New phosphabenzenes by [4 + 2] cycloaddition of stannoles to 1-phospha-1-alkynes – determination of signs of coupling constants $[^nJ(^{31}P, ^{13}C), {}^nJ(^{31}P, {}^1H), {}^2J(^{31}P, {}^{29}Si), {}^2J(^{119}Sn, {}^{31}P)]$ [1]

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Abstract

Stannoles bearing dialkylboryl groups in 3-position react with 1-phospha-1-alkynes $P{\equiv}C-{}^tBu$ (1) and $P{\equiv}C-CH_2{}^tBu$ (2) by [4 + 2] cycloaddition and elimination of stannylene to give phosphabenzenes in high yield. The stannylenes oligomerise to give $[R^1{}_2Sn]_n$ with $n \geq 7$ (R = Me, Et, $-(CH_2)_5-$ or, in the case of $R^1 = {}^tBu$, react with the stannole itself. All phosphabenzenes are characterised by their consistent sets of NMR data. The absolute signs of the coupling constants ${}^nJ(^{31}P, {}^1H)$, ${}^nJ(^{31}P, {}^{13}C)$, ${}^2J(^{31}P, {}^{29}Si)$ and ${}^2J(^{119}Sn, {}^{31}P)$ were determined by appropriate 1D and 2D NMR experiments.

Keywords: Phosphabenzenes; 1-Phospha-1-alkynes; Stannoles; [4 + 2] Cycloadditions; Stannylenes; Multinuclear NMR; Coupling constants

1. Introduction

Among various methods for the synthesis of phosphabenzenes [1], the [4 + 2] cycloaddition of suitable dienes to phosphaalkynes, followed by elimination of a leaving group, is an attractive route. So far, such reactions have been carried out for tert-butyl phosphaalkyne (1) and cyclopentadienones [2], α-pyrones [2] and phosphole sulf.des [3] with CO, CO_2 and PhPS respectively as leaving groups. [4 + 2] Cycloadditions with conjugated dienes were reported to proceed under relatively harsh reaction conditions [4]. We have found that 1,1-organoboration [5] of 1-alkynyltin compounds opens a convenient access to stannole derivatives [6], electron-rich reactive dienes which could prove useful in cycloaddition reactions [7]. Therefore, we have studied the reactivity of various stannole derivatives 3–10 [Eqs. (2)–(4)] towards the 1-phospha-1-alkynes 1 and 2 [Eq. (1)].

It was hoped that these reactions would lead to organometallic-substituted phosphabenzenes, for which only a few examples are known [8]. This [4 + 2] cycloaddition should generate monomeric stannylenes which could oligomerise or react with the respective 1-phospha-1-alkyne or with the stannole. Furthermore, we wanted to apply advanced NMR techniques to phosphabenzenes with the aim of determining the absolute signs of the coupling constants involving the ${}^{31}P$ nucleus. Although calculations on $J(^{31}P, {}^{13}C)$ of phosphabenzenes were carried out [9], and some coupling signs were proposed [10], to the best of our knowledge experimental confirmation of the signs is still lacking.
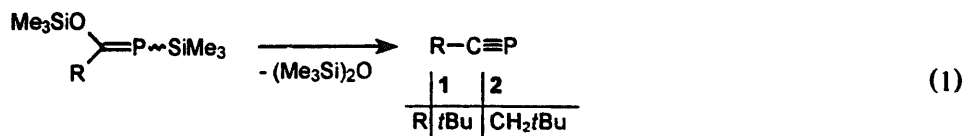
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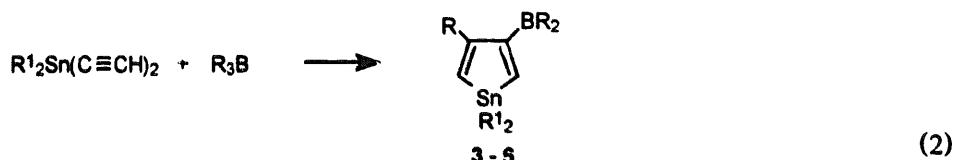[1] In memory of Hidemasa Takaya († 4 October 1995).

2. Results and discussion
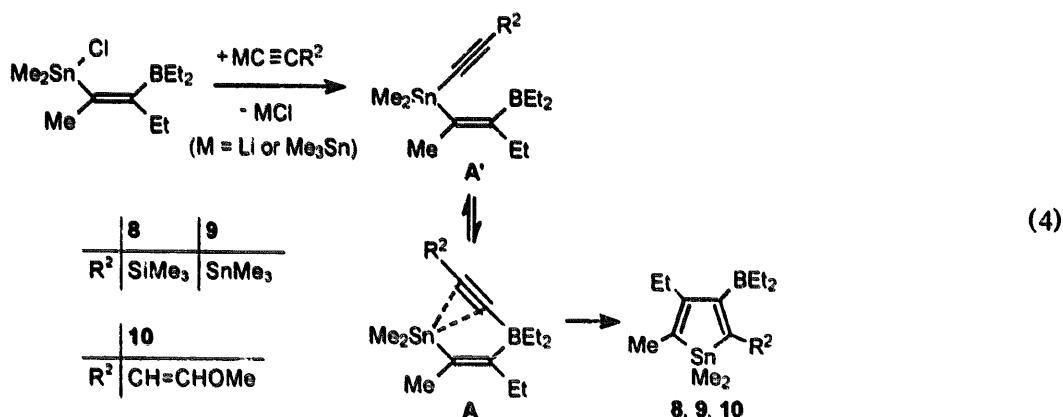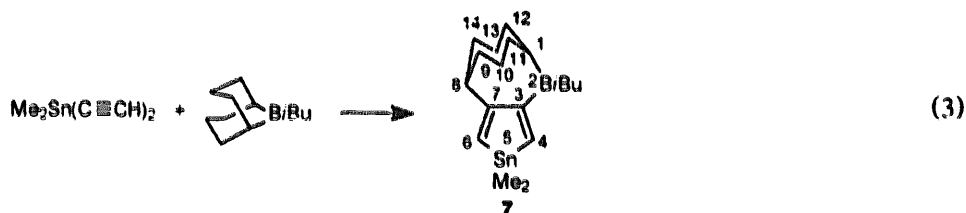
2.1. Synthesis of the starting materials

The 1-phospha-1-alkynes **1** [11] and **2** [12] were prepared as described in the literature according to Eq. (1):

$$Me_3SiO$$

R—C≡P

(1)

	1	2
R	tBu	CH₂tBu

The stannole derivatives **2–7** were obtained from the quantitative reaction [6a–c] between the respective diethynyltin compounds and the trialkylboranes [Eqs. (2) and (3)] and were ready for use without further purification. The stepwise synthesis [6d,e] according to Eq. (4) affords the stannoles **8–10** with different substituents in 2,5-positions. Several of these stannoles have not been described as yet, and their NMR data are given in Table 1.

$$R^1_2Sn(C≡CH)_2 + R_3B \longrightarrow$$

3 - 6

(2)

	3a	3b	4a	4b	5a	5b	6a
R	Et	iPr	Et	iPr	Et	iPr	Et
R¹/R¹	Me	Me	Et	Et	tBu	tBu	-(CH₂)₅-

$$Me_2Sn(C≡CH)_2 + \quad BtBu \longrightarrow$$

7

(3)

$$Me_2Sn \quad + MC≡CR^2$$

(4)

	8	9
R²	SiMe₃	SnMe₃

	10
R²	CH=CHOMe

In the case of **10** (R² = CH=CHOMe), the zwitterionic intermediate **A** was detected by monitoring the progress of the reaction using ¹¹B and ¹¹⁹Sn NMR. The deshielding of the ¹¹⁹Sn nucleus (δ ¹¹⁹Sn 187.9) and the shielding of the ¹¹B nucleus (δ ¹¹B 10.9), measured at room temperature, indicate that the equilibrium between **A** and **A'** is shifted to **A**. These data correspond to complete NMR data sets available for similar zwitterionic intermediates [13].

Table 1
^{119}Sn, ^{13}C and ^{11}B NMR data [a] of stannoles.

No.	R^1	R	δ^{119}Sn	δ^{11}B	δ^{13}C/C2	C3	C4	C5	SnR_2^1
3a [b]	Me	Et	19.5	82.0	128.1 [410.4]	175.3 (br)	162.7 [89.5]	121.1 [482.3]	−9.4 [330.4]
4b [c]	Et	^{i}Pr	48.6	84.8	123.7 [365.6]	175.7 (br)	170.6 [75.7]	117.8 [435.8]	3.4 [339.4]
5a [d]	^{t}Bu	Et	48.5	88.2	127.5 [303.2]	177.2 (br)	164.9 [63.0]	120.8 [364.2]	31.3 [368.2]
5b [e]	^{t}Bu	^{i}Pr	54.2	89.8	124.7 [301.2]	176.6 (br)	171.9 [60.1]	118.9 [365.2]	31.5 [366.2]
7 [f]	Me	g	5.0	83.7	145.0 [402.2]	172.0 (br)	169.8 [74.1]	122.4 [471.9]	−9.9 [332.4]
10 [h]	Me	Et	−2.9	90.9	129.7 [482.8]	154.2 (br)	152.4 [117.8]	136.6 [426.6]	−9.1 [337.5]

[a] In toluene-d_8 (50%) at 25 ± 1°C; $^nJ(^{119}$Sn, ^{13}C) in hertz are given in square brackets; (br) denotes broad ^{13}C resonances of boron bonded carbon atoms.
[b] Other δ^{13}C: 30.9 [63.2], 13.1 [8.0] (Et); 21.3 (br), 9.2 (BEt_2).
[c] Other δ^{13}C: 36.7 [54.3], 23.9 [6.7] (^{i}Pr); 24.3 (br), 18.8 (B^{i}Pr$_2$); 11.6 [25.6] (Et).
[d] Other δ^{13}C: 31.1, 13.4 (Et); 21.3 (br), 9.3 (BEt_2); 31.9 (^{t}Bu).
[e] Other δ^{13}C: 36.9 [47.3], 24.1 (^{i}Pr); 24.5 (br), 18.9 (B^{i}Pr$_2$); 31.9 (^{t}Bu).
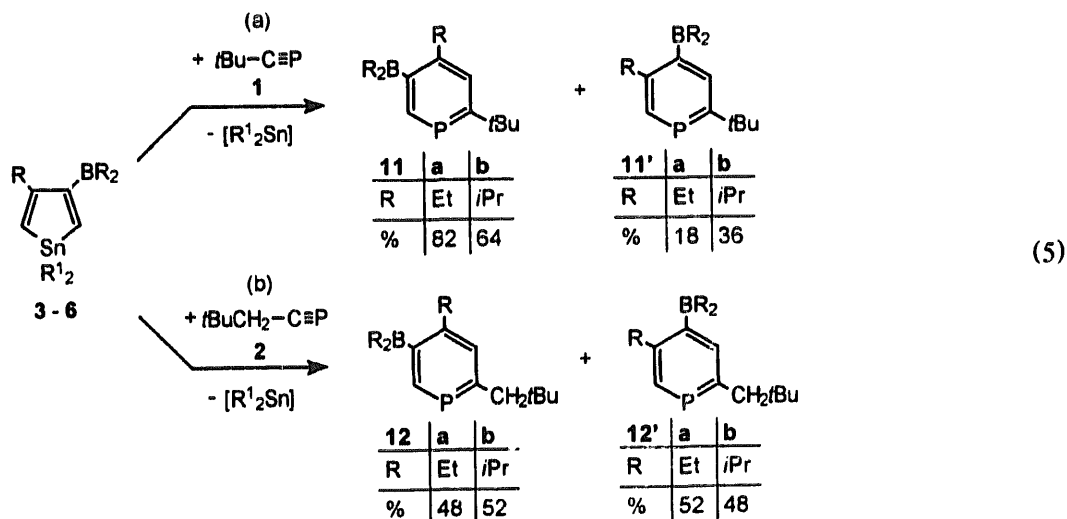[f] Other δ^{13}C: 43.5 [66.5] (8); 31.4 (9, 14), 22.4 (10, 13), 33.8 (11, 12), 33.4 (1), 43.5 (br), 26.5, 26.0 (^{t}Bu). For numbering see Eq. (3).
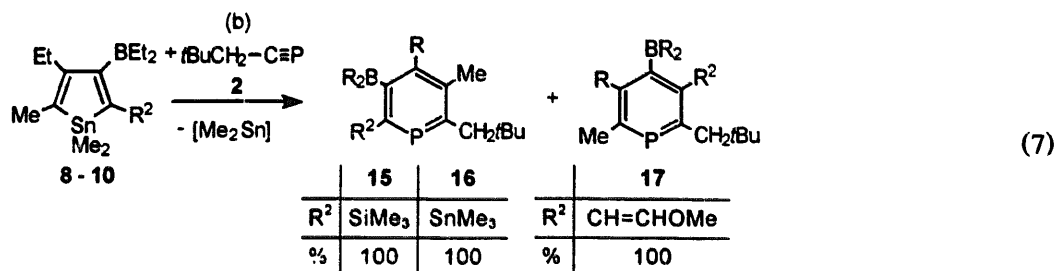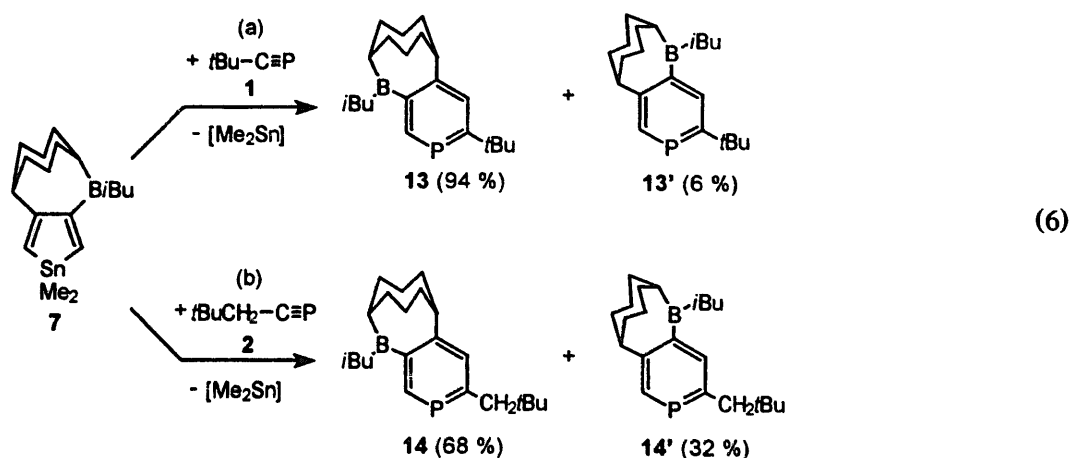[g] R-BR$_2$ = -CH[(CH$_2$)$_3$]$_2$CHB(^{t}Bu)-
[h] Other δ^{13}C: 25.8 [47.6], 14.1 [8.5] (Et); 17.7 [67.1] (Me); 110.8 [64.1], 144.8 [13.4], 59.0 (CH=CHOMe); 22.6 (br), 9.2 (BEt_2).

## 2.2. [4 + 2] Cycloadditions of stannoles to 1-phospha-1-alkynes

As expected, the steric hindrance exerted by substituents attached to the alkynyl carbon atom in 1 or 2 and to the diene system has a pronounced influence on the rate of [4 + 2] cycloadditions. In general, the 1-phospha-1-alkyne 2 proved to be more reactive than 1. In the case of the reactions of 3a–6a with 1 or 2, the reactivity of the stannoles decreased with the groups R^1/R^1 linked to the tin atom: -(CH$_2$)$_5$-> Me > Et ≫ ^{t}Bu. Therefore, it is most convenient to use the dimethyltin compounds 3a, 3b, 7 for the cycloadditions [Eqs. (5), (6)] in order to obtain the phosphabenzenes 11–14 after 1–2 h at room temperature. If there are substituents in 2,5-positions of the stannole ring, most of the [4 + 2] cycloadditions become very slow or do not take place at all. Thus, 1 does not react with any of the stannoles 8–10, whereas 2 reacts slowly to give the corresponding phosphabenzenes 15–17 [Eq. (7)]:

(5)

(a)

+ tBu–C≡P
1

→ (– [Me₂Sn])

13 (94 %)   +   **13' (6 %)**

(b)

+ tBuCH₂–C≡P
2

→ (– [Me₂Sn])

14 (68 %)   +   **14' (32 %)**

(6)

(b)

+ tBuCH₂–C≡P
2

→ (– [Me₂Sn])

8 – 10

15   **16**   +   **17**

	15	16		17
R²	SiMe₃	SnMe₃	R²	CH=CHOMe
%	100	100	%	100

(7)

Except for **15–17**, mixtures of isomers are obtained and their composition is determined by the mutual steric effects exerted by the substituent in the phosphaalkyne, the boryl group and the substituent in 4-position of the stannole ring. The ratio of the isomers given by Eqs. (5) and (6) indicates that **1** reacts more selectively than **2**, and that the boryl group in the tricyclic stannole **7** further increases the selectivity. The stannoles **15** and **16** are formed selectively, presumably as a result of the great difference in steric demand of the methyl and SiMe₃ or SnMe₃ group. The reason for the selective formation of **17**, with a substituent pattern opposite to that of **15** and **16**, is less obvious. However, the exocyclic C=C bond together with the cyclic diene system may form a polar unit which attracts the 1-phospha-1-alkyne in a specific way.

It was not possible to detect the primary [4 + 2] cycloaddition product **B**, although all reactions were carefully monitored by ³¹P NMR starting at low temperature. Unfortunately, the reaction of the stannoles bearing more bulky groups at the tin atom [e.g. **5a** (R¹ = ᵗBu)] with **1** or **2** required prolonged heating. This induced side reactions (vide infra), and under these conditions it appears that the kinetic stabilisation of **B** is insufficient.

B   **B'**
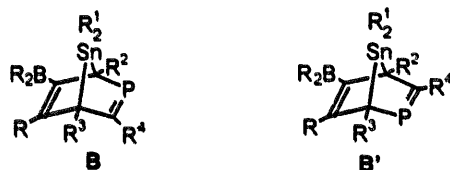
The stannylenes with R¹ = Me, Et or R¹/R¹ = –(CH₂)₅– form oligomers [R₂Sn]ₙ after their elimination, presumably with n > 6 (see Table 2 for ¹¹⁹Sn NMR data). Interestingly, for R¹ = Me a material was formed exclusively which was described previously [14] as the pure hexamer. However, the majority of the spectroscopic data, and in particular the poorly resolved published ¹¹⁹Sn NMR spectrum [14], are not conclusive with respect to the proposed hexameric structure. The relative intensities of the ¹¹⁷Sn satellites in our better resolved ¹¹⁹Sn NMR spectrum (Fig. 1) of this material, showing more clearly essentially the same features as the published spectrum, prove that n = 6 is impossible, since this would require an intensity pattern of 2:2:1 for the ¹¹⁷Sn satellites. The ¹¹⁹Sn NMR spectrum shown in the literature [14] for a minor product, assigned to [Me₂Sn]₅ for reasons unknown, would fit [Me₂Sn]₆ (see Table 2). In the case of R¹ = ᵗBu, the expected tetramer [15] [ᵗBu₂Sn]₄ (δ ¹¹⁹Sn +99.0; ¹J(¹¹⁹Sn, ¹¹⁷Sn) = 1195 Hz; ²J(¹¹⁹Sn, ¹¹⁷Sn) = 1638 Hz) was not observed. The ³¹P NMR spectra did not show

Table 2
^{119}Sn NMR data [a] of some oligomeric stannylenes

Compound	δ^{119}Sn	$^1J(^{119}$Sn, ^{117}Sn)	$^2J(^{119}$Sn, ^{117}Sn)	$^3J(^{119}$Sn, ^{117}Sn)	$^4J(^{119}$Sn, ^{117}Sn)
[Me$_2$Sn]$_6$ [b]	−241.4	1176.0	755.0	83.0	—
[Me$_2$Sn]$_n$ [c]	−231.0	938.3	273.7	193.0	21.0
[Et$_2$Sn]$_n$ [d]	−173.6	145.3	105.9	68.7	37.0
[(CH$_2$)$_5$Sn]$_n$ [e]	−264.0				

[a] In toluene-d_8 at 25°C.

[b] Values taken from the spectrum published in Ref. [14]. The ^{117}Sn satellites appear in a ratio of 2:2:1, the ^{117}Sn satellites with $^3J(^{119}$Sn, ^{117}Sn) = 83 Hz were originally assigned to $J(^{119}$Sn, ^{13}C), although no reason was given.

[c] See Fig. 1(a); the ^{119}Sn NMR data of this material correspond closely to those published and assigned to the hexamer [14].

[d] See Fig. 1(b); there is no way to assign the coupling constants $^nJ(^{119}$Sn, ^{117}Sn) for $n = 1, 2, 3, 4$.

[e] The ^{117}Sn satellites are not resolved.

prominent signals with $^{117/119}$Sn satellites, which excludes potential products arising from the reaction of ^{t}Bu$_2$Sn with the 1-phospha-1-alkyne. In all relevant ^{119}Sn NMR spectra two signals (singlets, 1:1 ratio; δ^{119}Sn −104.4 and −135.1) appear in addition to that of the stannole **5a** (δ^{119}Sn +43.1). The $^{117/119}$Sn satellites belonging to these signals indicate an Sn–Sn bond ($^1J(^{119}$Sn, ^{119}Sn) = 1545.6 Hz), and therefore we propose that a six-membered ring **C** was formed, in accord with the δ^{119}Sn values. This ring enlargement can be the result either of insertion of a
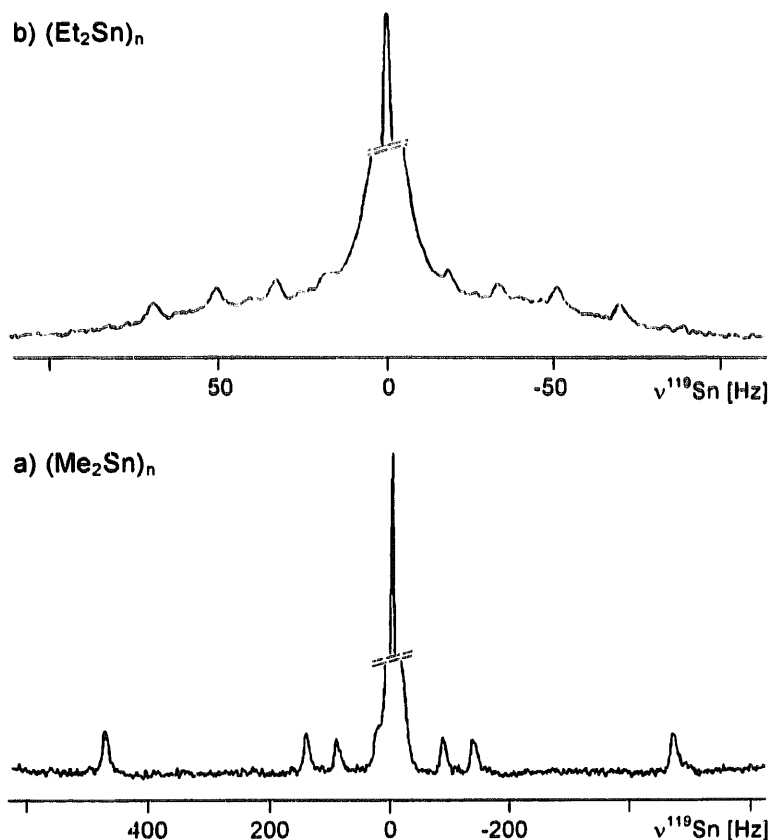

Fig. 1. ^{119}Sn NMR spectra of the oligomeric stannylenes [Me$_2$Sn]$_n$ and [Et$_2$Sn]$_n$. (a) 111.9 MHz ^{119}Sn{^{1}H} NMR spectrum of [Me$_2$Sn]$_n$ measured using the refocused INEPT pulse sequence [28] with ^{1}H decoupling. Three types of ^{117}Sn satellite are clearly resolved; their intensity ratio is not in agreement (in contrast to Ref. [14]) with $n = 6$, but with $n \geq 7$ another pair of ^{117}Sn satellites close to the parent signal is not fully resolved. (b) 93.3 MHz ^{119}Sn{^{1}H-inverse gated} NMR spectrum of [Et$_2$Sn]$_n$. Four types of ^{117}Sn satellite (ratio 1:1:1:1) are clearly resolved, which means that $n \geq 9$.

stannylene $^t Bu_2 Sn$ into one of the Sn–C= bonds in the stannole **5a** or of cycloaddition of the unstable distannene $^t Bu_2 Sn=Sn^t Bu_2$ to the stannole **5a** followed by elimination of $^t Bu_2 Sn$.

C
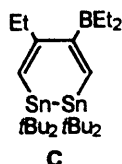
These experiments have shown that the oligomerisation of the monomeric stannylenes bearing sterically non-demanding groups R^1 is faster than their reaction with the stannoles or the 1-phospha-1-alkynes. More bulky groups R^1, e.g. $R^1 = ^t Bu$, reduce the rate of oligomerisation, and $^{119} Sn$ NMR spectra indicate that the stannole system itself may trap monomeric or dimeric stannylenes.

2.3. Reactions of the boryl-substituted phosphabenzenes

Protodeborylation of the compounds **11/11′** to **18/18′** is readily achieved by treatment with methanol [Eq. (8a)] or aminoethanol [Eq. (8b)]; this does not affect the ratio of the isomers.
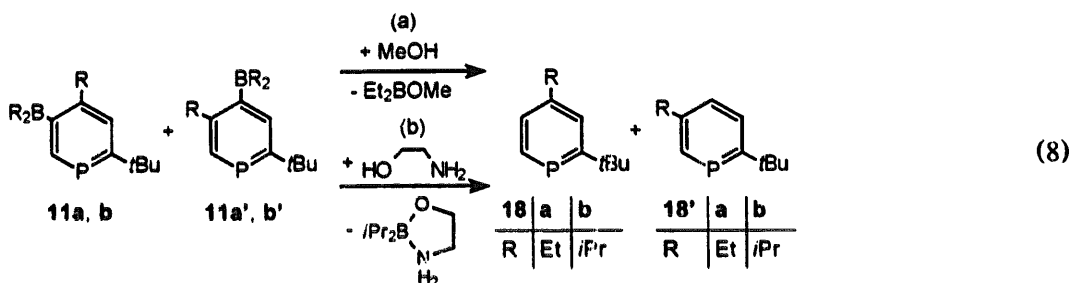

(8)

Table 3
$^{31} P$, $^{13} C$ and $^{11} B$ NMR data [a] of phosphabenzenes **11** and **13**

No.	11a [b]	11b [c]	13 [d]	11a′ [e]	11b′ [f]
R =	Et	$^i Pr$		Et	$^i Pr$
[%]	82	64	94	18	36
$\delta^{31} P$	182.2	186.3	180.9	193.6	191.6
$\delta^{13} C/C2$	183.0	182.1	186.0	179.4	178.5
	(−56.6)	(56.4)	(57.2)	(55.7)	(55.6)
C3	130.7	127.5	131.7	129.2	129.3
	(−11.7)	(11.6)	(12.0)	(12.6)	(12.8)
C4	143.7	148.4	154.7	n.m	150.2
	(+18.9)	(18.2)	(18.0)		(br)
C5	151.9	150.4	148.9	145.5	150.4
	(10.8) (br)	(br)	(12.0)	(14.4)	(14.4)
C6	149.9	149.8	155.4	150.9	147.9
	(−55.6)	(55.8)	(54.0)	(48.2)	(49.1)
$^t Bu$	38.8	38.8	38.5	38.5	n.m.
	(+19.8)	(19.9)	(19.6)	(20.7)	
	33.2	33.3	32.7	n.m.	33.2
	(+11.7)	(11.8)	(8.2)		(11.8)
R	32.1	38.5	44.3	31.9	38.4
	(−2.7)	(2.2)	(1.4)	(2.7)	(2.3)

[a] In $C_6 D_6$ (50%) at 25 ± 1°C; $^n J(^{31} P, ^{13} C)$ in hertz are given in parentheses; (br) denotes broad $^{13} C$ resonances of boron bonded carbon atoms; n.m. not measured.
[b] $\delta^{11} B$: 86.2; $\delta^{13} C$: 16.9 (+3.6) ($C^4 CH_2 Me$), 22.2 (br), 9.2 (BEt_2).
[c] $\delta^{11} B$: 84.7; $\delta^{13} C$: 25.1 ($C^4 CH Me_2$), 25.8 (br), 18.9 ($B^i Pr_2$).
[d] Toluene-d_8; other $\delta^{13} C$: 43.1 (br), 26.4, 25.3 ($B^i Bu$); other $\delta^{13} C$ values were not assigned. **13′**: $\delta^{31} P$: 210.9; abundance 6%.
[e] $\delta^{13} C$: 16.4 ($C^5 CH_2 Me$), 22.5 (br), n.m. (BEt_2).
[f] $\delta^{11} B$: 84.7; $\delta^{13} C$: 25.0 ($C^5 CH Me_2$), 26.5 (br), 18.8 ($B^i Pr_2$).

Oxidation of **11/11′** using Me_3NO [16] proceeds stepwise by oxidation of the two B–Et bonds [Eq. (9)], and enables one to characterise the products **19** and **20** by NMR. The final oxidation of the B–aryl bond leads to an inhomogeneous mixture of unidentified products.
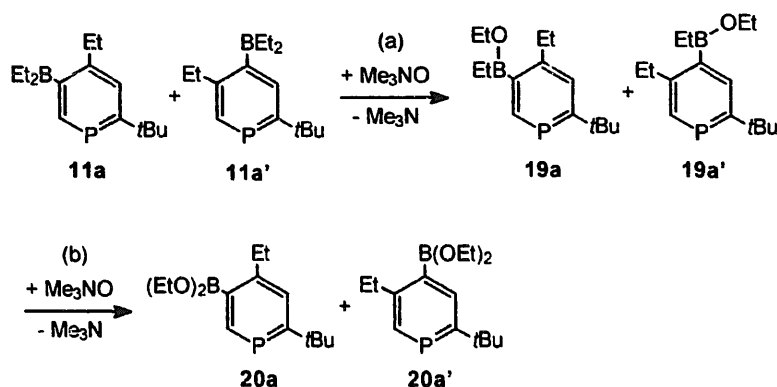
$$(9)$$

Table 4
^{31}P, ^{13}C and ^{11}B NMR data[a] of phosphabenzenes **12** and **14**

No.	12a[b]	12b[c]	14[d]	12a′[e]	12b′[f]	14′[g]
R =	Et	^{i}Pr		Et	^{i}Pr	
[%]	48	52	68	52	48	32
δ^{31}P	192.9	195.3	190.7	203.6	203.8	214.5
δ^{13}C/C2	167.2	166.1	170.9	163.8	162.9	164.9
	(51.9)	(51.6)	(51.6)	(50.6)	(50.8)	(49.4)
C3	135.7	132.5	137.4	134.1	133.9	139.4
	(11.9)	(12.0)	(11.8)	(12.9)	(13.0)	(11.6)
C4	142.8	147.3	154.6	148.9	n.m.	146.2
	(18.7)	(18.4)	(18.0)	(18.0)		(16.8)
				(br)		(br)
C5	151.9	n.m.	152.2	145.5	150.1	156.4
	(11.8)		(13.7)	(15.0)	(15.2)	(14.4)
	(br)		(br)			
C6	150.1	149.7	155.1	151.2	148.1	152.5
	(56.5)	(56.7)	(55.1)	(50.3)	(50.1)	(50.2)
CH_2^iBu	53.4	53.3	53.9	53.0	53.1	53.7
	(27.7)	(27.8)	(27.0)	(28.2)	(28.2)	(28.0)
	31.5	31.5	32.1	31.5	31.6	32.1
	(3.5)	(3.4)	(3.2)	(3.5)	(3.4)	(3.2)
	29.5	29.5	30.1	29.6	29.5	30.1
R	31.4	38.2	45.1	31.7	37.8	44.2
	(2.4)	(< 1)	(2.5)	(2.6)	(< 1)	(< 1)

[a] In toluene-d_8 (50%) at 25 ± 1°C; $^nJ(^{31}P, ^{13}C)$ in hertz are given in parentheses; (br) denotes broad ^{13}C resonances of boron bonded carbon atoms; n.m. not measured.
[b] δ^{11}B: 85.4; other δ^{13}C: 16.5 (3.1) (C^4CH_2Me); 21.9 (br), 8.9 (BEt_2).
[c] δ^{11}B: 84.5; other δ^{13}C: 24.6 (2.3) (C^4CHMe_2), 25.2 (br), 18.5 (B^iPr_2).
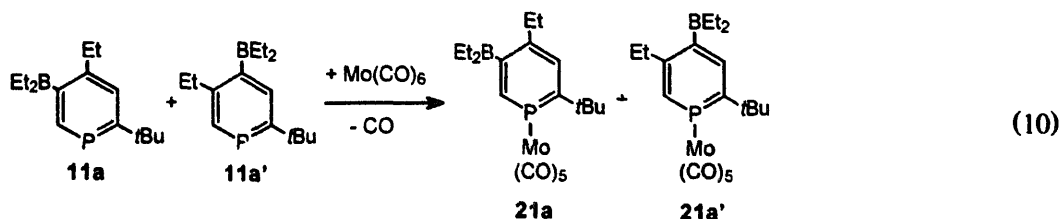[d] Other δ^{13}C: 43.4 (br) (BCH_2), 30.5 (BCH); other δ^{13}C values were not assigned.
[e] Other δ^{13}C: 16.1 (C^5CH_2Me), 22.2 (br), 8.9 (BEt_2).
[f] δ^{11}B: 84.5; other δ^{13}C: 23.8 (C^5CHMe_2), 25.6 (br), 18.5 (B^iPr_2).
[g] Other δ^{13}C: 43.4 (br) (BCH_2), 30.3 (BCH); other δ^{13}C values were not assigned.

The mixture of **11a/11a'** reacts with $Mo(CO)_6$ [17] by substitution of one CO ligand to give the complexes **21a** and **21a'**, as shown in Eq. (10).

(10)

Reactions of **11a/11a'** with $Mo(CO)_3(NCMe)_3$ did not lead to η^6-phosphabenzene complexes but to mixtures in which two of the acetonitrile ligands were substituted.

(11)
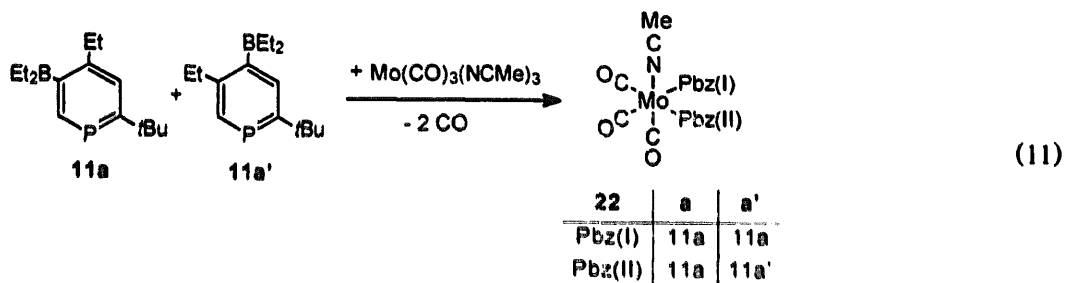
22	a	a'
Pbz(I)	11a	11a
Pbz(II)	11a	11a'

Table 5
^{31}P, ^{13}C, ^{11}B, ^{119}Sn and ^{29}Si NMR data [a] of phosphabenzenes 15, 16 and 17

No.	$\delta^{31}P$	$\delta^{13}C$						
		C2	C3	C4	C5	C6	CH_2	^tBu
15 [b]	232.4	163.4	158.0	138.9	139.5	163.8	48.0	32.7	30.6
	{37.2}	(78.7)	(10.8)	(22.4)	(10.6)	(58.5)	(32.1)	(2.9)	(3.6)
16 [c]	230.9	163.2	160.5	139.9	139.7	165.1	48.5	33.3	30.6
	[352.5]	(86.7)	(10.9)	(24.8)	(10.9)	(62.1)	(30.5)	(2.7)	(3.8)
		[412.0]				[56.7]	[6.5]		
17 [d]	204.9	163.6	137.4	152.9	142.9	161.6	47.5	32.8	30.1
		(50.9)	(13.1)	(14.3)	(12.9)	(46.6)	(28.9)	(2.7)	(3.9)

[a] In toluene-d_8 (50%) at 25 ± 1°C; $^nJ(^{31}P,X)$ in hertz are given in parentheses; $^nJ(^{119}Sn,X)$ in hertz are given in square brackets; $^nJ(^{29}Si,X)$ in hertz are given in braces; (br) denotes broad ^{13}C resonances of boron bonded carbon atoms.
[b] $\delta^{11}B$: 87.7; $\delta^{29}Si$ = -10.3 (37.2); other $\delta^{13}C$: 2.4 (10.7) (Me_3Si); 29.9 (< 1), 14.4 (3.9) (C^4Et); 16.6 (1.6) (C^3Me); 22.4, 9.5 (BEt_2).
[c] $\delta^{11}B$ = 87.8; $\delta^{119}Sn$ = -43.0 (325.5); other $\delta^{13}C$: -5.6 (9.3) [336.8] (Me_3Sn); 30.8 (< 1), 15.1 (3.8) (C^4Et); 17.1 (1.6) (C^3Me); 22.8, 9.9 (BEt_2).
[d] Other $\delta^{13}C$: 21.0 (43.6) (C^6Me); 28.1 (< 1). 14.4 (1.6) (C^5Et); 105.7 (1.9), 147.6 (< 1). 58.9 ($C^3CH=CHOMe$); 21.8 (br), 9.6 (BEt_2).

Table 6
^{31}P and ^{13}C NMR data [a] of phosphabenzenes 18

No.	R	δ^{31}P	δ^{13}C						
			C2	C3	C4	C5	C6	^{t}Bu	
18a [b]	Et	185.8	185.2	132.1	145.7	132.0	153.8	38.8	33.0
			(−58.2)	(−13.0)	(+17.4)	(−14.3)	(−51.4)	(+20.1)	(+12.1)
18b [c]	^{i}Pr	186.3	185.0	130.8	150.2	130.2	153.4	38.8	32.9
			(57.1)	(12.6)	(17.1)	(14.3)	(50.4)	(19.8)	(11.9)
18a' [d]	Et	201.8	181.7	132.0	130.0	147.1	150.7	38.4	n.m.
			(57.2)	(12.5)	(17.0)	(14.2)	(51.2)	(20.2)	
18b' [e]	^{i}Pr	191.6	181.8	131.8	128.6	151.4	149.6	38.3	32.9
			(56.5)	(12.5)	(17.4)	(14.7)	(51.0)	(20.1)	(11.9)

[a] In C_6D_6 (50%) (18a, 18a'); in $CDCl_3$ (30%) (18b, 18b') at 25 ± 1°C; $^nJ(^{31}P, ^{13}C)$ in hertz are given in parentheses; n.m. not measured.
[b] Other δ^{13}C: 31.6 (−2.4), 16.1 (+3.0) (C^4Et).
[c] Other δ^{13}C: 36.3 (1.7), 24.0 (2.4) ($C^{4i}Pr$).
[d] Other δ^{13}C: 31.6 (2.8), 15.7 (< 1) (C^5Et).
[e] Other δ^{13}C: 36.3 (1.5), 23.9 (0.9) ($C^{5i}Pr$).

Table 7
^{31}P, ^{13}C and ^{11}B NMR data [a] of phosphabenzenes 19 and 20

No.	δ^{31}P	δ^{13}C						
		C2	C3	C4	C5	C6	^{t}Bu	
19a [b]	182.8	184.1	131.1	146.0	145.3	154.5	38.8	33.1
		(57.1)	(11.8)	(18.4)	(br)	(55.0)	(19.7)	(11.8)
20a [c,d]	181.7	184.9	131.4	147.8	n.m.	156.8	38.8	33.0
		(57.3)	(11.9)	(18.4)		(54.4)	(19.7)	(11.8)
19a' [e]	198.2	179.8	n.m.	n.m.	n.m.	151.3	38.4	33.1
		(54.5)				(49.3)	(19.6)	(11.8)

[a] In C_6D_6 (20%) at 25 ± 1°C; $^nJ(^{31}P, ^{13}C)$ in hertz are given in parentheses; n.m. not measured.
[b] δ^{11}B = 51.5; other δ^{13}C: 31.9 (2.3), 16.7 (3.0) (4-Et); 63.1, 17.4 (OEt); 14.4, 8.4 (BEt).
[c] δ^{11}B = 29.3; other δ^{13}C: 32.3 (2.1), 16.9 (3.2) (4-Et); 60.4, 17.5 (OEt).
[d] δ^{31}P: 193.4 (20a').
[e] Other δ^{13}C: 31.7 (2.8), 16.2 (< 1) (5-Et); 63.0, 17.5 (OEt), n.m. (BEt).

Table 8
^{31}P, ^{13}C and ^{11}B NMR data [a] of the phosphabenzene pentacarbonyl molybdenum(0) complex 21a

δ^{31}P [b]	δ^{11}B	δ^{13}C					δ^{13}C							
		C2	C3	C4	C5	C6	^{t}Bu		Et		BEt$_2$		CO$_{trans}$	CO$_{cis}$
166.9	84.7	178.1	134.1	143.3	155.6	150.9	39.1	33.1	31.6	16.3	22.1	8.7	211.6	205.1
		(3.3)	(13.4)	(31.3)	(br)	(7.2)	(12.2)	(8.8)	(4.5)	(5.3)			(29.6)	(10.6)

[a] In CD_2Cl_2 (20%) at 25 ± 1°C; $^nJ(^{31}P, X)$ in hertz are given in parentheses; (br) denotes broad ^{13}C resonances of boron bonded carbon atoms.
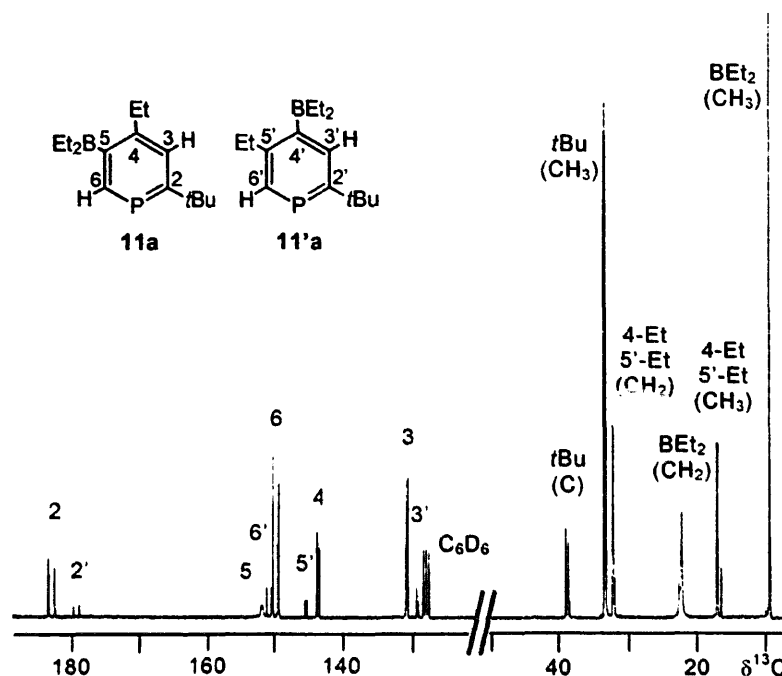[b] δ^{31}P: 177.0 (21a').

Fig. 2. 67.8 MHz ^{13}C{^{1}H} NMR spectrum of the phosphabenzenes **11a** and **11'a** (around 40% in C_6D_6 at $25 \pm 1°C$). The assignments are given. Note the typical broad ^{13}C resonances of the boron bonded carbon atoms C5 and $BEt_2(CH_2)$. The ^{13}C(C4') resonance was not observed due to its low intensity.

2.4. NMR spectroscopic studies of the phosphabenzenes

The proposed structures of the phosphabenzenes follow conclusively from the sum of the NMR data as given in Tables 3 (**11** and **13**), 4 (**12** and **14**), 5 (**15–17**), 6 (**18**), 7 (**19** and **20**) and 8 (**21**). ^{31}P NMR spectroscopy proved
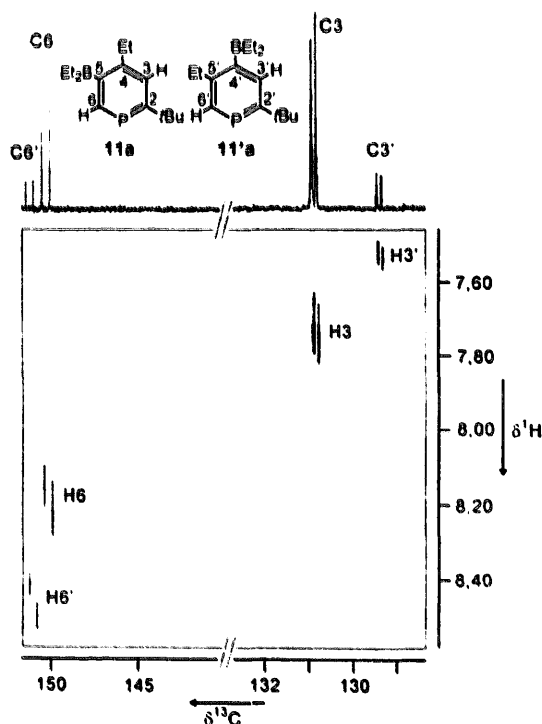

Fig. 3. Contour plot of the 2D 125.8 MHz ^{13}C/^{1}H HETCOR experiment [based on $^1J(^{13}C, ^1H)$] of the phosphabenzenes **11a/11a'** showing the region of the ring carbon atoms C-3 and C-6 in F2 and H-3 and H-6 in F1. The negative tilt of the respective cross-peaks indicates opposite signs of the coupling constants $^1J(^{31}P, ^{13}C-6)$, $^2J(^{31}P, ^1H-6)$ and $^2J(^{31}P, ^{13}C-3)$, $^3J(^{31}P, ^1H-3)$ in both isomers (see also Scheme 1).
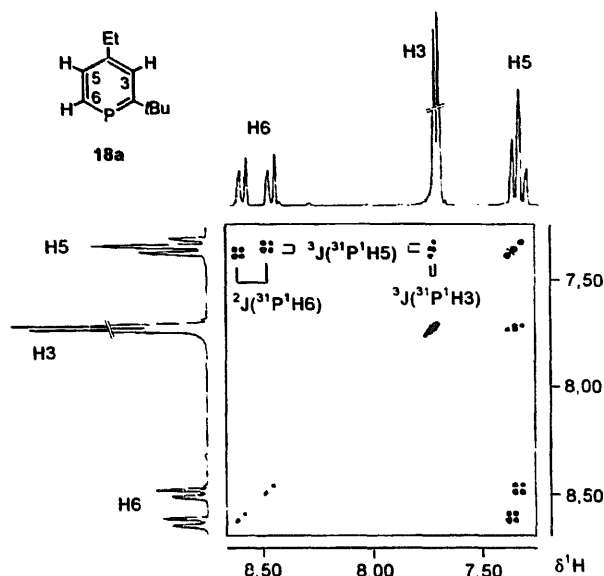
Fig. 4. Contour plot of the 300.13 MHz 2D ^{1}H/^{1}H COSY experiment showing the region of the aromatic protons of the phosphabenzene 18a. Some of the cross-peaks are marked to indicate the coupling constants $^nJ(^{31}P, ^1H)$, and the positive tilts prove that the sign of the three coupling constants $^nJ(^{31}P, ^1H)$ ($n = 2, 3$) are alike (see also Scheme 1).

extremely valuable for monitoring the progress of the reaction and to establish the ratio of isomers for the reaction solutions. The substituent pattern of the phosphabenzenes follows from the ^{1}H and ^{13}C NMR spectra (see Figs. 2–4). ^{11}B NMR spectroscopy played a minor role, except for confirming the stepwise oxidation of the B–C bond with
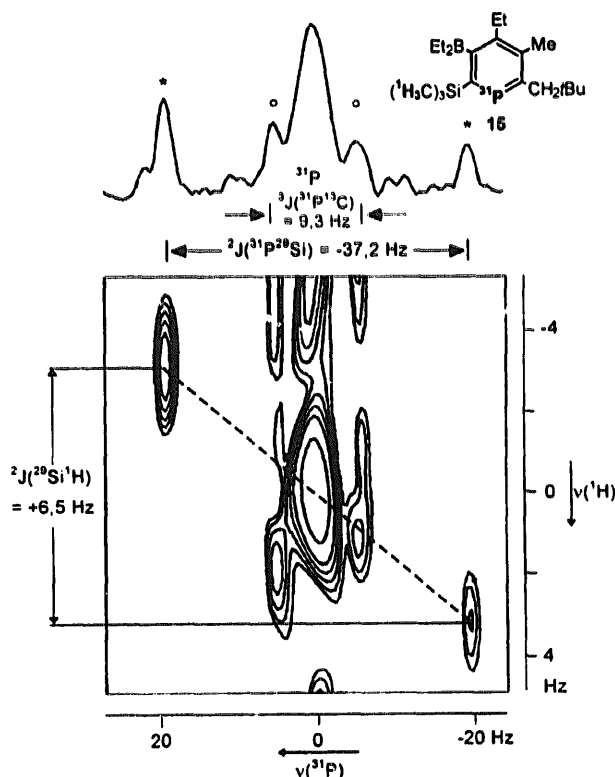

Fig. 5. Contour plot of the 2D 101.3 MHz ^{31}P/^{1}H z-filtered [20] HETCOR experiment [based on $^4J(^{31}P, ^1H_{SiMe_3})$] of the phosphabenzene 15. The ^{29}Si satellites in F2 (ν^{31}P) are marked by asterisks [^{13}C satellites according to $^3J(^{31}P, ^{13}C_{SiMe_3})$ are marked by open circles]. The negative tilt of the cross-peaks for the ^{29}Si satellites prove the opposite sign of the reduced coupling constants $^2K(^{31}P, ^{29}Si)$ and $^2K(^{29}Si, ^1H_{SiMe_3})$. Since the sign of $^2K(^{29}Si, ^1H_{SiMe_3})$ is known to be negative [19], it follows that $^2K(^{31}P, ^{29}Si)$ is positive and that $^2J(^{31}P, ^{29}Si) < 0 (\gamma^{29}Si < 0!)$.

Me$_3$NO (see Table 7). ^{119}Sn NMR spectroscopy proved useful for studying the fate of the stannylenes (vide supra) and also for 16, like ^{29}Si NMR for 15, to indicate the position of the SnMe$_3$ group.

Information on signs of coupling constants can be gained by numerous heteronuclear correlation experiments, if there are three magnetically active nuclei involved which always form one pair of active spins and one passive spin. In our case these nuclei are, in general, ^{1}H, ^{13}C and ^{31}P, or in special cases ^{1}H, ^{29}Si, ^{31}P (see Fig. 5 for the phosphabenzene 15) or ^{1}H, ^{119}Sn, ^{31}P (16). Scheme 1 shows a large set of experiments, many of which are routine 2D COSY or HETCOR experiments [18] carried out (see Figs. 3 and 4) in order to obtain the absolute coupling signs [based on $^1J(^{13}C, {}^1H) > 0$ [19]]. If the detection of cross-peaks d⁻ ₌ ₎ low intensity satellites (e.g. arising from coupling to ^{29}Si) becomes difficult, z-filtering [20] is a useful method for suppressing most of the intensity of the parent signal, as shown for the phosphabenzene 15 in Fig. 5.

The results of the coupling sign determinations are given in Scheme 1, and we note the agreement with calculated [9] and proposed [10] signs. The additional experiments for 15 and 16 have shown that both $^2K(^{31}P, {}^{29}Si)$ and $^2K(^{119}Sn, {}^{31}P)$ possess a positive sign [$^2J(^{31}P, {}^{29}Si)$ and $^2J(^{119}Sn, {}^{31}P)$ are negative because of $\gamma^{29}Si < 0$ and $\gamma^{119}Sn < 0$]. This is in agreement with $^2J(^{31}P, {}^1H) > 0$ and $^2J(^{31}P, {}^{13}C) > 0$. In general, the signs and trends in the magnitude of the coupling constants in the phosphabenzenes are reminiscent of analogous couplings involving the ^{15}N nucleus in pyridines where the influence of the lone pair of electrons was convincingly demonstrated [21]. As an example, the lone pair of electrons at the phosphorus atom induces a large negative contribution to the Fermi contact term, the major mechanism describing the one-bond $^{31}P–^{13}C$ spin–spin coupling. If this lone pair of electrons becomes engaged in chemical bonding, e.g. in the Mo–P bond in the pentacarbonyl molybdenum complex 21a, the values $^1J(^{31}P, {}^{13}C-2) = 3.3$ Hz and $^1J(^{31}P, {}^{13}C-6) = 7.2$ Hz become fairly small and may be of either sign, whereas they are large and negative for example in 11a (-56.6 and -55.6 Hz).

3. Conclusions

[4 + 2] Cycloadditions of stannoles provide a useful route to new organometallic-substituted phosphabenzenes and first reactions have been carried out with these compounds. In addition to these findings the fate of the stannylenes generated in the course of these reactions is of some interest and should be the subject of further systematic studies. There is a wealth of NMR data, considering only ^{1}H, ^{13}C and ^{31}P nuclei, and for the first time the absolute signs of coupling constants for phosphabenzenes were determined.

4. Experimental

All synthetic work and the handling of samples was carried out under an inert atmosphere (Ar), using carefully dried glassware and dry solvents. The 1-phospha-1-alkynes 1 [11a,b], 2 [11c], diethynyltin compounds R$^1_2$Sn(C≡CH)$_2$ (R^1/R^1 = Me [22a], Et [22], ^{t}Bu [23], -(CH$_2$)$_5$- [6c]), and 3-boryl-stannoles 3a [6a], 4a [6a], 5a [23], 3b [6a], 5b [23], 8 [24], 9 [24] were prepared following literature procedures. This is also true for other starting materials such as 2-(chlorodimethylstannyl)-3-diethylboryl-2-pentene [25], Me$_3$SnC≡CSnMe$_3$ [22b], HC≡CSiMe$_3$ [26] and 2-alkyl-1-(trimethylsilyl)-2-(trimethylsiloxy)-1-phospha-1-ethen (alkyl =^{t}Bu, CH$^t_2$Bu) [27]. Deuterated solvents were stored over molecular sieves and saturated with argon.

NMR spectra were recorded using Bruker AM 500, AC 300, ARX 250 and JEOL JNM-EX 270 instruments equipped with multinuclear units. If not mentioned otherwise, samples were dissolved in toluene-d_8, C$_6$D$_6$ or CD$_2$Cl$_2$ in 5 mm (o.d.) tubes and measured at 25 ± 1°C. Chemical shifts are given with respect to solvent signals [δ^1H (C$_6$D$_5$H) = 7.15; (C$_6$D$_5$CD$_2$H) = 2.03; δ^{13}C (C$_6$D$_6$) = 128.0; (C$_6$D$_5$CD$_3$) = 20.4] and external references [δ^{11}B (BF$_3$·OEt$_2$) = 0, Ξ^{11}B = 32.083971 MHz; δ^{29}Si (Me$_4$Si) = 0, Ξ^{29}Si = 19.867184 MHz; δ^{31}P (85% H$_3$PO$_4$) = 0, Ξ^{31}P = 40.480747 MHz; δ^{119}Sn (Me$_4$Sn) = 0, Ξ^{119}Sn = 37.290665 MHz].

IR spectra were recorded with a Perkin-Elmer 983 G spectrometer as hexane solutions in a CaF$_2$ cell with a film thickness of 0.1 mm at 298 K. Elemental analyses were carried out at Dornis and Kolbe (Mülheim an der Ruhr).

4.1. 3-Boryl-stannoles (3–7) (general procedure, NMR tube)

1.0 mmol of trialkylborane (BEt$_3$, B^{i}Pr$_3$, 9-^{i}Bu-9-BBN) were added to a solution of 1.0 mmol of R$^1_2$Sn(C≡CH)$_2$ (R^1 = Me, Et, ^{t}Bu, -(CH$_2$)$_5$-) in 0.3 ml of toluene-d_8 at -78°C. The reaction mixture was warmed slowly to ambient temperature.

isotopomer	experiment	coupling constants	result
Et₂B ... ¹H ³¹P (structure)	$^{31}P / ^{1}H$	$\dfrac{^{1}J(^{13}C^{1}H(6))}{^{1}J(^{31}P^{13}C(6))} < 0$	$^{1}J(^{13}C^{1}H) > 0$ $^{1}J(^{31}P^{13}C) < 0$
Et₂B ... ¹³C ¹H P (structure)	$^{13}C / ^{1}H$	$\dfrac{^{2}J(^{31}P^{1}H)}{^{1}J(^{31}P^{13}C)} < 0$	$^{2}J(^{31}P^{1}H) > 0$
Et₂B ... ¹³C ¹H P (structure)	$^{13}C / ^{1}H$	$\dfrac{^{2}J(^{31}P^{1}H)}{^{3}J(^{31}P^{13}C)} > 0$	$^{3}J(^{31}P^{13}C) > 0$
Et₂B ... ¹H ¹³C P (structure)	$^{13}C / ^{1}H$	$\dfrac{^{2}J(^{31}P^{1}H)}{^{1}J(^{31}P^{13}C)} < 0$	$^{1}J(^{21}P^{13}C) < 0$
Et₂B ... ¹³C C¹H₃ (structure)	$^{13}C / ^{1}H$	$\dfrac{^{4}J(^{31}P^{1}H)}{^{1}J(^{31}P^{13}C)} < 0$	$^{4}J(^{31}P^{1}H) > 0$
Et₂B ... ¹³C C¹H₃ (structure)	$^{13}C / ^{1}H$	$\dfrac{^{4}J(^{31}P^{1}H)}{^{2}J(^{31}P^{13}C)} > 0$	$^{2}J(^{31}P^{13}C) > 0$
Et₂B ... ¹³C¹H₃ (structure)	$^{13}C / ^{1}H$	$\dfrac{^{4}J(^{31}P^{1}H)}{^{3}J(^{31}P^{13}C)} > 0$	$^{3}J(^{31}P^{13}C) > 0$
¹H ... ¹H P (structure)	$^{1}H / ^{1}H$	$\dfrac{^{2}J(^{31}P^{1}H)}{^{3}J(^{31}P^{1}H)} > 0$	$^{3}J(^{31}P^{1}H) > 0$
¹H ¹³C ... P (structure)	$^{13}C / ^{1}H$	$\dfrac{^{3}J(^{31}P^{1}H)}{^{2}J(^{31}P^{13}C)} < 0$	$^{2}J(^{31}P^{13}C) < 0$
¹H ... ¹H P (structure)	$^{1}H / ^{1}H$	$\dfrac{^{3}J(^{31}P^{1}H)}{^{3}J(^{31}P^{1}H)} > 0$	$^{3}J(^{31}P^{1}H) > 0$
Et₂B ... ¹³C¹H P (structure)	$^{13}C / ^{1}H$	$\dfrac{^{3}J(^{31}P^{1}H)}{^{2}J(^{31}P^{13}C)} < 0$	$^{2}J(^{31}P^{13}C) < 0$
Et₂B ¹H₂ ... ¹³C P (structure)	$^{13}C / ^{1}H$	$\dfrac{^{5}J(^{31}P^{1}H)}{^{2}J(^{31}P^{13}C)} < 0$	$^{5}J(^{31}P^{1}H) > 0$
¹H₂ ... ¹³C P (structure)	$^{13}C / ^{1}H$	$\dfrac{^{5}J(^{31}P^{1}H)}{^{2}J(^{31}P^{13}C)} < 0$	$^{5}J(^{31}P^{1}H) > 0$
¹H₂¹³C ... Et₂B P (structure)	$^{13}C / ^{1}H$	$\dfrac{^{5}J(^{31}P^{1}H)}{^{4}J(^{31}P^{13}C)} < 0$	$^{4}J(^{31}P^{13}C) < 0$
¹H₂ ¹³C ... Et₂B P (structure)	$^{13}C / ^{1}H$	$\dfrac{^{5}J(^{31}P^{1}H)}{^{5}J(^{31}P^{13}C)} > 0$	$^{5}J(^{31}P^{13}C) > 0$

Scheme 1. Experiments for comparison of signs of coupling constants in phosphabenzenes. Each experiment involves three spin-1/2 nuclei which are labelled as the active spins (e.g. ^{1}H and ^{13}C) and the passive spin (*).

4b: ^{1}H NMR (toluene-d_8): $\delta\,^{1}H$ [$^{n}J(^{119}Sn, ^{1}H)$] = 0.96–1.06 (q, 4H, SnCH₂); 1.17 (t, 6H, SnEt₂); 2.12 (m, 1H, ^{i}Pr); 1.08 (d, 6H, ^{i}Pr); 1.51 (m, 2H, B$^{i}Pr_2$); 0.99 (d, 12H, B$^{i}Pr_2$); 5.76 [152.6] (s, 1H, =CH); 6.08 [154.5] (s, 1H, =CH).

5a: ^{1}H NMR (toluene-d_8): δ^1H [$^9J(^{119}$Sn, ^{1}H)] = 1.21 [67.1] (s, 18H, Sn^{t}Bu$_2$); 2.17 (dq, 2H, Et); 0.97 (t, 3H, Et); 1.23 (q, 4H, BEt$_2$); 0.91 (t, 6H, BEt$_2$); 5.89 [144.9] (s, 1H, =CH); 5.98 [145.7] (t, 1H, =CH).

5b: ^{1}H NMR (toluene-d_8): δ^1H [$^nJ(^{119}$Sn, ^{1}H)] = 1.30 [66.7] (s, 18H, Sn^{t}Bu$_2$); 2.14 (m, 1H, ^{i}Pr); 1.12 (d, 6H, ^{i}Pr); 1.56 (m, 2H, B^{i}Pr$_2$); 1.04 (d, 12H, B^{i}Pr$_2$); 5.76 [144.5] (s, 1H, =CH); 6.10 [145.0] (s, 1H, =CH).

7: ^{1}H NMR (toluene-d_8): δ^1H [$^nJ(^{119}$Sn, ^{1}H)] = 0.14 [57.6] (s, 6H, SnMe$_2$); 0.85 (d, 6H, ^{i}Bu); 3.07 (m, 1H, =C–CH); 5.85 [162.2] (s, 1H, =CH); 6.75 [158.8] (s, 1H, =CH); 0.9–2.0 (other δ^1H values were not assigned).

4.2. 3-Diethylboryl-4-ethyl-2-(1'-methoxyethen-2'-yl)-1,1,5-trimethylstannole 10

A solution of 3.0 mmol of 2-(chlorodimethylstannyl)-3-diethylboryl-2-pentene in 10 ml of hexane was added slowly to a suspension of 3.0 mmol of lithiated 1-methoxy-but-1-en-3-ine in 10 ml of hexane at −78°C. After stirring overnight LiCl was filtered off and all volatile material was removed in vacuo (10^{-3} mbar). After one day at ambient temperature the intermediate A/A′ had completely reacted to the stannole 10.

10: ^{1}H NMR (toluene-d_8): δ [$^nJ(^{119}$Sn, ^{1}H)] = 0.15 [56.6] (s, 6H, SnMe$_2$); 1.95 [40.1] (s, 3H, =C–CH$_3$); 1.95 (q, 2H, =C–CH$_2$); 0.83 (t, 3H, CH$_3$); 1.12 (q, 4H, BCH$_2$); 0.90 (t, 6H, CH$_3$); 5.01 [111.3] (d, 1H, –CH=); 5.44 [5.1] (d, 1H, =CH–O); 3.11 (s, 3H, OMe).

4.3. Phosphabenzenes 11–17 (general procedure, NMR tube)

A solution of 1.0 mmol of 1-phospha-1-alkine **1** or **2** in (Me$_3$Si)$_2$O (10–20%) was added to 1.0 mmol of stannole (**3–10**) in 0.3 ml of C$_6$D$_6$ or toluene-d_8 at ambient temperature. The progress of the reaction was followed by ^{31}P NMR.

11a: b.p. 87°C (10^{-2} mbar); ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.12 (+40.5) (d, 1H, H^6); 7.69 (+5.8) (d, 1H, H^3); 1.43 (+1.3) (d, 9H, ^{t}Bu); 2.41 (+1.9) (dq, 2H, Et^4); 1.09 (< 1) (dt, 3H, Et^4); 1.45 (q, 4H, BEt$_2$); 0.92 (t, 6H, BEt$_2$). Anal. Found: C, 70.92; H, 10.41. Calc.: C, 72.60; H, 10.56.

11a′: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.41 (39.9) (d, 1H, H^6); 7.49 (5.6) (d, 1H, H^3); 1.44 (n.m.) (d, 9H, ^{t}Bu); 2.40 (< 1) (dq, 2H, Et^5); 1.07 (< 1) (dt, 3H, Et^5); 0.97 (t, 6H, BEt$_2$).

11b: ^{1}H NMR (C$_6$D$_6$): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.09 (40.2) (d, 1H, H^6); 7.84 (5.8) (d, 1H, H^3); 1.45 (1.3) (d, 9H, ^{t}Bu); 2.23 (< 1) (m, 1H, ^{i}Pr^4); 1.26 (< 1) (d, 3H, ^{i}Pr^4); 1.73 (m, 2H, B^{i}Pr$_2$); 0.97 (d, 6H, B^{i}Pr$_2$).

11b′: ^{1}H NMR (C$_6$D$_6$): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.51 (38.7) (d, 1H, H^6); 7.39 (5.6) (d, 1H, H^3); 1.43 (1.4) (d, 9H, ^{t}Bu); 2.13 (< 1) (m, 1H, ^{i}Pr^5); 1.19 (< 1) (d, 3H, ^{i}Pr^5); 1.70 (m, 2H, B^{i}Pr$_2$); 0.99 (d, 6H, B^{i}Pr$_2$).

12a: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.03 (37.9) (d, 1H, H^6); 7.34 (5.8) (d, 1H, H^3); 2.76 (16.2) (d, 2H, CH$_2$); 0.90 (< 1) (s, 9H, ^{t}Bu); 2.30 (< 1) (q, 2H, Et^4); 1.04 (< 1) (dt, 3H, Et^4); 1.37 (q, 4H, BEt$_2$); 0.84 (t, 6H, BEt$_2$).

12a′: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.29 (37.1) (s, 1H, H^6); 7.19 (6.3) (d, 1H, H^3); 2.77 (16.2) (d, 2H, CH$_2$); 0.89 (< 1) (s, 9H, ^{t}Bu); 2.27 (< 1) (q, 2H, Et^5); 1.02 (< 1) (dt, 3H, Et^5); 1.34 (q, 4H, BEt$_2$) 0.84 (t, 6H, BEt$_2$).

12b: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 7.82 (37.5) (d, 1H, H^6); 7.28 (6.5) (d, 1H, H^3); 2.64 (16.1) (d, 2H, CH$_2$); 1.45 (< 1) (s, 9H, ^{t}Bu); 2.0 (< 1) (m, 1H, ^{i}Pr^4); 1.04 (< 1) (d, 3H, ^{i}Pr^4); 1.52 (m, 2H, B^{i}Pr$_2$); 0.83 (d, 6H, B^{i}Pr$_2$).

12b′: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.26 (36.1) (d, 1H, H^6); 6.89 (6.2) (d, 1H, H^3); 2.62 (16.1) (d, 2H, CH$_2$); 1.43 (< 1) (s, 9H, ^{t}Bu); 2.0 (< 1) (m, 1H, ^{i}Pr^5); 1.04 (< 1) (d, 3H, ^{i}Pr^5); 1.38 (m, 2H, B^{i}Pr$_2$); 0.83 (d, 6H, B^{i}Pr$_2$).

13: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.58 (41.2) (d, 1H, H^6); 7.42 (6.0) (d, 1H, H^3); 1.33 (1.1) (d, 9H, ^{t}Bu); 3.11 (m, 1H, CH^4); 0.80 (d, 6H, ^{t}Bu); (other δ^1H values were not assigned).

14: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.45 (38.4) (d, 1H, H^6); 7.05 (6.4) (d, 1H, H^3); 2.64 (15.8) (d, 2H, CH$_2$); 0.80 (< 1) (s, 9H, ^{t}Bu); 3.07 (m, 1H, CH^4); (other δ^1H values were not assigned).

14′: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 7.94 (42.3) (d, 1H, H^6); 7.43 (6.6) (d, 1H, H^3); 0.80 (< 1) (s, 9H, ^{t}Bu); 3.07 (m, 1H, CH^4); (other δ^1H values were not assigned).

15: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 0.25 (+1.4) (u, 9H, SiMe$_3$); 2.90 (18.9) (d, 2H, CH$_2$); 0.83 (< 1) (s, 9H, ^{t}Bu); 2.15 (2.0) (d, 3H, Me); 2.14 (< 1) (2H, q, Et); 0.93 (3H, t, Et); 1.42 (q, 4H, BEt$_2$); 0.82 (t, 6H, BEt$_2$).

16: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) [$^nJ(^{119}$Sn, ^{1}H)] = 0.18 (0.4) [53.8] (d, 9H, SnMe$_3$); 2.82 (18.3) (d,

2H, CH$_2$); 0.80 ($<$ 1) (s, 9H, ^{t}Bu); 2.15 (1.5) (d, 3H, Me); 2.10 ($<$ 1) (2H, q, Et); 0.91 (3H, t, Et); 1.41 (q, 4H, BEt$_2$); 0.76 (t, 6H, BEt$_2$).

17: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 5.52 ($<$ 1) (d, 1H, =CH–O); 4.95 (1.5) (dd, 1H, =CH); 3.00 (s, 3H, OMe); 2.85 (18.4) (d, 2H, CH$_2$); 0.92 ($<$ 1) (s, 9H, ^{t}Bu); 2.43 (16.0) (d, 3H, Me); 2.15 ($<$ 1) (q, 2H, Et); 0.94 ($<$ 1) (t, 3H, Et); 1.35 (q, 4H, BEt$_2$); 0.89 (t, 6H, BEt$_2$).

4.4. Deborylation of 11a/11a′ (NMR tube)

28 mg (0.88 mmol) of methanol was added to a solution of 0.22 g (0.88 mmol) of **11a/11a′** in 0.3 ml of C$_6$D$_6$. After 24 h at ambient temperature the reaction was complete.

18a: ^{1}H NMR (C$_6$D$_6$): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.53 (+40.0) (dd, 1H, H^6); 7.71 (+5.6) (dd, 1H, H^3); 7.33 (+8.7) (dt, 1H, H^5); 1.40 (+1.5) (d, 9H, ^{t}Bu); 2.47 (+2.3) (dq, 2H, Et^4); 1.06 ($<$ 1) (t, 3H, Et^4).

18a′: ^{1}H NMR (C$_6$D$_6$): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.36 (40.1) (dd, 1H, H^6); 7.68 (5.8) (dd, 1H, H^3); 7.07 (3.5) (m, 1H, H^4); 1.38 (1.4) (d, 9H, ^{t}Bu); 2.45 ($<$ 1) (q, 2H, Et^5); 1.06 ($<$ 1) (t, 3H, Et^5).

4.5. Deborylation of 11b/11b′ (NMR tube)

0.12 g (1.6 mmol) of 2-aminoethanol was added to a solution of 0.46 g (1.6 mmol) of **11b/11b′** in 0.3 ml of toluene-d_8 at ambient temperature. After heating overnight at 100°C the reaction was complete.

18b: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.62 (39.7) (dd, 1H, H^6); 7.80 (5.7) (dd, 1H, H^3); 7.60 (+9.0) (dt, 1H, H^5); 1.45 (1.3) (d, 9H, ^{t}Bu); 2.9 (n.m.) (m, 1H, ^{i}Pr^4); 1.28 ($<$ 1) (d, 6H, ^{i}Pr^4).

18b′: ^{1}H NMR (toluene-d_8): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.49 (39.6) (dd, 1H, H^6); 7.86 (5.7) (dd, 1H, H^3); 7.32 (3.5) (m, 1H, H^4); 1.45 (1.3) (d, 9H, ^{t}Bu); 2.9 (n.m.) (m, 1H, ^{i}Pr^5); 1.27 ($<$ 1) (d, 6H, ^{i}Pr^5).

4.6. Oxidation of 11a/11a′ with Me$_3$NO

75 mg (1.0 mmol)/150 mg (2.0 mmol) of Me$_3$NO was added to a solution of 0.25 g (1.0 mmol) of **11a/11a′** in 4 ml of toluene at ambient temperature. After stirring for 1 h all volatile material was removed in vacuo (10^{-2} mbar).

19a: yield 0.24 g (91.4%). ^{1}H NMR (C$_6$D$_6$): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.48 (40.7) (d, 1H, H^6); 7.76 (5.9) (d, 1H, H^3); 1.45 (1.3) (d, 9H, ^{t}Bu); 2.58 (1.5) (dq, 2H, Et^4); 1.00 ($<$ 1) (t, 3H, Et^4); 3.68 (q, 2H, OEt); 1.17 (t, 3H, OEt).

19a′: ^{1}H NMR (C$_6$D$_6$): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.44 (39.9) (d, 1H, H^6); 7.76 (6.0) (d, 1H, H^3); 1.43 (1.4) (d, 9H, ^{t}Bu); 2.54 ($<$ 1) (q, 2H, Et^5).

20a: ^{1}H NMR (C$_6$D$_6$): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.67 (+39.0) (d, 1H, H^6); 7.78 (5.5) (d, 1H, H^3); 1.45 ($<$ 1) (s, 9H, ^{t}Bu); 1.22 ($<$ 1) (t, 3H, Et^4); 3.80 (q, 4H, OEt); 1.07 (t, 6H, OEt).

4.7. Reaction of 11a/11a′ with Mo(CO)$_6$

0.38 g (1.4 mmol) of Mo(CO)$_6$ was added to a solution of 0.35 g (1.4 mmol) of **11a/11a′** in 10 ml of heptane. After heating at reflux for 6 h (IR controlled) all volatile material was removed in vacuo (10^{-2} mbar). Filtration over silica gel of the product **21a/21a′** led to decomposition.

21a: ^{1}H NMR (C$_6$D$_6$): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.04 (30.2) (d, 1H, H^6); 7.96 (16.1) (d, 1H, H^3); 1.69 (0.5) (d, 9H, ^{t}Bu); 2.63 (4.0) (q, 2H, Et^4); 1.30 ($<$ 0.5) (t, 3H, Et^4); 1.07 (t, 6H, BEt$_2$); IR ν(CO) = 2073 cm^{-1} (w), 1948 cm^{-1} (s).

21a′: ^{1}H NMR (C$_6$D$_6$): δ^1H ($^nJ(^{31}$P, ^{1}H)) = 8.36 (28.6) (d, 1H, H^6); 7.67 (16.9) (d, 1H, H^3) (other δ^1H values were not assigned).

4.8. Reaction of 11a/11a′ with Mo(CO)$_3$(NCMe)$_3$

0.61 g (2.0 mmol) (I)/0.30 g (1.0 mmol) (II) of Mo(CO)$_3$(NCMe)$_3$ were added to a solution of 0.50 g (2.0 mmol) of **11a/11a′** in 2 ml of THF. After 2 h at ambient temperature all volatile material was removed in vacuo (10^{-2} mbar) and the residue was dissolved in 4 ml of hexane. The solution was decanted from the residue. In case (I) 0.3 g

of yellow $Mo(CO)_3(NCMe)_3$ was left. Hexane was removed in vacuo (10^{-2} mbar). In both cases the same resonances in the NMR spectra were obtained. ^{31}P NMR (C_6D_6): $\delta^{31}P = 166.9$ (22a), 179.9, 191.6 ($^2J(^{31}P, ^{31}P) = 36.7$) (22a').

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