (6H, $B(CH_2CH_3)_2$, signals for $BCH_2$ overlap with other signals); 1.76 (q), 0.62 (t) (5H, Et); 3.01 (m), 0.91 (d) (7H, =C$^{i}$Pr); 2.33 (m), 0.91 (d), (7H, ≡C$^{i}$Pr).

*4.2.1.6. Complex* ***8***. $^{1}$H-NMR ($CDCl_3$/213 K): $\delta$ [$^{n}J(^{119}Sn^{1}H)$] = 0.25 [54.6] (s, 6H, $SnMe_2$); 0.64 (br), 0.51 (br) (10H, $BEt_2$); 2.18 (br), 1.03 (t) (5H, Et); 3.42 (m), 1.27 (d) (7H, ≡C$^{i}$Pr); 2.72 (m), 1.36 (d) (7H, ≡C$^{i}$Pr).

#### 4.2.2. Reactions of the compounds **1** with $Bu_4NF$ in THF (NMR scale; complexes **10**, **11**, **12**, and 2,5-dihydro-1,2,5-oxoniastannaboratole derivatives **13**, **14**, **15**, **16**)

A solution of **1** (0.2 mmol) in THF-$d_8$ (0.35 ml) is cooled to − 78°C, $Bu_4NF$ in THF (1.1 M; 0.24 mmol) is added in one portion, and the mixture is warmed to − 30°C. and studied by NMR spectroscopy. The compounds **10, 11** and **12** can be identified, and these decompose when volatile material is removed in a vacuum. If the reaction mixtures in THF are warmed to ambient temperature, the compounds **13**–**16** are formed quantitatively. These compounds can then be isolated, after removing of all volatile material in vacuo (0.1 Torr), as colourless, oily liquids. Monitoring of the reaction of **1d** with $Bu_4NF$–THF shows that **16** is already present at − 65°C.

*4.2.2.1. Complex* ***11***. $^{1}$H-NMR (243 K): $\delta$ [$^{n}J(^{119}Sn^{1}H)$] = 0.52 [63.2], $^{3}J(^{19}F,^{1}H) = 3.6$ Hz (d, 6H, $SnMe_2$); 1.36 (m), 0.82 (d) (14H, B$^{i}Pr_2$); 2,68 (m), 0.85 (d) (7H, $^{i}$Pr); 1.43 (q), 1.03 (t) (5H, =CEt); 2.13 (q), 1.10 (t) (5H, ≡CEt); 3.38 (br), 1.73 (br), 1.49 (m), 1.06 (t) (36H, $NBu_4$).

*4.2.2.2. Complex* ***12***. $^{1}$H-NMR (THF-$d_8$/243 K): $\delta$ [$^{n}J(^{119}Sn^{1}H)$] = 0.38 [66.2] (s, 6H, $SnMe_2$); 0.80 (t), (6H, $B(CH_2CH_3)_2$, $^{1}H(BCH_2)$ signals overlap with other signals); 1.10 (t, 3H, $CH_2CH_3$, $^{1}H(CH_2)$ signals overlap with other signals); 3.40 (s), 2.32 (s) (8H, =$CCH_2NMe_2$); 3.38 (s), 2.37 (s) (8H, ≡$CCH_2NMe_2$); 3.59 (br), 1.92 (m, br), 1.62 (m, br), 1.24 (t) (36H, $NBu_4$).

*4.2.2.3. Complex* ***13***. $^{1}$H-NMR ($CDCl_3$): $\delta$ [$^{n}J(^{119}Sn^{1}H)$] = 0.16 [65.1] (s, 6H, $SnMe_2$); 0.55 (t), (6H, $B(CH_2CH_3)_2$, $^{1}H(BCH_2)$ signals overlap with other signals); 1.73 (q), 0.82 (t) (5H, Et); 2.28 (t), 1.60 (m), 0.84 (t) (7H, Pr); 3.24 (br), 1.61 (m), 135 (m), 0.95 (t) (36H, $NBu_4$).

*4.2.2.4. Complex* ***14***. $^1$H-NMR ($CDCl_3$): $\delta$ [$^nJ(^{119}Sn^1H)$] = 0.18 [63.2] (s, 6H, $SnMe_2$); 0.67 (d), 0.71 (d) (12H, $B(CHMe_2)_2$, $^1$H(BCH) signals overlap with other signals); 2.48 (m), 1.09 (d) (7H, $^i$Pr); 2.46 (q), 0.96 (t) (5H, Et); 3.17 (br), 1.58 (m), 1.39 (m), 0.96 (t) (36H, $NBu_4$).

*4.2.2.5. Complex* ***15***. $^1$H-NMR (THF-$d_8$/243 K): $\delta$ [$^nJ(^{119}Sn^1H)$] = 0.21 [66.8] (s, 6H, $SnMe_2$); 0.03 (br), 0.65 (t) (10H, $BEt_2$); 2.12 (q), 0.92 (t) (5H, Et); 3.19[59.5] (s), 2.22 (s) (8H, $CH_2NMe_2$); 3.38 (br), 1.72 (m), 1.46 (m), 1.03 (t) (36H, $NBu_4$).

*4.2.2.6. Complex* ***16***. $^1$H-NMR ($C_7D_8$): $\delta$ [$^nJ(^{119}Sn^1H)$] = 0.34 [65.1] (s, 6H, $SnMe_2$); 0.70 (br), 0.77 (t) (10H, $BEt_2$); 3.26 (q, br), 0.90 (t) (5H, Et); 2.13 (m), 1.23 (d) (7H, $^i$Pr); 2.90 (br), 1.31 (m), 1.22 (m), 0.83 (t) (36H, $NBu_4$).

### *4.2.3. Reactions of* ***2*** *with pyridine and 2,2′-bipyridyl (adducts* ***17*** *and* ***18****)*

A solution of **2** (0.5 g; 1.1 mmol) in toluene (20 ml) is cooled to −78°C, and pyridine (3.7 mmol) or 2,2′-bipyridyl (1.1 mmol) is added in one portion. The reaction starts already at −78°C. After removing all volatile material in a vacuum ($10^{-3}$ Torr) at 0°C, a colourless solid **17** (fast decomp. >20°C) is obtained in the case of pyridine, and a yellow solid **18** (fast decomp. >40°C) in the case of 2,2′-bipyridyl.

*4.2.3.1. Adduct* ***17***. $^1$H-NMR ($CD_2Cl_2$/243 K): $\delta$ [$^nJ(^{119}Sn^1H)$] = 2.21 [74.5] (s, 6H, =CMe); 1.90 [9.0] (s, 6H, ≡CMe); 1.76(q), 0.64(t) (10H, =CEt); 0.70 (br), 0.52 (br) (20H, $BEt_2$); 8.68 (d, 4H; $H^2$-py); 7.92 (t, 2H; $H^4$-py); 7.47 (t, 4H; $H^3$-py).

*4.2.3.2. Adduct* ***18***. $^1$H-NMR ($C_7D_8$/243 K): $\delta$ [$^nJ(^{119}Sn^1H)$] = 2.30 (m, 2H), 2.19 (m, 2H), 0.76 (t, 6H) (=CEt); 1.97 (s, 6H, ≡CMe); 1.67 (t, 6H), 1.40 (t, 6H), 1.08(m, 4H), 0.95(m, 4H) ($BEt_2$); 1.30 (s, 6H, =CMe); 9.29 (d, 2H; $H^6$-bpy); 7.15–6.75 (m, 4H; $H^3$/$H^4$-bpy); 6.64 (t, 2H; $H^5$-bpy); $^1$H-NMR ($C_7D_8$/293 K): $\delta$ [$^nJ(^{119}Sn^1H)$] = 2.19 (q), 0.78 (t), 0.76 (t) (6H; =CEt); 1.84[9.8] (s, 6H, ≡CMe); 1.45 [114.0] (s, 6H; =CMe); 1.30 (t), 0.84 (q) (20H; $BEt_2$); 8.91 (br) (2H; $H^6$-bpy); 7.61 (br) (2H; $H^3$-bpy); 7.07 (m, 2H; $H^4$-bpy); 6.71 (m, 2H; $H^5$-bpy).

### *4.2.4. Reactions of* ***2*** *with* $PMe_3$, $PEt_3$ *and depe (zwitterionic complexes* ***19***, ***20***, ***21***, ***22****)*

A solution of compound **2** (0.5 g; 1.1 mmol) in $CH_2Cl_2$ (20 ml) is cooled to −78°C and the respective phosphane (2.5 mmol) is added in one portion. Removing all volatile material in a vacuum ($10^{-3}$ Torr) at 0°C leaves the products, which start to decompose at temperatures >0°C. The products are highly viscous oils (**21**, **22**) or colourless solids (**19**/**20** = 1:1 after crystallisation from pentane).

*4.2.4.1. Complex* ***19*** *in mixture with complex* ***20***. $^1$H-NMR ($CH_2Cl_2$/$CD_2Cl_2$/243 K): $\delta$ = 2.47 $^3J(^{31}P^1H)$ = 12.6 Hz (d, 3H, C(3)Me); 2.30(br), 2.02(br) (2H, 2H; =CEt); 2.14 (s, 3H; C(6)Me); 1.89 (s, 3H; C(1′)Me); 1.88 (s, 3H; ≡CMe). **20**: $\delta$ = 2.43 $^4J(^{31}P^1H)$ = 3.4 Hz (d, 3H; C(2)Me); 2.24(br), 2.00(br) (4H; =CEt); 2.07 (s, 3H; C(6)Me); 1.83 (s, 3H; C(1′)Me); 2.00 (s, 3H; ≡CMe);-not assigned $^1$H resonances of the **19**/**20** mixture: $\delta$ = 2.98 $^2J(^{31}P^1H)$ = 12.3 Hz (d), 1.92 $^2J(^{31}P^1H)$ = 12.3 Hz (d) ($PMe_3$); 0.99, 0.95, 0.95, 0.91 (=CEt); 0.79(br), 0.61(br), 0.55(br) ($BEt_2$).

*4.2.4.2. Complex* ***21***. $^1$H-NMR ($CH_2Cl_2$–$CD_2Cl_2$/263 K) $\delta$ = 2.50 $^3J(^{31}P^1H)$ = 10.5 Hz (d, 3H, C(3)Me); 2.31(m), 2.05(m), 1.04(t), 0.94(t) (10H; =CEt); 2.37 $^2J(^{31}P^{13}C)$ = 12.0 Hz (m), 1.28 $^3J(^{31}P^{13}C)$ = 17.6 Hz (dt) (15H; $PEt_3$); 2.18(s), 1.92(s) (6H; =CMe); 1.92 (s, 3H; ≡CMe); 0.81(br), 0.63(br), 0.30(br) (20H; $BEt_2$).

*4.2.4.3. Complex* ***22***. $^1$H-NMR ($CH_2Cl_2$–$CD_2Cl_2$/263 K): $\delta$ = 2.45 $^3J(^{31}P^1H)$ = 10.5 Hz (d, 3H, C(3)Me); 2.14(s), 1.89(s), 1.88(s) (3H, 3H; =CMe, ≡CMe); 0.81(br), 0.63(br), 0.28(br) (20H, $BEt_2$).

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