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Plumboles bearing organometallic substituents. Their synthesis and reaction mechanism, as studied by multinuclear magnetic resonance spectroscopy

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Abstract

Reaction of bis(trimethylsilylethynyl)dimethyllead (**1**) with trialkylboranes (**2**) gives the 3-dialkylboryl-4-alkyl-2,5-bis(trimethylsilyl)-1,1-dimethylplumboles (**4**). The course of the reactions was monitored by multinuclear NMR (^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{207}Pb), and various intermediates were identified, including two non-cyclic bis(alkenyl)lead compounds (**8**, **9**) and a zwitterionic species (**5**) in which a triorganolead cation is stabilized by intramolecular side-on coordination to the C≡C triple bond of an alkylnylborate moiety. The presence of at least one trimethylsilylethynyl group is necessary for the formation of plumboles from zwitterionic compounds analogous to **5**, as was shown by the synthesis of 3-diethylboryl-4-ethyl-1,1,5-trimethyl-2-trimethylsilylplumbole (**11**). Positive and negative signs of coupling constants $^1J(^{207}\text{Pb}^{13}\text{C})$ in the plumboles have been determined by two-dimensional ^{13}C/^{1}H heteronuclear shift correlations. Features of these data and of the δ^{207}Pb values are compared with ^{119}Sn NMR parameters of comparable tin compounds.

Introduction

There is considerable interest in metallacyclopentadienes, owing to the reactivity of the metal-carbon bonds and to the special aspects of the reactivity of the diene system in such compounds. Metallacyclopentadienes are considered to be intermediates in the oligomerization of alkynes [1], and electron delocalization across the metal may occur. In the latter context the boroles [2] and the higher homologues of cyclopentadienes, the siloles [3], germoles [4] stannoles [5] (e.g. as potential precursors of boroles or reactive dienes in cycloadditions) have been the subject of numerous investigations. Derivatives with M = Ti [6], Zr [7], or Pt [8] have also received some attention. However, relatively little is known about plumboles, except for the 2,3,4,5-tetraaryl derivatives [9] that are available from the reaction between the readily accessible 1,4-dilithiotetraarylbutadiene and a diorganolead dihalide.

We have shown that organoboration [10] of bis(alkynyl) derivatives of boron, silicon and tin leads to boroles (**A**) [11], siloles (**B**) [12] or stannoles (**C**) [13–15],

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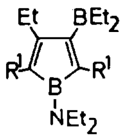
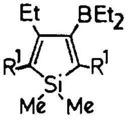
respectively, with some dependence on the substituents R^1 on the respective C≡C triple bonds.



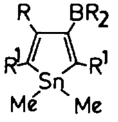
A

($R^1 = SnMe_3$)



B

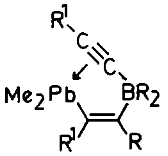
(R^1 = Me, $SnMe_3$)



C

(R^1 = H[13], ${}^tBu$[14], $SiMe_3$ [14,15];
R = Me, Et, Pt, ${}^iPr$, Bu)

In particular, this type of reaction allowed preparation of a wide variety of stannoles, and now we report on our attempts to make comparable plumboles. When we started to investigate the organoboration of bis(alkynyl)plumbanes, $Me_2Pb(C{\equiv}CR^1)_2$, we found that the first stable product had the structure **D**, which was assigned from spectroscopic data (IR, ^1H-, ^{11}B-, ^{13}C- and ^{207}Pb NMR) and by X-ray crystallography [16]. In the light of the results for the stannoles **C** with $R^1 = SiMe_3$, we studied the reaction of bis(trimethylsilylethynyl)dimethylplumbane



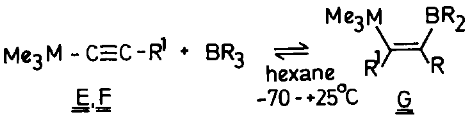
D

(R^1 = Me, Bu, ${}^tBu$, Ph; R = Et, Pr, ${}^iPr$, C_5H_9)

(**1**) with trialkylboranes BR_3 [**2a** (R = Et), **2b** (R = Pr) and **2c** (R = ${}^iPr$)]. Furthermore, we have tried to convert an intermediate of type **D** (**3**, R^1 = Me, R = Et) into a plumbole. All the reactions were monitored by multinuclear magnetic resonance spectroscopy and the final structure of the products was deduced from a large set of NMR data.

Results and discussion

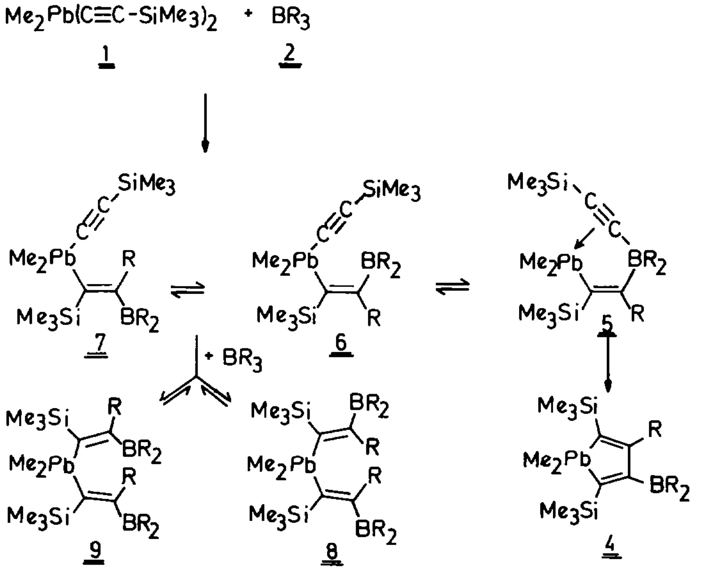
For most groups R^1 attached to the C≡C triple bond in alkynylstannanes and -plumbanes, e.g. of the type $Me_3SnC{\equiv}CR^1$(**E**) or $Me_3PbC{\equiv}CR^1$ (**F**), respectively, the organoboration is a quantitative and stereoselective reaction [10], leading to the products **G** shown in Eq. 1.



(1)

(M = Sn, Pb) (R^1 = H, alkyl, aryl;
R = alkyl, aryl)

If R^1 is another organometallic group a mixture of (*E*/*Z*)-isomers is obtained [10,17]. The organoboration of bis(alkynyl) derivatives of various elements requires a stereochemistry, as shown in Eq. 1 for **G**, in the first step of the reaction if the



Scheme 1. Proposed intermediates from the organoboration of bis(trimethylsilylethynyl)dimethylplumbane (**1**) and triorganoboranes (**2**). The structure of the compounds **5**, **8**, **9** follows from the NMR data for the reaction mixture (see Table 1, 2 and Fig. 1) (R = Et (**a**), Pr (**b**), ^{i}Pr (**c**)).

heterocyclic systems are to be formed in the final step. Fortunately, the organoboration is readily reversible, especially if R^1 is an organometallic substituent such as $R^1 = SiMe_3$ [10]. Thus, the desired stereochemistry eventually results from a series of organo- and deorgano-borations and the final irreversible cyclization will drive the reaction to completion. In any case, such reactions are expected to proceed slowly and, observation of intermediates should be possible, corroborating the mechanistic assumptions. In the case of the stannoles **C** ($R^1 = SiMe_3$), one of the various possible intermediates (corresponding to **7**) had been identified in the reaction solutions [15].

By monitoring the reaction between **1** and trialkylboranes by NMR spectroscopy, we have obtained fairly complete NMR data sets for three of the proposed intermediates (**8**, **9**, **5**, Scheme 1). The complex reaction mixtures (see Fig. 1) finally yield a single species, the plumbole **4**. Thus the formation of the plumboles is the major irreversible reaction (accompanied by the formation of some metallic lead, triorganoboranes and alkynes, $Me_3SiC{\equiv}CR$), and the intermediate **5** analogous to **D** ($R^1 = SiMe_3$) is considered to be the direct precursor of **4**. When the reaction mixtures contain mainly ($\approx 90\%$) the plumbole **4**, compound **8** is still present. This is in accord with Scheme 1 which shows that for compound **8** the greatest number of rearrangement processes is required to reach the plumbole **4**. Compounds **4** are obtained as yellowish oily liquids which are thermally unstable (undergoing extensive decomposition at $> 40\,^\circ C$), sensitive to air and moisture, and which slowly deposit lead, even when stored at $-20\,^\circ C$ in the dark. The difficulty of handling the plumboles **4** complicates most analytical procedures, their composition and structure follows unambiguously from the NMR data in solution.

The mechanism proposed in Scheme 1 attributes a central role to the intermediate **5**. However, the compounds **D** (analogous to **5**) do not rearrange to plumboles. So far, the only useful rearrangement of **D** is that leading to a

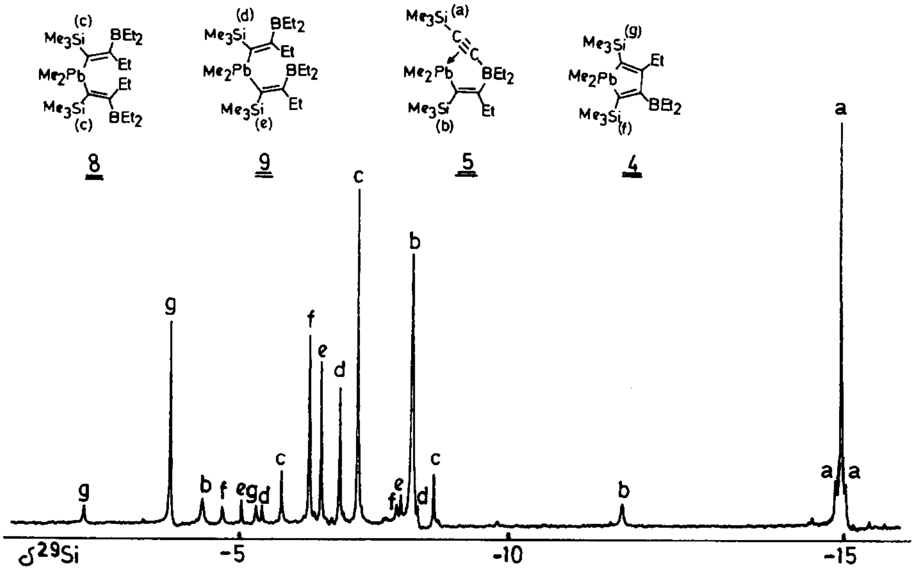
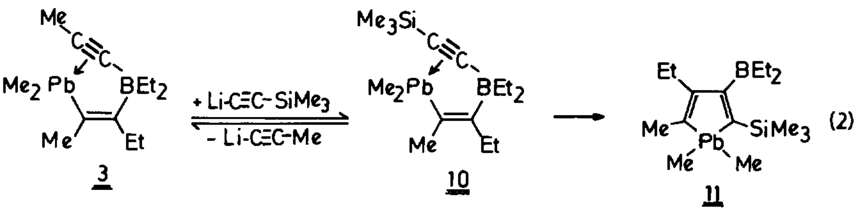


Fig. 1. 59.6 MHz ^{29}Si NMR spectrum (refocused INEPT pulse sequence, 6s recycle time, 32 scans) at −30 °C in CD_2Cl_2 of the solution from the reaction between $Me_2Pb(C{\equiv}CSiMe_3)_2$ (**1**) and BEt_3 (**2a**). The assignment of the various ^{29}Si resonance signals is based on their relative intensities as a function of time, on the δ^{29}Si values and the magnitude of $^{2}J(^{207}Pb^{29}Si)$ (e.g., for **5**) and on the appearance of the respective ^{207}Pb-, ^{1}H- and ^{13}C NMR spectra which were taken in the same intervals.

1,4-plumbabora-2,5-cyclohexadiene derivative (R^1 = Me, R = ^{i}Pr) [16,18]. It thus appears that R^1 must be $SiMe_3$ for the plumbole ring to be formed. If this is true, treatment of **D** with $LiC{\equiv}CSiMe_3$ should give the intermediate **10**, at least in equilibrium with **D**, and from **10** the rearrangement to the plumbole is conceivable. In accord with to Eq. 2, the plumbole **11** was in fact obtained in high yield from the reaction between **3** and $LiC{\equiv}CSiMe_3$. Compound **11** is even less stable than the plumboles **4**. Its structure was deduced from the NMR data (Table 3), by comparison with data that were obtained for the corresponding stannole [14b].



(2)

NMR spectroscopic results

In Table 1 ^{13}C, ^{29}Si and ^{207}Pb NMR data are given for the non-cyclic alkenes **8**, **9**, and, for comparison, for alkenes obtained from the reaction between trimethylsilylethynyltrimethylplumbane ($Me_3Pb{-}C{\equiv}C{-}SiMe_3$) and BR_3. Table 2 list relevant NMR data for **5** and **3** (for comparison). The ^{13}C, ^{29}Si and ^{207}Pb NMR data for the plumboles **4** and **11**, and some data for analogous stannoles (**4**-Sn, **11**-Sn), are listed in Table 3.

Table 1

^{11}B-, ^{13}C-, ^{29}Si and ^{207}Pb NMR spectra [a,b] of **8a**, **9a** and the *E*/*Z*-isomers from the organoboration of $Me_3PbC{\equiv}CSiMe_3$ with Et_3B for comparison

Parameters	(*Z*)-$\begin{matrix}Me_3Pb\\Me_3Si\end{matrix}C{=}C\begin{matrix}Et\\BEt_2\end{matrix}$	(*E*)-$\begin{matrix}Me_3Si\\Me_3Pb\end{matrix}C{=}C\begin{matrix}Et\\BEt_2\end{matrix}$	(*Z*/*Z*)-**8a**	(*Z*/*E*)-**9a**
δ^{13}C(PbC=)	144.9 [141.9]	143.0 [230.7]	152.6 [48.5]	151.8, 150.9 [43.1] [82.8]
δ^{13}C(BC=)	177.9 [br]	181.7 [br]	174.2 [br]	177.2, 176.9 [br] [br]
δ^{13}C(PbMe)	1.0 [142.7]	1.0 [149.0]	8.1 [n.o.]	9.0 [n.o.]
δ^{13}C(SiMe$_3$)	1.0 [22.0]	2.5 [25.5]	1.8 [16.3]	2.4, 1.2 [n.o.] [n.o.]
δ^{13}C(=CEt)	35.4, 14.3 [222.5] [15.6]	32.5, 14.6 [246.6] [17.0]	38.9, 13.5 [195.1] [n.o.]	38.0, 37.2 [212.5] [n.o.] 13.8, 13.9 [n.o.] [21.8]
δ^{13}C(BEt$_2$)	19.3, 9.6 [br]	21.4, 9.3 [br]	22.6, 10.0 [br]	22.7, 22.2, [br] [br] 9.8, 9.8
δ^{11}B [c]	+85.0	+85.0	+85.0	+85.0
δ^{29}Si	−5.8 [172.0]	−7.2 [171.5]	−6.9 [149.6]	−6.6, −6.3 [153.1] [157.7]
δ^{207}Pb	−109.1	−81.3	−137.0 [d]	−139.0 [d], −164.0 [d]

[a] In toluene-d_8 at −40 °C and in CD_2Cl_2 (**8a**, **9a**) at −30 °C. [b] Chemical shifts δ with respect to Me_4Si [$\delta^{13}C(C_6D_5CD_3) = 20.4$; $\delta^{13}C(CD_2Cl_2) = 50.3$], external Et_2O–BF_3 (δ^{11}B), external Me_4Si (δ^{29}Si), and external Me_4Pb (δ^{207}Pb). Coupling constants $^nJ(^{207}PbX)$ are given in square brackets; [br] denotes the ^{13}C resonance signal of a carbon atom linked to boron; [n.o.] means not observed. [c] ^{11}B resonances were extremely broad ($h_{1/2} > 700$ Hz). [d] Assignment uncertain.

All ^{1}H-, ^{11}B-, ^{13}C-NMR data were obtained by routine procedures. The ^{11}B NMR spectra for **4**, **8**, **9**, **11** show extremely broad resonances typical [19] of three-coordinate boron atoms in the region of $\delta^{11}B \approx 84 \pm 2$. Only compounds **5** show a relatively sharp ^{11}B NMR signal at low frequencies typical [19] of tetracoordinate boron atoms. The assignment of the ^{13}C NMR spectra is straightforward from the δ^{13}C values, the coupling constants $^nJ(^{207}Pb^{13}C)$, and the broadening of ^{13}C resonances of carbon atoms linked directly to boron [19]. The ^{29}Si NMR spectra were recorded using the refocused INEPT pulse sequence [20] based on the almost identical $^2J(^{29}Si^1H)$ values (≈ 6.5 Hz) for all Me_3Si groups involved. All ^{207}Pb resonance signals (except for **1**) are broad owing to partially relaxed scalar coupling $^3J(^{207}Pb^{11}B)$.

Chemical shifts $\delta^{13}C$, $\delta^{29}Si$ and $\delta^{207}Pb$

The δ^{13}C data for the plumboles in Table 3 show that there is the expected striking resemblance to the data for the corresponding stannoles, which were discussed previously [15]. Similarly, the δ^{29}Si values are found in the typical range

Table 2
^{11}B-, ^{13}C-, ^{29}Si- and ^{207}Pb NMR data [a,b] of the zwitterionic intermediates **5** and **3** (for comparison)

Parameters	**5a** (R = Et)	**5b** (R = Pr)	**3** (R = Et) [c]
δ^{13}C(PbC=)	148.2	148.2	146.1
	[116.6]	[n.o.]	[640.9]
δ^{13}C(BC=)	206.9	206.0	181.4
	[br. ≈ 60]	[br]	[br]
δ^{13}C(BC≡C)	150.7, 109.4	151.8,109.5	108.7, 106.6
	[br. ≈ 116.0] [105.0]	[br] [n.o.]	[br] [28.0]
δ^{13}C(PbMe$_2$)	23.1	23.2	19.6
	[177.5] [d]	[141.0] [d]	[60.5] [d]
δ^{13}C(=CSiMe$_3$)	1.9	2.0	22.5 (=CMe)
	[n.o.]	[n.o.]	[307.4]
δ^{13}C(≡CSiMe$_3$)	0.9	1.0	4.2 (≡CMe)
	[< 2]	[< 2]	[10.9]
δ^{13}C(R)	35.4, 16.6	45.3, 25.4, 15.7	28.4, 14.5
	[424.0] [31.6]	[415.8] [30.8]	[262.7] [28.9]
δ^{13}C(BR$_2$)	17.9, 12.4	30.9, 22.0, 17.9	18.8, 13.0
	[br]	[br]	[br]
δ^{11}B	−9.2	−9.5	−8.6
δ^{29}Si(=CSi)	−7.8	−7.6	–
	[413.5]	[408.8]	
δ^{29}Si(≡CSi)	−14.9	−15.1	–
	[9.8]	[< 6]	
δ^{207}Pb	+767.0	+773.0	+722.7

[a] In CD$_2$Cl$_2$ at −30 °C. [b] See Footnote *b* in Table 1. [c] Ref. [16,18]. [d] Sign is negative with respect to $^2J(^{207}\text{PbC}^1\text{H}) < 0$.

[17], slightly deshielded compared with these for **4**-Sn and **11**-Sn. The changes in the δ^{207}Pb values with the number of Me$_3$Si-groups and the nature of R follow the trend shown by δ^{119}Sn values. The range of the δ^{207}Pb data is approximately three times greater than that of the δ^{119}Sn values, in accord with expectations [21]. The larger deshielding of the ^{207}Pb nuclei in **4** than in **11** indicates the influence of the increasing number of electropositive substituents on the conjugated cyclic π-system. The δ^{207}Pb values for **8**, **9** and compounds of type **G** (Table 1) are also instructive. Of all known tetraorganolead compounds, **4c** has its ^{207}Pb resonance at the highest frequency [21]. The decrease in ^{207}Pb nuclear shielding observed for **4** (in contrast to non-cyclic or cyclic non-conjugated π-systems) reflects the presence of low lying excited electronic states involving at least partially the lead atom.

Coupling constants $^nJ(^{207}Pb^{13}C)$, $^2J(^{207}Pb^{29}Si)$

The extreme NMR spectroscopic properties of heavy nuclei within a group of the Periodic Table often serves to establish useful trends. The variation in $^1J(^{119}\text{Sn}^{13}\text{C})$ values of stannoles with the number of electropositive substituents on the ring have been discussed [15]. The trends noticed for the stannoles are also found, much more explicitly, in the case of the plumboles **4** and **11**. The small $|^1J(^{207}\text{Pb}^{13}\text{C(Me)})|$ values indicate an unusual bonding situation at the lead atom. By two-dimensional (2D) ^{13}C/^{1}H heteronuclear shift correlations we have established a positive sign for these coupling constants (compared with a negative sign of $^2J(^{207}\text{PbC}^1\text{H})$) [22]. Interestingly, the $|^1J(^{207}\text{Pb}^{13}\text{C(2,5)})|$ values are also rather small, except for

Table 3

^{11}B-, ^{13}C-, ^{29}Si- and ^{207}Pb NMR data [a,b] for the plumboles **4** and **11**, together with data for three coressponding stannoles (**4a**-Sn, **4c**-Sn [15], **11**-Sn [14b]) for comparison.

Parameter	**4a** (R = Et)	**4a**-Sn	**4b** (R = Pr)	**4c**-(R = ^{i}Pr)	**4c**-Sn	**11**	**11**-Sn
δ^{13}C(2)	147.6	145.0	147.4	146.1	144.5	139.8	136.1
	[31.6] [c]	[194.2]	[29.4] [c]	[54.5] [c]	[179.2]	[45.2] [d]	[231.1]
δ^{13}C(3)	177.7	181.8	175.0	178.0	183.4	175.6	182.2
	[br]	[br]	[br]	[br]	[br]	[br]	[br]
δ^{13}C(4)	161.5	166.7	160.6	166.3	171.8	151.8	153.3
	[185.3]	[94.8]	[188.3]	[182.6]	[93.0]	[330.2]	[173.2]
δ^{13}C(5)	145.1	139.1	146.3	144.7	138.2	147.5	139.0
	[64.3] [d]	[260.4]	[59.9] [d]	[48.0] [d]	[240.7]	[316.1] [d]	[451.4]
δ^{13}C(PbMe$_2$)	9.2	−5.6 (SnMe$_2$)	9.5	11.6	−3.9 (SnMe$_2$)	5.3	−7.6 (SnMe$_2$)
	[33.8] [d]	[259.1]	[32.7] [d]	[7.0] [d]	[250.5]	[88.3] [d]	[278.2]
δ^{13}C(SiMe$_3$)	2.5, 2.1	1.9, 1.7	2.8, 2.7	4.5, 2.5	4.0, 2.1	2.3, 22.9 (C^5–Me)	1.8, 17.4 (C^5–Me)
	[15.3] [19.6]	[9.0] [11.7]	[n.o.] [n.o.]	[21.3] [20.1]	[11.8] [11.3]	[22.9] [119.4]	[13.1] [75.2]
δ^{13}C(R)	32.5, 17.1	31.4, 16.0	42.8, 26.3, 15.2	42.8, 24.3	41.6, 24.1	26.5, 14.4	27.2, 13.9
	[145.0] [13.5]	[92.2] [9.7]	[142.8] [13.1]	[140.1] [14.7]	[88.2] [9.3]	[90.5] [12.0]	[58.2] [7.5]
δ^{13}C(BR$_2$)	22.7, 10.0	22.3, 9.3	34.3, 19.7, 18.0	26.6, 20.5, 20.2	25.8, 20.4, 20.1	22.7, 9.6	22.2, 9.2
	[br]	[br]	[br]	[br]	[br]	[br]	[br]
δ^{11}B [e]	+83.0	+83.0	+83.0	+84.0	+84.0	+85.0	+86.0
δ^{29}Si [f]	−6.1, −3.8	−9.7, −8.2	−6.4, −4.0	−7.4, −6.7	−10.5, −10.3	−7.2	−10.0
	[171.3] [168.8]	[97.4] [98.2]	[172.2] [170.7]	[175.5] [162.4]	[98.0] [88.0]	[164.5]	[93.7]
δ^{207}Pb	+543.2	+133.5(δ^{119}Sn)	+551.6	+630.1	+157.0 (δ^{119}Sn)	+319.0	+59.2 (δ^{119}Sn)

[a] In CDCl$_2$ at −30°C and in C$_6$D$_6$ (**11**) at 25°C. [b] See Footnote b in Table 1. [c] Sign is negative with respect to $^{2}J(^{207}PbC^{1}H) < 0$. [d] Sign is positive with respect to $^{2}J(^{207}PbC^{1}H) < 0$. [e] All ^{11}B resonance signals are very broad ($h_{1/2}$ > 700 Hz). [f] No assignment of the ^{29}Si resonances has been made.

$^1J(^{207}Pb^{13}C(5))$ in **11**. Correlations between $^1J(^{119}Sn^{13}C(C=))$ and $^1J(^{207}Pb^{13}C(C=))$ values [22] indicate that some of the coupling constants $^1J(^{207}Pb^{13}C(2,5)$ in **4** and **11** may have a negative sign. Recently, we reported that the 2D $^{13}C/^1H$ heteronuclear shift correlation can also be based on small long range coupling constants [23], e.g. on $^3J(^{13}C(2,5)PbC^1H)$ (≈ 1 Hz), which allows comparison of the signs of $^1J(^{207}Pb^{13}C(2,5))$ and $^2J(^{207}PbC^1H)$. Such an experiment was carried out for **4b**, and showed that $^1J(^{207}Pb^{13}C(2)) < 0$ and $^1J(^{207}Pb^{13}C(5)) > 0$ (again a negative sign of $^2J(^{207}PbC^1H)$ is assumed [22]). On the basis of this result, the sign of the other coupling constants $^1J(^{207}Pb^{13}C(2,5))$ in **4a**, **4b** and **11** follows from the linear correlation between these data and the $^1J(^{119}Sn^{13}C(2,5))$ values of the stannoles given in Table 3 [$^1J(^{119}Sn^{13}C(2,5)) = -0.74\ ^1J(^{207}Pb^{13}C(2,5)) - 211.5$ for stannoles and plumboles].

The $^2J(^{207}Pb^{13}C(4))$ values reflect the coupling across two and three bonds. Inspection of the data for **4** (≈ 185 Hz) and **11** (330.2 Hz) shows that the contributions from the two-bond pathways must be markedly different, assuming similar contributions from the three-bond pathway. The vicinal coupling constants $^3J(^{207}Pb^{13}C(R))$ of **4** are smaller than of comparable non-cyclic compounds (Table 1). However, the correct trend is observed for the $^3J(^{207}Pb^{13}C(R))$ values in **4** and **11**. The greater values for **4** are in accord with the general observation [24] that electropositive substituents at the C=C double bond cause an increase in the magnitude of vicinal coupling constants across the C=C double bond.

The $^2J(^{207}Pb^{29}Si)$ values for **4** and **11** are of the same order of magnitude as those observed for noncyclic compounds (Table 1). In respect of ^{119}Sn- and ^{207}Pb NMR data for stannyl- and plumbyl-amines, we have shown [25] that there is a linear relationship between geminal coupling constants $^2J(^{119}Sn^{29}Si)$ and $^2J(^{207}Pb^{29}Si)$ [$^2J(^{119}Sn^{29}Si) = -0.486\ ^2J(^{207}Pb^{29}Si) + 11.8$]. The magnitude of $^2J(^{207}Pb^{29}Si)$ does not show any spend influence of the conjugated π-system.

Experimental

All compounds were handled under N_2, with exclusion of traces of moisture and oxygen. The starting materials were prepared by literature procedures: **1** [26], **2a** [27], **2b** [28], **2c** [29], **3** [16,18] and $LiC\equiv CSiMe_3$ from $Me_3SiC\equiv CH$ and BuLi (1.6 *M* in hexane).

3-Dialkylboryl-4-alkyl-1,1-dimethyl-2,5-bis(trimethylsilyl)plumboles (4a, b, c)

The reactions between **1** (2.16 g, 5 mmoles) and **2** (5.5 mmoles) were carried out in hexane or methylene chloride (≈ 15 ml) at −78 °C. The reaction mixtures were slowly warmed to −20 °C, when samples were taken for ^{29}Si NMR to allow monitoring of the progress of the reaction. In the case of **4a** the mixture had to be kept at −10 to −20 °C for several weeks in order to avoid extensive decomposition during the reaction. In contrast, in the case of **4b** and **4c** the reaction mixtures had to be warmed to 0 °C and finally to +20 °C in order to bring about complete rearrangement of all the intermediates to the plumboles. Since the decomposition products from **4** and from the intermediates are either insoluble solids (metallic lead) or volatile materials (trialkylboranes, alkynes $Me_3SiC\equiv CR$), fairly pure samples (^{1}H NMR: $\geq 90\%$) of **4** (yield ≈ 60 to 80% with respect to **1**) are readily available as oily, yellow, extremely air-sensitive liquids. Compounds **4** slowly deposit lead, even when kept in solution at −20 °C in the dark. ^{1}H NMR of **4a** (CD_2Cl_2, −30 °C, 300 MHz): $\delta^1H[J(^{207}Pb^1H)] = 0.11$ s, 0.22 s, 18H, $SiMe_3$; 0.94 [45.0] s, 6H, $PbMe_2$; 1.2–0.9 m, 10H, BEt_2; 2.30 [3.6] q, 1.09 [4.7] t, 5H, =CEt.

3-Diethylboryl-4-ethyl-1,1,5-trimethyl-2-trimethylsilylplumbole (11)

A solution of 0.83 g **3** (2 mmoles) in 5 ml of hexane was added to a freshly prepared suspension of $Me_3SiC{\equiv}CLi$ (2 mmoles) in 10 ml of hexane at −55 °C. The mixture was allowed to warm slowly (8 h) to 20 °C and solid material (lead and $LiC{\equiv}CMe$) was filtered off, leaving a greenish solution. After all the volatile material was removed at 0 °C/0.1 Torr, 0.8 g of a greenish, oily liquid was left and this consisted of > 90% of **11** (yield ≈ 80%). This liquid decomposes completely within several hours at 25 °C. ^{1}H NMR (C_6D_6, 300 MHz): $\delta^1H[J(^{207}Pb^1H)] = 0.14$ s, 9H, $SiMe_3$; 0.86 [51.0] s, 6H, $PbMe_2$; 1.3 m, 1.04 t, 10H, BEt_2; 2.04 q, 0.99 t, 5H, =CEt; 2.08 [63.8] s, 3H, =CMe.

The NMR spectra were measured with a Bruker AC 300 spectrometer, equipped with a multinuclear unit and a variable temperature control unit (for experimental conditions, see the Tables 1 to 3 and Fig. 1). Since the chemical shift anisotropy (CSA) provides an efficient relaxation mechanism for longitudinal ^{207}Pb nuclear spin relaxation at the field strength $B_0 = 7.05\ T$ [21,30,31], short acquisition times (≈ 0.2 s) and fairly large pulse angles (≈ 45 to 60°) without any relaxation delay were used for recording the ^{207}Pb NMR spectra.

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