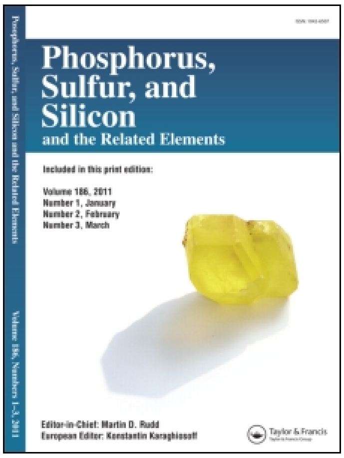

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1,1-ORGANOBORATION OF STANNYLETHYNYLPHOSPHANES

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1,1-ORGANOBORATION OF STANNYLETHYNYLPHOSPHANES

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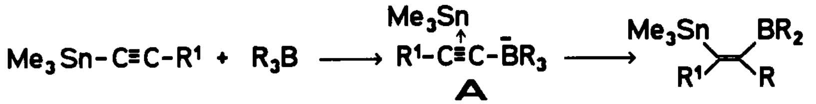
Bis(trimethylstannylethynyl)phenylphosphane (**1**) reacts regio- and stereoselectively via 1,1-organoboration with one equivalent of triethylborane (**4a**) or triisopropylborane (**4b**) to give the (Z)-alkene derivatives **5a** and **5b**, respectively, in quantitative yield. With an excess of **4a** the bis(alkenyl)phosphane **6a** is formed ((Z)-configuration of both alkenyl groups). The reaction between bis(dimethylphosphanylethynyl)dimethyltin (**2**) and **4a** leads to a complex reaction mixture, whereas bis(diphenylphosphanylethynyl)dimethyltin (**3**) reacts with **4a** to give selectively the organometallic substituted stannole derivative **8a**. In this case, a zwitterionic intermediate (**9a**) was identified by ^{1}H-, ^{11}B-, ^{13}C-, ^{31}P and ^{119}Sn NMR. In **9a** a positively charged triorganotin fragment is stabilized by intramolecular π-coordination to the C≡C bond of an alkynylborate group. The reaction between **3** and **4b** affords a mixture (12:1) of the stannole derivative **8b** and the 1-stanna-4-bora-2,5-cyclohexadiene derivative **10b**. All compounds were characterized by multinuclear NMR, and various coupling signs have been determined for the first time.

Key words: 1-Alkynylphosphanes, organotin substituted, 1,1-organoboration, tin cations, triorgano, coordination, σ and π, multinuclear NMR, coupling signs.

INTRODUCTION

The 1,1-organoboration of alkynyltin compounds has opened convenient routes to numerous organometallic-substituted alkenes and heterocyclic compounds.[1,2] Recently, the mechanism of this reaction has been firmly established by the isolation and structural characterization of zwitterionic intermediates[3,4] in which a triorganotin cation is coordinated to the C≡C bond of an alkynylborate fragment, as shown schematically in **A** in Equation (1).



(1)

If the substituent R^1 is a functional group or contains a donor group (e.g., R^1 = CH$_2$NMe$_2$) the synthetic potential increases further, and zwitterionic intermediates similar to **A** have been observed.[5] The reactivity of the Sn—C≡ bond ensures that the 1,1-organoboration proceeds under mild reaction conditons for a wide range of different substituents R^1. When ethynylphosphanes of the type Me$_2$P—C≡CH,

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$Ph_2P—C≡CH$ or $PhP(C≡CH)_2$ are treated with triethylborane no reaction takes place, even after prolonged heating up to 100°C in boiling triethylborane. It is expected that the replacement of the terminal ≡C—H bond by the ≡C—Sn bond activates these alkynylphosphanes in order to carry out 1,1-organoboration reactions. One object of the present study concerns the question whether the usual stereochemistry in the products from 1,1-organoborations [cis position of stannyl and boryl group at the C=C bond as shown in Equation (1)] is affected by the presence of the phosphanyl substituent. Other interesting problems are related to ^{31}P NMR parameters, in particular to coupling constants and their signs in the organometallic substituted alkene derivatives as the expected products. For these purposes we have prepared the compounds **1–3** studied their reactivity towards triethylborane (Et_3B, **4a**) and triisopropylborane (iPr_3B, **4b**).

$Ph\text{-}P(C≡C\text{-}SnMe_3)_2$ **1** $\quad Me_2Sn(C≡C\text{-}PMe_2)_2$ **2** $\quad Me_2Sn(C≡C\text{-}PPh_2)_2$ **3**

RESULTS AND DISCUSSION

Synthesis of the Stannylethynylphosphanes 1–3

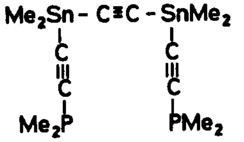
For the synthesis of **1–3**, the ethynylphosphanes $PhP(C≡CH)_2$, $Me_2P—C≡CH$ and $Ph_2P—C≡CH$ were lithiated[6] in hexane by treatment with two equivalents (**1**) or one equivalent (**2**, **3**) of butyllithium. The reactions between these lithiated alkynes and trimethyltin chloride or dimethyltin dichloride afforded the alkynes **1**, **2**, and **3**, respectively [Equations (2, 3, 4)].

$$Ph\text{-}P(C≡CH)_2 \xrightarrow[-\,2\,n\text{BuH}]{+\,2\,n\text{BuLi}} Ph\text{-}P(C≡CLi)_2 \xrightarrow[-\,2\,\text{LiCl}]{+\,2\,Me_3SnCl} \underset{\mathbf{1}}{Ph\text{-}P(C≡C\text{-}SnMe_3)_2} \quad (2)$$

$$2\,Me_2P\text{-}C≡CH \xrightarrow[-2\,n\text{BuH}]{+2\,n\text{BuLi}} 2\,Me_2P\text{-}C≡CLi \xrightarrow[-2\,\text{LiCl}]{+\,Me_2SnCl_2} \underset{\mathbf{2}}{Me_2Sn(C≡C\text{-}PMe_2)_2} \quad (3)$$

$$2\,Ph_2P\text{-}C≡CH \xrightarrow[-2\,n\text{BuH}]{+\,2\,n\text{BuLi}} 2\,Ph_2P\text{-}C≡CLi \xrightarrow[-\,2\,\text{LiCl}]{+\,Me_2SnCl_2} \underset{\mathbf{3}}{Me_2Sn(C≡C\text{-}PPh_2)_2} \quad (4)$$

Table I lists ^{13}C, ^{31}P and ^{119}Sn NMR data of **1–3**. The compounds **1** and **3** were obtained in high purity, whereas several attempts at the synthesis of **2** always gave



2'

TABLE I

^{13}C, ^{31}P and ^{119}Sn NMR data[a] of the stannylethynylphosphanes **1**–**3**

Comp. No.	δ^{13}C P-C≡	δ^{13}C Sn-C≡	δ^{13}C P-*Ph*/P-*Me*	δ^{13}C Sn-*Me*	δ^{31}P	δ^{119}Sn
1	103.9 [56.9] (13.8)	115.8 [368.1] (4.9)	134.4 (i), 132.4(o) [5.0] (21.7) (< 1.0) 129.0 (m), 129.4 (p) (7.9) (< 1.0)	-8.2 [402.6]	-55.6 [16.6]	-63.0 (16.6)
2	113.4 [94.3] (30.9)	106.5 [555.2] (10.6)	14.1 [7.0] (8.2)	-6.1 [495.4] (7.0)	-65.8 [12.5]	-160.8 (12.5)
2′	114.6 [n.m.] (33.7)	106.6[b] [554.8] (11.1) 113.4[c]	13.7 [7.9] (8.0)	-6.1 [495.4]	-65.1 [12.5]	-167.0 (12.5)
3	107.7 [90.8] (17.6)	112.6 [532.6] (6.1)	135.9 (i), 132.5 (o) (6.1) (20.6) 128.6(m), 129.2 (p) (7.6) (< 1.0)	-5.6 [495.9]	-32.7 [29.1]	-157.1 (29.1)

[a] Compound **1** in C_6D_6 and compounds **2**, **2′** and **3** in $CDCl_3$, all at 25°C.

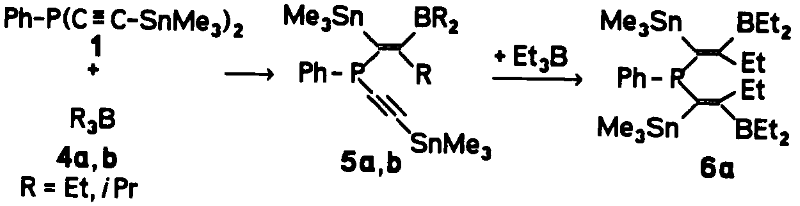
[b] $^4J(^{119}Sn^{13}C)$ = 1.8 Hz.

[c] Sn-*C*≡*C*-Sn

mixtures. The NMR spectroscopic analysis of these mixtures showed that the major impurity is **2′** which decomposes further, because of the lability of the Sn—C≡ bond, when the solutions are kept at room temperature. This is evident from ^{31}P and ^{119}Sn NMR spectra which show an increasing number of additional signals, all typical of the structural units in **2′**, indicative of further exchange processes.

1,1-Organoboration of the Stannylethynylphosphanes

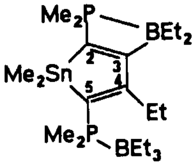
The reaction between **1** and one equivalent of Et_3B (**4a**) proceeds slowly between −30°C and room temperature to give selectively the (Z)-alkene **5a** [Equation (5a)], and in the presence of an excess of **4a**, the bis(alkenyl)phosphane **6a** is formed [Equation (5b)]. Treatment of **1** with *i*Pr_3B (**4b**) affords only **5b** [Equation (5a)], even in the presence of a large excess of **4b** and after heating to 60°C for 6 h. Heating for longer periods or at higher temperature causes extensive decomposition. All alkenes **5** and **6** are formed selectively free of other isomers, and they are obtained in quantitative yield. Prolonged UV irradiation or heating to reflux in benzene solution induces decomposition. Rearrangement of the (Z)-alkenes **5a**,**b**



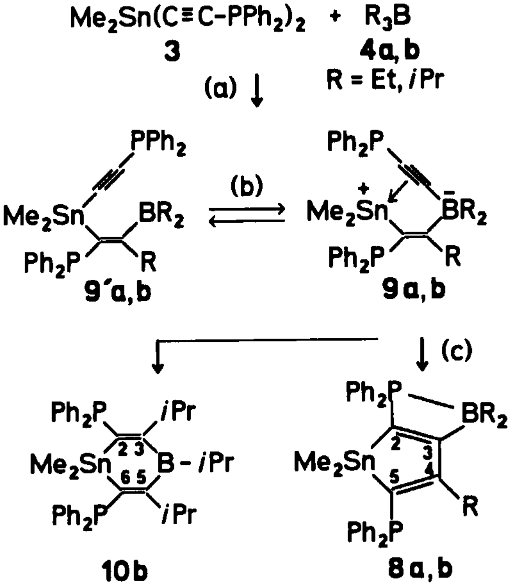
(5)

or **6a** to the (E)-alkenes (potential precursors of heterocycles such as phospholes) was not observed.

Treatment of a $CDCl_3$-solution containing **2** and **2'** (ratio ca. 4:1), together with a small amount of other alkynes of similar type, with an excess of triethylborane leads to a complex reaction mixture containing many different species which could not be analysed by ^1H or ^{13}C NMR as yet. ^{31}P NMR spectra are also not very helpful since the nature of this mixture is further complicated by the fact that Et_3B is coordinated more or less strongly to the various Me_2P-groups. In addition, intramolecular P—B coordination is also possible, once the sequence of 1,1-organoboration reactions has reached the stage of stannole formation (as in **8**, vide infra). There are also several ^{119}Sn NMR signals of appreciable intensity. One signal at δ ^{119}Sn = +35.8 [$^2J(^{119}Sn^{31}P)$ = 40.0 and 78.0 Hz] is tentatively assigned to the stannole **7a** with a structure analogous to that of the stannoles **8** [see Equation (6)].



7a



(6)

TABLE II

^{13}C, ^{11}B, ^{31}P and ^{119}Sn NMR data[a] of the alkenyl derivatives **5** and **6** and of the zwitterionic intermediate **9a**

Comp.	$\delta^{13}C$						$\delta^{11}B$	$\delta^{31}P$	$\delta^{119}Sn$
No.	P-*C*=	B-*C*=	=C-*R*	P-*Ph*	Sn-*Me*	BR$_2$			
5a	131.7 [449.5] (28.6)	185.1 (17.7) (br)	28.1, 14.5 (48.2) (4.9)	139.5(i)[b] (9.8)	-4.4[c] [321.9]	21.8, 9.3 (br)	+86.5	-32.3 [66.4]	-29.3[d] (66.4)
5b	130.1 [446.0] (35.1)	188.5 (14.8) (br)	35.3 [90.0][h] (37.4) 23.5, 23.4 (6.9) (5.9)	139.4(i)[e] (9.9)	-3.3[f] [319.0]	27.0,25.5 (br) (br) 20.0,20.7 19.6,19.9	+84.7	-31.7 [62.3[i] 14.2]	-41.6[g] (62.3)
6a	137.5 [418.5, 18.0] (65.0)	179.6 [40.0] (7.0) (br)	30.4, 13.6 [88.5] [7.8] (30.5)[l] (2.0)	140.4(i)[j] [13.7] (9.8)	-4.7 [314.0] (2.0)	22.3, 9.5 (br)	+85.7	-2.7[k] [125.0]	-50.2 [68.0] (125.0)
9a[m]	134.8 [658.0] (4.9)	207.3 (br)	29.4, 15.3 [156.4] (4.6) (30.0)	139.1[n] (12.0)	3.0 [281.6] (6.7)	18.6,12.6 (br)	-1.5	-14.0[o] [102.5]	+203.9 (102.5)

[a] In C_6D_6 at 25°C, if not mentioned otherwise; coupling constants $J(^{119}SnX)$ (X = ^{13}C, ^{31}P) are given in square brackets and $J(^{31}PX)$ in parentheses (X = ^{13}C, ^{31}P, ^{119}Sn); (br) denotes the broadened ^{13}C resonance signal of boron-bonded carbon atoms.

[b] Other $\delta^{13}C$ data: 130.5 (o) (16.7), 128.6 (m) (3.9), 127.4 (p); 110.2 (19.7) (P-*C*=), 115.4 (5.9) (Sn-*C*=).

[c] =C-Sn*Me*$_3$: $\delta^{13}C$ = -8.0 [401.7].

[d] =C-*Sn*Me$_3$: $\delta^{119}Sn$ = -63.0 (16.5).

[e] Other $\delta^{13}C$ data: 131.1 (16.7) (o), 128.5 (3.9) (m), 127.5 (p); 110.3 (21.7) (P-*C*=), 115.8 [402.8] (5.9) (Sn-*C*=).

[f] =C-Sn*Me*$_3$: $\delta^{13}C$ = -7.8 [402.8].

[g] =C-*Sn*Me$_3$: $\delta^{119}Sn$ = -71.6 [14.2].

[h] $^{13}C/^{1}H$ HETCOR [based on $^{1}J(^{13}C^{1}H)$]: negative tilts of crosspeaks show opposite signs of $^{4}J(^{31}P^{1}H)$ and $^{3}J(^{31}P^{13}C)$, and also of $^{3}J(^{119}Sn^{13}C)$ and $^{4}J(^{119}Sn^{1}H)$ (see Fig. 2).

[i] $^{31}P/^{1}H$ HETCOR [based on $^{4}J(^{31}PC{=}CC^{1}H)$ = 7.2 Hz]: postive tilt of cross peaks shows alike signs of $^{2}J(^{119}Sn^{31}P)$ and $^{4}J(^{119}Sn^{1}H)$.

[j] Other $\delta^{13}C$ data: 134.5 (o) (18.7), 128.5 (m), 128.2 (p).

[k] ^{13}C Satellites according to $^{1}J(^{31}P^{13}C_{(P-C=)})$ = 65.0 Hz with isotope induced shift $^{1}\Delta^{13/12}C(^{31}P)$ = - 31.7 ppb

[l] $^{13}C/^{1}H$ HETCOR [based on $^{1}J(^{13}C^{1}H)$]: negative tilt of croos peaks shows opposite signs of $^{4}J(^{31}P^{1}H)$ and $^{3}J(^{31}P^{13}C)$.

[m] At 243 K in $CDCl_3$.

[n] Other $\delta^{13}C$ data: 132.5 (21.5), 132.3 (17.4) (o), 129.0 (5.8), 128.9 (8.3) (m), 129.7, 128.7 (p); B-*C*=*C*-P*Ph*$_2$: 106.5 (7.2) (br), 117.4 [39.1] (27.3), 133.6 (4.9) (i).

[o] =C-*P*Ph$_2$: $\delta^{31}P$ = -34.3 [53.7].

The reaction of the alkyne **3** with an excess of Et_3B (**4a**) leads quantitatively to the stannole **8a** [Equation (6)]. The first step of this reaction is an intermolecular 1,1-ethyloboration that leads to **9a′**. Then the alkynyl group is shifted from the tin to the boron atom, affording the zwitterionic compounds **9a** [Equation (6b)] in which the triorganotin cation is stabilized by π-coordination to the C≡C bond. This proposed structure is fully consistent with the NMR data (vide infra), and it corresponds to that of analogous intermediates for which the molecular structures have been determined by X-ray analyses.[3-5] Thus, the presence of the Ph_2P groups does not change the fundamental mechanism of the 1,1-organoboration reaction. Intramolecular 1,1-vinyloboration in **9a** leads to the stannole **8a** [Equation (6c)] which can be isolated as a colorless powder. The reaction between **3** and $i Pr_3B$ (**4b**) gave a 2:1 mixture of the stannole **8b** and the 1-stanna-4-bora-2,5-cyclohexadiene **10b**. The latter compound **10b** is formed by intramolecular 1,1-alkyloboration in **9b**. These results are in agreement with previous observations when the reactions between di-, tri- and tetra-1-alkynyltin compounds and **4b** were studied.[3-5,7]

NMR Spectroscopic Results

Relevant NMR data (except for ^1H NMR; see experimental part) are listed in the Tables I (**1–3**), II (**5**, **6** and **9**) and III (**8**, **10b**).

TABLE III

^{13}C, ^{11}B, ^{31}P, ^{119}Sn NMR data[a] of the stannole **8a**

Comp.	$\delta^{13}C$						$\delta^{11}B$	$\delta^{31}P$	$\delta^{119}Sn$
No.	C(2)	C(3)	C(4)	C(5)	Sn-*Me*	BR_2			
8a[b]	142.4 [281.9] (12.5) 140.7[e] [10.8] (9.9)	186.3 [40.0] (43.0) (br)	165.3 [85.2] (22.5,25.2) 29.9,13.8 [67.9] (2.7) (21.1)	142.8 [340.6] (26.9,1.8) 140.9[e] [8.1] (7.2)	-5.6 [317.7]	22.0,9.6 (br) (3.6)	-5.1	-12.1[c] [45.7] (2.8) -13.8[d] [62.5] (2.8)	39.6 (45.7, 62.3)

[a] In $CDCl_3$; 25°C; coupling constants $J(^{119}SnX)$ ($X = {}^{13}C, {}^{31}P$) are given in square brackets and $J(^{31}PX)$ in parentheses ($X = {}^{13}C, {}^{31}P, {}^{119}Sn$); (br) denotes the broadened ^{13}C resonance signal of a boron-bonded carbon atoms.

[b] Some relevant NMR data of the mixture containing **8 b** and **10b**: $\delta^{11}B$ (**8b**) = +53.0 ($h_{1/2}$ = 500 Hz); $\delta^{31}P$ (**8b**) = -14.5 [41.0] (4.0), -10.6 [71.0] (4.0); $\delta^{119}Sn$ (**8b**) = -9.3 [67.0]; $\delta^{31}P$ (**10b**) = -9.3 [68.5]; $\delta^{119}Sn$ (**10b**) = -100.0 (68.5).

[c] Tentatively assigned to P-C(2).

[d] Tentatively assigned to P-C(5).

[e] No assignment of $\delta^{13}C$(i,o,m,p) of the *Ph*$_2$P-C(2) and *Ph*$_2$P-C(5): $\delta^{13}C$ = 132.6 (16.9) and 132.9 (19.4) (o), 128.2 (6.4) and 128.3 (6.7) (m), 128.1 and 129.0 (p).

The stereochemistry of the alkenes **5** and **6** at the C=C bond follows from the δ ^{13}C values, the $^{117/119}Sn$ satellites according to $^nJ(Sn^{13}C)$ (n = 1–4), the appearance of broad ^{13}C NMR signals[8] for the boron-bonded olefinic carbon atom and from $^1H/^1H$ NOE difference spectra[9] [irradiation of the $^1H(SnMe_3)$ or $^1H(=CR)$ transitions]. The unambiguous assignment of the ^{13}C NMR signals for the olefinic and alkynyl carbon atoms linked directly to a tin atom requires the observation of $^{117/119}Sn$ satellites. This was achieved by using the refocused INEPT pulse sequence[10] based on long range coupling constants $^3J(^{13}C^1H_{SnMe})$ (range between 1 to 4 Hz).[11] After optimizing the delays in the pulse sequence, meaningful spectra were obtained within 1 to 2 h (see Figure 1). The magnitude of the coupling constants $^nJ(^{119}Sn^{13}C)$ and $^nJ(^{119}Sn^1H)$ lie in the expected range.[3–5,7] This is also true for $^nJ(^{31}P^{13}C)$ of the PPh group.[12] In contrast, the values $|^1J(^{31}P^{13}C_{PC=})|$ are fairly large already in **5a** (28.6 Hz) and **5b** (35.1 Hz) and increase further to 65.0 Hz in **6a** (compare with $|^1J(^{31}P^{13}C^{2,6})|$ = 14.3 Hz in 4,4-dimethyl-1-phenyl-1-phospha-4-stanna-2,5-cyclohexadiene[13]). The magnitude of the long range coupling constant $|^4J(^{119}Sn^{119}Sn)|$ (68 Hz) for **6a** is also remarkable. However, there are no data available for comparison.

In the case of **5b**, the signs of coupling constants $^4J(^{119}Sn^1H_{(R)})$ and $^2J(^{119}Sn^{31}P)$ were determined by combining the information from 2D $^{13}C/^1H$ and $^{31}P/^1H$ het-

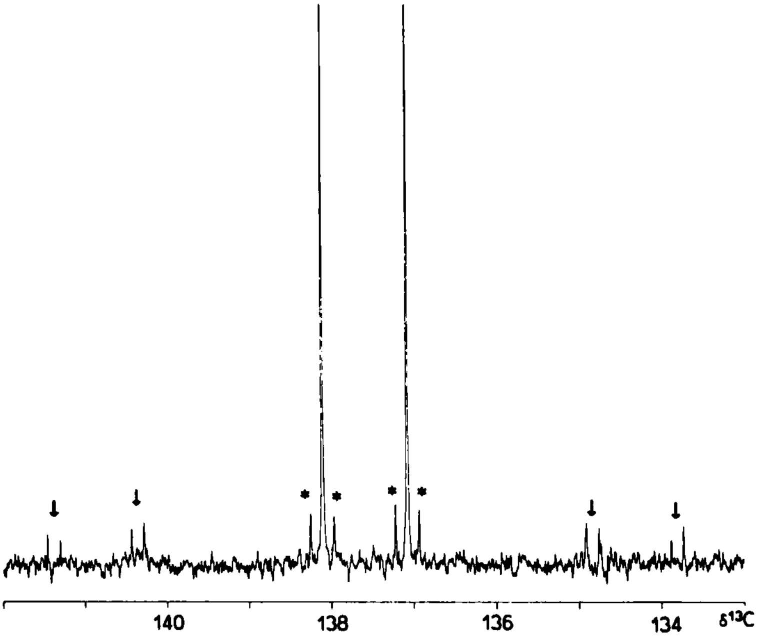


FIGURE 1 62.9 MHz ^{13}C NMR spectrum of the bis(alkenyl)phosphane **6a** showing the ^{13}C resonance signal of the olefinic carbon atom linked directly to tin and phosphorus. The spectrum was recorded by using the refocused INEPT pulse sequences (based on $^3J(^{13}CSnC^1H) \approx 1.0$ Hz, repetition delay 2.5 s, acquisition time 1.5 s, 2.5 h of spectrometer time) with ^1H decoupling. The $^{117/119}Sn$ satellites corresponding to $^1J(Sn^{13}C)$ and $^3J(SnCP^{13}C)$, marked by arrows and asterisks, respectively, can be observed undisturbed by other signals. In contrast, in normal $^{13}C\{^1H\}$ NMR spectra, it was not possible to assign the $^{117/119}Sn$ satellites belonging to $^1J(Sn^{13}C)$ with certainty because of severe overlap with other ^{13}C resonance signals in that particular region.

eronuclear shift correlations (HETCOR), based on ${}^1J({}^{13}C^1H)$ and the long range coupling constant ${}^4J({}^{31}PC{=}CC^1H)$, with regard to the cross peaks for the ${}^{117/119}Sn$ satellites. The contourplot of the ${}^{13}C/{}^1H$ HETCOR for the $=C—CH$ moiety (Figure 2) shows a negative tilt[14] of the ${}^{117/119}Sn$ satellites, which means that the signs of ${}^3J({}^{119}Sn^{13}C)$ and ${}^4J({}^{119}Sn^1H)$ are opposite; the former is known to be negative[15,16] and therefore, ${}^4J({}^{119}Sn^1H) > 0$. In the ${}^{31}P/{}^1H$ HETCOR for the $P—C{=}C—CH$ moiety, a positive tilt of the cross peaks for the ${}^{117/119}Sn$ satellites indicates alike signs of ${}^2J({}^{119}Sn^{31}P)$ and ${}^4J({}^{119}Sn^1H)$ and therefore, ${}^2J({}^{119}Sn^{31}P) > 0$. The information on the coupling sign of ${}^2J({}^{119}Sn^{31}P)$ in **5**, **6** and **8a** (Ph_2P-group in 5-position), was also gained by 1D selective ${}^1H\{{}^{31}P\}$ heteronuclear double resonance experiments.[17] Although the long range coupling ${}^4J({}^{31}P^1H_{SnMe})$ across the olefinic carbon atom was not resolved in the ${}^1H$ NMR spectra, the central ${}^1H({=}CSnMe)$ signal became sharper upon ${}^{31}P$ irradiation. If the ${}^{31}P$ irradiation frequency was set selectively with low power level to either of the ${}^{117/119}Sn$ satellites according to ${}^2J(Sn^{31}P)$, differential effects were observed for ${}^{117/119}Sn$ satellites in the ${}^1H$ NMR spectrum. From this it followed that the signs of ${}^2J(Sn^1H_{SnMe})$ (>0[18]) and ${}^2J(Sn^{31}P)$ are alike, meaning that ${}^2J({}^{119}Sn^{31}P) > 0$ and the reduced coupling constant ${}^2K({}^{119}Sn^{31}P) < 0$.

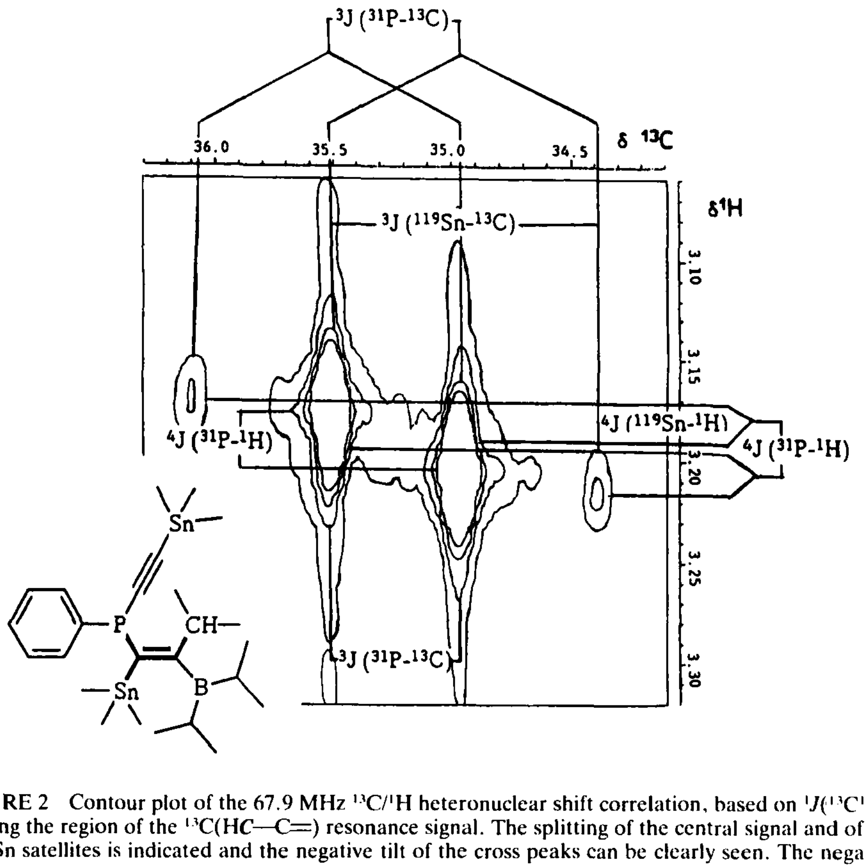


FIGURE 2 Contour plot of the 67.9 MHz ${}^{13}C/{}^1H$ heteronuclear shift correlation, based on ${}^1J({}^{13}C^1H)$, showing the region of the ${}^{13}C(HC—C{=})$ resonance signal. The splitting of the central signal and of the ${}^{117/119}Sn$ satellites is indicated and the negative tilt of the cross peaks can be clearly seen. The negative tilt proves that the signs of the coupling constants ${}^4J({}^{31}P^1H)$ and ${}^3J({}^{31}P^{13}C)$, as well as of ${}^4J(Sn^1H)$ and ${}^3J(Sn^{13}C)$ are opposite.

When the reaction between **3** and Et_3B was first monitored by ^{11}B and ^{31}P NMR, the formation of **9a** was indicated by the appearance of an ^{11}B NMR signal (δ -1.9) typical of tetra-coordinate boron,[8,19] and of two new ^{31}P NMR signals (δ -34.3 [53.7], -14.0 [102.5]) in a 1:1 ratio, both accompanied by $^{117/119}Sn$ satellites. One of these signals, close to that of **3** (δ -32.7 [29.1]), can be assigned to the $\equiv C—PPh_2$ group and the other one to the $=C—PPh_2$ group. In the ^{119}Sn NMR spectrum the signal for **3** was absent and only one signal as double doublet was observed at rather high frequency [δ $+203.9$ (102.5, 53.7)], the low ^{119}Sn nuclear shielding being in accord with that of other zwitterionic intermediates.[3-5] The characteristic pattern in the ^{13}C NMR spectrum in the range for alkynyl and olefinic carbon atoms (one sharp and one broad signal, each, see Table II) confirms the proposed structure. The rather large coupling constant between ^{119}Sn and ^{31}P, attached to the bridging alkynyl group, $|J(^{119}Sn^{31}P_{\equiv C—P})|$ (53.7 Hz), also supports the bonding interaction between the cationic triorganotin fragment and the $C{\equiv}C$ bond.

The stannole ring of **8a** is readily identified by the splitting pattern, different line widths [C(3)] and $^{117/119}Sn$ satellites of the ^{13}C NMR signals of the ring-carbon atoms C(2-5). Consistent ^{31}P and ^{119}Sn NMR data support this structural assignment and the δ ^{11}B value at low frequency (δ -5.1) indicates the presence of P—B coordination. The linewidth of the corresponding ^{31}P resonance signal is slightly greater than that for the ^{31}P nuclei attached to C(5). The mixture of the heterocycles **8b** and **10b** gives exceedingly complex ^{13}C and ^{1}H NMR spectra which were not analysed. However, the NMR data of the heteronuclei ^{11}B, ^{31}P and ^{119}Sn are indicative (see Table III, footnote [b]). Owing to steric hindrance, the P—B coordination is weak, as shown by the broad ^{11}B NMR signal with δ ^{11}B $+53$. The presence of the six-membered ring is readily shown by the typical $\delta^{119}Sn$ value[1,3-5,7,16] [δ -100.0 (68.5)] and the fitting ^{31}P NMR data.

EXPERIMENTAL

All preparative work and handling of compounds was carried out in a dry N_2 atmosphere, using carefully dried glassware and purified solvents. Trimethyltin- and dimethyltin chloride, diphenyl-chlorophosphane and *n* butyl-lithium (1.6 M in hexane) were commercial products. Triethylborane [**4a**][20] was available, triisopropylborane [**4b**],[21] dimethyl-chlorophophane,[22] bis(trimethylstannylethynyl)phenylphosphane (**1**),[6] ethynyldimethyl-[23,24] and ethynyl-diphenylphosphane[23a,24] were prepared following the literature procedures reported for the same or related compounds. – NMR spectra: JEOL FX 90 Q (^{31}P, ^{119}Sn NMR), JEOL EX 270 (^{1}H, ^{13}C NMR), Bruker AC 300, AM 500 and ARX 250 (^{1}H, ^{11}B, ^{13}C, ^{31}P, ^{119}Sn NMR); chemical shifts are given with respect to internal Me_4Si (δ $^{1}H(CHCl_3/CDCl_3) = 7.24$, δ $^{1}H(C_6D_6) = 7.15$; δ ^{13}C $(CDCl_3) = 77.0$, δ $^{13}C(C_6D_6) = 128.0$), external $Et_2O—BF_3$ (δ ^{11}B, $\Xi(^{11}B) = 32.083791$ MHz), external H_3PO_4(aqu. 85%) (δ ^{31}P, $\Xi(^{31}P) = 40.480747$ MHz) and external Me_4Sn (δ ^{119}Sn, $\Xi(^{119}Sn) = 37.290665$ MHz). – IR: Perkin-Elmer 983. – EI (70 eV) – MS: VARIAN MAT CH 7 (direct inlet).

Bis(dimethylphosphanylethynyl)dimethyltin (**2**). A solution (183 ml) of $Me_2P—C{\equiv}CH$ (64 mmol) in THF (0.35 M; IR: $\nu(C{\equiv}C) = 2244$ cm^{-1}; ^{31}P NMR: δ ^{31}P -71.0) was cooled to −78°C before adding of 39 ml of *n* butyl-lithium/hexane (1.6 M) within 1 h. After warming the reaction mixture to room temp. and stirring for 12 h, the suspension was cooled again to −78°C and 7 g (32 mmol) of dimethyltin dichloride were added in one portion. The mixture was warmed up to room temp. and stirred for 12 h. All volatile material was removed in vacuo and the residue was extracted with hexane. After filtration, the hexane was removed in vacuo and a beige solid was left which was identified as impure **2**. Attempts at further purification by recrystallization from pentane or sublimation were not successful. ^{1}H NMR (in $CDCl_3$, 300 MHz): δ ^{1}H = 0.30 s, 6 H, $SnMe_2$, $^{2}J(^{119}Sn^{1}H)$ = 68.5 Hz; 1.50 d, $^{2}J(^{31}P^{1}H)$ = 3.4 Hz, 12 H, PMe_2.

Bis(diphenylphosphanylethynyl)dimethyltin (**3**). A freshly prepared suspension of 18.4 g (85 mmol) of LiC$\equiv$CPPh$_2$ in 100 ml of toluene was cooled to −78°C and 8.3 g (38 mmol) of Me$_2$SnCl$_2$ were added in one portion. The mixture was allowed to reach room temp. and was stirred for 12 h. After filtration, all volatile material was removed in vacuo and the solid residue was recrystallized from pentane to give 9.1 g (41%) of the compound **3** as colorless crystalline material (m.p. 94–96°C) which turns yellow and dark after several days. – IR: ν(C$\equiv$C) 2250, 2157 cm^{-1}. – ^{1}H NMR (300 MHz, CDCl$_3$): δ ^{1}H [$J(^{119}\mathrm{Sn}^1\mathrm{H})$] = 0.61 [69.2] s, 6H (SnMe$_2$); 7.31 m, 7.64 m, 20H (PPh$_2$). – EI-MS: m/z (%) = 553 (100) [M$^+$ −15], 209 (17).

C$_{30}$H$_{26}$P$_2$Sn (567.19) calcd. C 63.53, H 4.62%; found C 63.35, H, 4.58%.

(Z)-1-Phenyl(trimethylstannylethynyl)phosphanyl-1-trimethylstannyl-2-diethylboryl-1-butene (**5a**). A solution of 0.7 g (1.15 mmol) of **1** in 3 ml of hexane was cooled to −78°C and 0.143 g of Et$_3$B were added in one portion (syringe). The cooling bath was removed, the mixture was stirred and warmed to room temp. After removing all volatile material in vacuo, a yellow oil was left. – ^{1}H NMR (270 MHz; C$_6$D$_6$): δ ^{1}H ($J(^{31}\mathrm{P}^1\mathrm{H})$) [$J(^{119}\mathrm{Sn}^1\mathrm{H})$] = 0.03 [60.1] s, 9H ($\equiv$C—SnMe$_3$); 0.02 [53.0] s, 9H (=CSnMe$_3$); 2.27 (3.2) d, d, q ($^2J(^1\mathrm{H}^1\mathrm{H})$ = 14.0, $^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.6 Hz) 1H, 2.72 (5.3) d, d, q ($^2J(^1\mathrm{H}^1\mathrm{H})$ = 14.0, $^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.6 Hz) 1H, 0.82 t, ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.6 Hz) 3H (=C—Et); 1.25–1.04 m, 4H, 0.92 t ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.6 Hz) 6H (BEt$_2$); 7.68 (8.1) d, d, d ($J(^1\mathrm{H}^1\mathrm{H})$ = 8.1, 1.2 Hz) 2H (o), 7.05 (2.0) d, d, d ($J(^1\mathrm{H}^1\mathrm{H})$ = 8.1, 7.5 Hz) 2H (m), 6.89 t, t ($J(^1\mathrm{H}^1\mathrm{H})$ = 7.5, 1.2 Hz) 1H (p) (P—Ph).

C$_{22}$H$_{38}$BPSn$_2$ (581.73) calcd. C 45.42, H 6.58%; found C 45.65, H 6.68%.

Compound **5b** was prepared in the same way as **5a**. ^{1}H NMR (C$_6$D$_6$, 270 MHz): δ ^{1}H ($J(^{31}\mathrm{P}^1\mathrm{H})$) [$J(^{119}\mathrm{Sn}^1\mathrm{H})$] = 0.15 [60.3] s, 9H ($\equiv$C—SnMe$_3$); 0.05 [52.9] s, 9H (=C—SnMe$_3$); 3.19 [5.0] (7.2) d, sept ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.3) 1H, 1.18 d ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.3 Hz) 3H, 1.16 d ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.3 Hz) 3H (=C—*i*Pr); 1.33 sept ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.0 Hz) 1H, 1.48 sept ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.0 Hz) 1H, 1.10 d, 1.098 d, 1.04 d, 1.06 d (all $^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.0 Hz) 12 H (B*i*Pr$_2$); 7.60 (7.0) d, d, d ($J(^1\mathrm{H}^1\mathrm{H})$ = 7.0, 1.4 Hz) 2H (o) 7.10 (1.5) d, d, d ($J(^1\mathrm{H}^1\mathrm{H})$ = 7.0, 7.2 Hz) 2H (m), 6.99 t, t ($J(^1\mathrm{H}^1\mathrm{H})$ = 7.2, 1.4 Hz) 1H (p) (P—Ph).

C$_{25}$H$_{44}$BPSn (623.81) calcd. C 48.14, H 7.11%; found C 48.22, H 7.21%.

Bis[(Z)-1-trimethylstannyl-2-diethylboryl-1-butenyl]phenylphosphane (**6a**). A solution of 0.331 g (0.684 mmol) of **1** in 10 ml of hexane was cooled to −78°C and an excess of Et$_3$B [0.2 g (2 mmol)] was added (syringe) in one portion. After warming to room temp., the mixture was stirred for 2 h until the reaction was complete (^{31}P NMR). The solvent and the excess of Et$_3$B were removed in vacuo. The residue, a brown oil, proved to be pure (>98%) **6a**. – ^{1}H NMR (C$_6$D$_6$, 270 MHz): δ ^{1}H ($J(^{31}\mathrm{P}^1\mathrm{H})$) [$J(^{119}\mathrm{Sn}^1\mathrm{H})$] = 0.23 [51.7] s, 18H (=C—SnMe$_3$), 3.07 (4.8) d, d, q ($^2J(^1\mathrm{H}^1\mathrm{H})$ = 14.0, $^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.6 Hz) 2H, 2.77 (1.8) d, d, q ($^2J(^1\mathrm{H}^1\mathrm{H})$ = 14.0, $^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.6 Hz) 2H, 1.19 t ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.6 Hz) 6H (=C—Et); 1.54 m, 8H, 1.28 t ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.6 Hz) 12H (BEt$_2$); 7.86 (7.0) d, d ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.5 Hz) 2H (o), 7.34 (1.5) d, t ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.5 Hz) 2H (m); 7.22 t ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.5 Hz) 1H (p) (P—Ph).

C$_{28}$H$_{53}$B$_2$PSn$_2$ (679.73) calcd. C 49.48, H 7.86%; found C 49.33, H 7.80%.

4-Ethyl-3-diethylboryl-1,1-dimethyl-2,5-bis(diphenylphosphanyl)stannole (**8a**). After cooling a solution of 2.27 g (4 mmol) of **3** in CH$_2$Cl$_2$ to −78°C, Et$_3$B (0.43 g, 4.4 mmol) was added in one portion (syringe). The resulting mixture was warmed to room temp., stirred for 24 h and then all volatile material was removed in vacuo. A colorless solid was left and recrystallization from pentane at −78°C gave 1.9 g (71%) of **8a** (m.p. 66–70°C). – ^{1}H NMR (300 MHz, C$_6$D$_6$): δ ^{1}H [$J(^{119}\mathrm{Sn}^1\mathrm{H})$] = −0.30 [56.6] s, 6H (SnMe$_2$); 1.30–0.9 m, 10H (BEt$_2$); 2.50 m, 2H, 1.18 t ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.6 Hz) 3H (=C—Et); 7.00 m, 7.43 m, 7.61 m, 20H (PPh$_2$, PPh$_2$).

C$_{36}$H$_{41}$BP$_2$Sn (665.25) calcd. C 65.00, H 6.21%; found C 64.76, H 6.15%.

The reaction between **3** and Et$_3$B (**4a**), carried out in CDCl$_3$ solution in an NMR tube, was monitored from −78 to −20°C, until the formation of the zwitterionic intermediate **9a** was complete. Further warming showed that **9a** rearranges to the stannole derivative **8a**.

9a: ^{1}H NMR (300 MHz, CDCl$_3$, −30°C): δ ^{1}H [$J(^{119}\mathrm{Sn}^1\mathrm{H})$] = 0.15 [53.4] s, 6H (SnMe$_2$); 0.19 m, 4H, 0.67 t ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.4 Hz) 6H (BEt$_2$); 1.84 m, 2H, 0.86 t ($^3J(^1\mathrm{H}^1\mathrm{H})$ = 7.6 Hz) 3H (=C—Et); 7.31–7.66 m, 20H (PPh$_2$, PPh$_2$).

The reaction between **3** and *i*Pr$_3$B (**4b**) did not start until room temp., and heating up to 60°C was required in order to produce a mixture of **8b** and **10b**. The complex ^{1}H and ^{13}C NMR data of the resulting mixture were not analysed. See Table III, footnote [b] for relevant ^{11}B, ^{31}P and ^{119}Sn MNR data.

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