(57, M$^+$), 340 (46, M$^+$ – CO), 312 (42, M$^+$ – 2CO); IR (hexane) ν(CO) 1978, 1907 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.82 (s, $C_6H_3Me_3$), 1.90 (s, $C_6H_3Me_3$).

Preparation of [(mes)Os(C_2H_4)$_2$] (18). A suspension of 1 (105 mg, 0.14 mmol for n = 2) in 12 mL of ethanol was treated with an excess of dry Na_2CO_3 (ca. 100 mg). While a slow stream of ethylene was passed through the suspension, it was heated to 80 °C under continuous stirring. After 6 h the reaction mixture was cooled to room temperature, and the solvent was removed in vacuo. The residue was extracted three times with 20 mL of petroleum ether, the solution was filtered, and the filtrate was concentrated to ca. 1 mL in vacuo. After chromatography on Al_2O_3 (neutral, activity grade III) with benzene/hexane (1:5) a yellow fraction was obtained. It was brought to dryness and dried in vacuo to give a pale yellow microcrystalline solid, yield 48 mg (48%). Anal. Calcd for $C_{13}H_{20}Os$: C, 42.60; H, 5.50; Os, 51.90. Found: C, 42.49; H, 5.64; Os, 52.05. MS (70 eV), m/z 368 (24, M$^+$); ^{1}H NMR (C_6D_6) δ 4.58 (s, $C_6H_3Me_3$), 1.72 (s, $C_6H_3Me_3$), 2.04 (m, [4H], C_2H_4), 0.94 (m, [4H], C_2H_4).

Preparation of [(mes)Os(C_7H_8)] (19) occurred analogously as described for 18, starting from 1 (89 mg, 0.12 mmol for n = 2) and norbornadiene (0.91 g, 9.9 mmol). The reaction mixture was heated to 80 °C for 1 h and further worked up as described for 18 by using only hexane for chromatography. A pale yellow powder was obtained, yield 56 mg (58%). Anal. Calcd for $C_{16}H_{20}Os$: C, 47.74; H, 5.01. Found: C, 48.27; H, 5.28. MS (70 eV), m/z 404 (71, M$^+$); ^{1}H NMR (C_6D_6) δ 4.77 (s, $C_6H_3Me_3$), 1.91 (s, $C_6H_3Me_3$), 3.74 (m, CH), 2.64 (m, =CH—), 1.07 (t, J_{HH} = 1.6 Hz, CH_2).

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Registry No. 1, 126724-08-1; 2, 126724-09-2; 3, 126724-10-5; 4, 123725-82-6; 5, 126724-11-6; 5-d_6, 126724-15-0; 6, 126724-13-8; 6-d_5, 126724-17-2; 7, 123725-77-9; 7-d_4, 123725-83-7; 8, 123725-75-7; 9, 126724-14-9; 10, 123725-76-8; 11, 109013-42-5; 12, 71652-17-0; 13, 126724-18-3; 14, 126724-19-4; 15, 126724-21-8; 16, 126724-23-0; 17, 123725-74-6; 18, 126724-24-1; 19, 126724-25-2; DMSO, 67-68-5; $OsCl_3$, 13444-93-4; [(mes)$OsCl_2$]$_2$, 94957-59-2; CO, 630-08-0; [CPh_3]PF_6, 437-17-2; 1,3,5-trimethylcyclohexa-1,4-diene, 4074-23-1; methylmagnesium iodide, 917-64-6; methyllithium, 917-54-4; ethylene, 74-85-1; norbornadiene, 121-46-0.

Dynamic Behavior and Rearrangements of Group 14 Organometallic Substituted Alkenylboranes

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Alkenylboranes 7 and 8 with a group 14 organometallic group ($R^2{}_3M$; M = Sn, Pb, R^2 = Me, Et, Ph) at the C=C double bond, in a cis position with respect to the boryl group, are obtained via organoboration of the corresponding alkynylstannanes (5) and -plumbanes (6) ($R^2{}_3M—C\equiv C—R^1$; R^1 = H, Me, ^{t}Bu, Ph) with trialkylboranes (R_3B, R = Et (**2a**), ^{i}Pr (**2b**)). Many of the lead compounds are thermally and photolytically unstable. The dialkylboryl group in 7 and 8 prefers the conformation 10, where the C_2B plane is perpendicular to the C=C—B plane as shown by dynamic ^{1}H and ^{13}C NMR spectra. In the alkene derivatives 7 and 8 cleavage of the =C—R bond occurs readily, re-forming the alkynylmetal compound (5, 6) and the trialkylboranes 2 (deorganoboration). Direct proof is given for this by two-dimensional ^{1}H/^{1}H exchange NMR spectra. The preferred structure 10 makes CB ($\sigma\pi$) interactions possible, weakening the =C—R bond, and together with a weak M—C= bond the organoboration becomes readily reversible. The structure 10 is also favorable for R^2/R exchange, which has been found to take place between lead and boron in 8, leading to alkenes 13 and 13′. Only one example for 8 has been found for cis/trans isomerization into 15. All products are characterized by their ^{11}B, ^{13}C, ^{119}Sn, and ^{207}Pb NMR data.

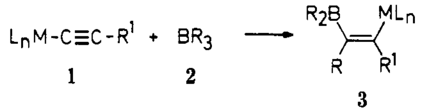
Introduction

Among the various reactive sites in alkynylmetal compounds (1)[1] the M—C≡C- fragment in particular offers great synthetic potential. Considering the polarity of that

$$L_nM-C\equiv C-R^1$$

1

fragment, an electrophile is likely to attack at either of the alkyne carbon atoms. The attack at the carbon atom adjacent to the metal may lead to cleavage of the M—C≡ bond, which is then followed by further reactions. We have found that triorganoboranes (2) react with various alkynylmetal compounds (M = Si,[2] Sn,[3] Pb,[4] Pt[5]) such that alkenes of type 3 are formed (eq 1). The metal fragment



(1)

$R^2{}_3M$ has migrated from one carbon atom to the other, and an organyl group (R) from boron together with the boryl group end up at the same carbon atom. In most cases these organoborations are quantitative and stereoselective (as shown). An intermediate (4) has been proposed[3] that

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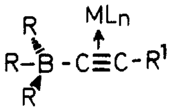


4

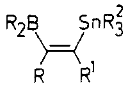
has a borate-like structure with the L_nM fragment side-on-coordinated to the C≡C triple bond. Recently this was confirmed by X-ray analysis for M = Pb.[4] Thus, the products **3** are formed in a way analogous to the reaction of alkynylborates with electrophiles,[6] e.g., trialkyltin chlorides.[7]

There is already some evidence that the reaction shown in eq 1 is reversible[8,9] (deorganoboration), although no direct relationship to the nature of the substituents on the C=C double bonds and their spatial arrangement has been established. Since the alkene derivatives **3** are attractive starting materials for organometallic synthesis, their structure in solution is of considerable interest. In this work we show that the preferred conformation of the boryl groups for the alkenes **7** (L_nM = R^2_3Sn) and **8** (L_nM = R^2_3Pb) is related to the chemical properties of these alkenes. The compounds **7**[3,10] and **8** are analogous to **3** and can be readily obtained (according to eq 1) by the reaction between the alkynylstannanes (**5**) and -plumbanes (**6**), respectively, with the triorganoboranes **2**. Owing to the weak and polar lead–carbon bonds, the alkenes **8** should be good models (stereochemistry comparable to that for L_nM = R^2_3Sn, R^2_3Si) for studying the deorganoboration and other possible rearrangements. Multinuclear magnetic resonance spectroscopy together with various two-dimensional (2D) NMR techniques has been used.

$R^2_3Sn{-}C{\equiv}C{-}R^1$ **5** $R^2_3Pb{-}C{\equiv}C{-}R^1$ **6** R_3B **2**

	a	b	c	d	e	f	g
R^2	Me	Me	Me	Me	Et	Et	Ph
R^1	H	Me	${}^tBu$	Ph	Me	${}^tBu$	Me

	a	b
R	Et	${}^iPr$



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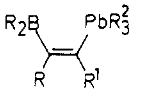


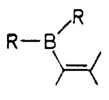
8

	a	b	c	d	e	f	g	h	i	j	k
R^2	Me	Me	Me	Me	Me	Me	Me	Et	Et	Ph	Ph
R^1	H	Me	Me	${}^tBu$	Ph	Ph	Me	Me	${}^tBu$	Me	Me
R	Et	Et	${}^iPr$	Et	Et	${}^iPr$	Et	${}^iPr$	Et	Et	${}^iPr$

Results and Discussion

The reactions between the alkynylmetal compounds **5** and **6** and the triorganoboranes **2** in hexane or toluene at low temperatures (between −78 and +25 °C) afford compounds **7** and **8** quantitatively. These are colorless, extremely air-sensitive, oily liquids or solids (**8j**, **8k**). The lead derivatives **8** with R = Et are much less stable to rearrangements and decomposition than **7**, and frequently their NMR spectroscopic characterization had to be carried out in solution at low temperature immediately after mixing the alkynylplumbane (**6**) and the triorganoborane (**2**) at −78 °C (e.g., for **8d,j**). The NMR data for the alkenes **7** and **8** are given in Table I, together with data for rearrangement products (**13**, **14**, **15**) and data from the literature for comparison.

Conformation of the Alkenylboranes 3, 7, and 8. For alkenyldiorganoboranes the two extreme conformations **9** and **10** can be considered. A structure close to that of **9** is stable if there is little steric hindrance, and BC (pp) π interactions may add to the stability. The structure **10** will be observed if bulky substituents are present on the C=C double bond and/or on the boron atom. This is the case for compounds **7** and **8** and, indeed, for all compounds **3**.[11]



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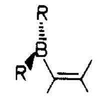

10

The alternative structures **9** and **10** in solution can be deduced from dynamic NMR measurements. In **9** the two groups R could be distinguished, whereas in **10** the two groups R are chemically equivalent. Of course, this equivalence could also result from fast rotation about the B—C= bond axis. Therefore, the organyl groups R must contain prochiral centers with groups that become diastereotopic[12] if structure **10** is preferred. This condition would be fulfilled with R = Et (BCH_2 protons) or R = ${}^iPr$ (methyl groups of the B^iPr_2 group). The ^1H NMR spectrum for the BEt_2 unit should show the pattern for an A_2M_3 spin system if fast rotation about the B—C= axis takes place or the pattern for an ABM_3 spin system for structure **10** in the case of slow rotation (see Figure 1 for **3** with L_nM = Me_3Si, R^1= Me, R = Et). In the case of R = ${}^iPr$ the ^1H (Me) und ^{13}C (Me) resonances for the B^iPr_2 group will be split into two doublets and two singlets, respectively, for structure **10** (see Figure 2 for **8f**). The ΔG^* values (e.g., 57.7 ± 2 kJ/mol for **8f**, 63.7 ± 2 kJ/mol for **7f**) are on the same order of magnitude as found for another alkene derivative of type **3** (L_nM = Me_2EtSn, R^1 = Me, R = Et, R_2B = $Et(C_4H_4N)B$; ΔG^* = 58.1 ± 1 kJ/mol[12d]). Thus, structure **9** can be ruled out, since it would require the nonequivalence of all ^1H and ^{13}C resonance signals for BEt_2 and B^iPr_2 groups, which has not been observed (see Figures 1 and 2).

Reversible Formation of the Alkenylboranes 3, 7, and 8. The deorganoboration of **7** and **8** requires the smooth cleavage of a carbon–carbon bond (=C—R). This calls for experimental evidence as well as for a mechanistic explanation. Thus far this deorganoboration has served to explain the rearrangement from kinetically controlled products to the thermodynamically stable products[13] and the formation of various products such as allenes[8a–c] and 3-borolenes.[8d] In the latter cases the compounds of type **3** react further with alkynylmetal compounds, which are thought to stem from the partial deorganoboration of **3**. It would be more conclusive to find direct evidence for the exchange between **7** or **8** and an excess of either the re-

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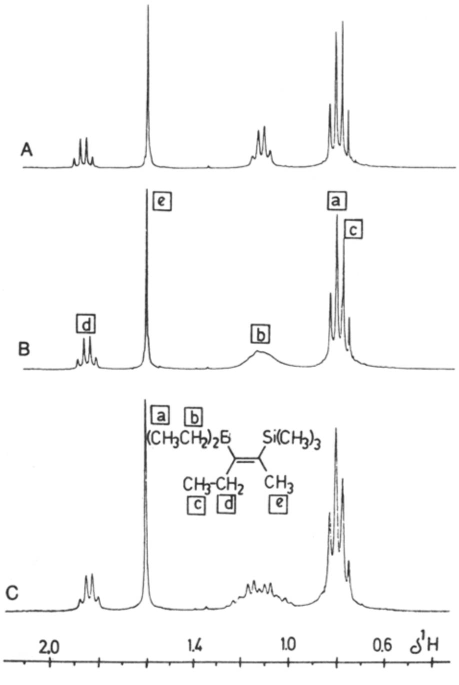

Figure 1. Part of the 300-MHz ^1H NMR spectra of (*E*)-2-(trimethylsilyl)-3-(diethylboryl)-2-pentene (**3**, $L_nM = Me_3Si$, R^1 = Me, R = Et; the ^1H $SiMe_3$ resonance is not shown) at various temperatures: (A) −20 °C, corresponding to the spectrum at 25 °C (the rotation of the Et_2B group about the =C—B bond is fast, and the ^1H BEt resonance shows the pattern for an A_2M_3 spin system); (B) −45 °C (the rotation of the Et_2B group about multiplet is observed, indicating coalescence); (C) −70 °C (the pattern of an ABM_3 spin system has emerged, which upon $^1H\{^1H\}$ decoupling yields the coupling constant $^2J(^1H^1H) = 18 \pm 0.3$ Hz; with use of the value $^2J(^1H^1H) = 18.0$ Hz and the shift difference $\Delta(^1H) = 20.9$ Hz, $\Delta G^*(-45\ ^\circ C) = 46.5 \pm 2$ kJ/mol for the barrier to rotation of the Et_2B group about the =C—B bond can be evaluated[28]). The quality of analogous spectra for **7b** ($L_nM = Me_3Sn$) and **8b** ($L_nM = Me_3Pb$) is poor, owing to smaller shift differences $\Delta(^1H)$ and broadening of all ^1H resonances at low temperature (<−70 °C).

spective alkynylmetal compound or the trialkylborane **2**. The former exchange reaction is not particularly suitable, as it may involve the formation of other products. An excess of **2** does not seem to affect the NMR spectra of the organoboration products **7** and **8**. Since many of these alkene derivatives are thermally unstable (uncontrolled decomposition), an increase of the exchange rate by heating the samples cannot be achieved. One alternative is an extension of the NMR time scale for the observation of slower processes by application of magnetization transfer experiments[14] (nuclear magnetization of R should be found for **2** and for **7** and **8**). The nuclei for this experiment must be either ^{13}C or ^1H, since the relaxation rate of the ^{11}B nuclei is dominated by efficient quadrupolar interactions. In the case of ^{13}C NMR we are dealing with simple spectra, but there is the inherent problem of low sensitivity. With ^1H NMR we encounter rather complex ^1H NMR spectra for R = Et (the compounds with R = Me are too unstable). Therefore, we turned again to R = ^iPr and used 2D exchange spectra[15] (preferable to 1D experiments because the relevant ^1H resonances (^iPr methyl groups) are found in a close range). A typical result is shown for **8h** in Figure

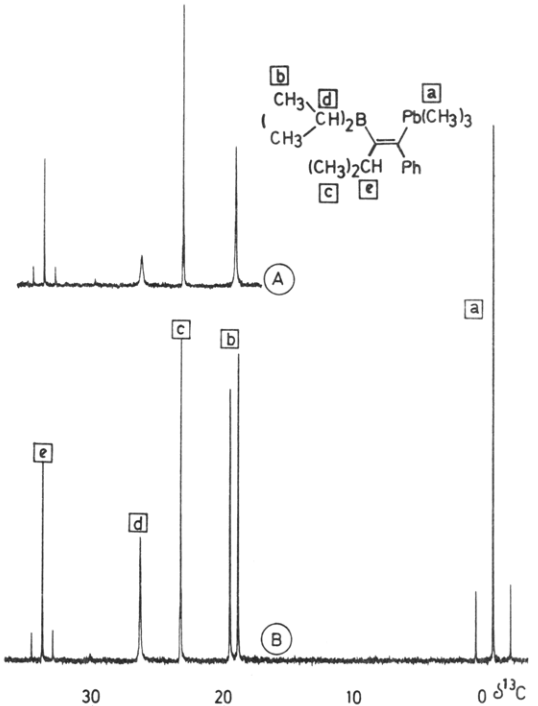

Figure 2. 75.5-MHz $^{13}C\{^1H\}$ NMR spectra at various temperatures for **8f** in CD_2Cl_2 (the region for olefinic carbon is not shown): (A) spectrum at 25 °C, showing a single slightly broadened ^{13}C Me resonance for the B^iPr_2 group (note also the ^{207}Pb satellites for other ^{13}C resonances and the broadened (partially relaxed scalar coupling $^1J(^{13}C^{11}B)$ ^{13}C BCH resonance); (B) spectrum at −20 °C (there are now two ^{13}C Me resonances for the B^iPr_2 group, but there is still a single ^{13}C BCH resonance in agreement with the conformation of the boryl group in structure **10**; from $\Delta(^{13}C)$ (37.9 Hz) $\Delta G^* = 57.7 \pm 2$ kJ/mol (at 5 °C, coalescence) can be evaluated[28] for the barrier to rotation about the =C—B bond (for the corresponding tin compound **7f** $\Delta G^* = 63.7 \pm 2$ kJ/mol has been determined)).

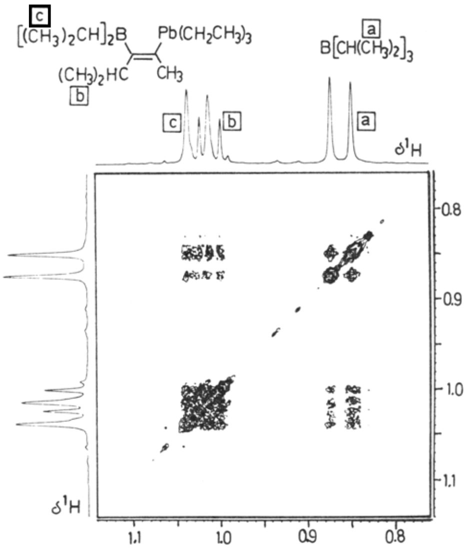

Figure 3. Two-dimensional (2D) $^1H/^1H$ exchange 300-MHz NMR spectrum[15] for a mixture of the alkene **8h** and triisopropylborane (**2b**) (the same experiment also works for **7f** or **8f** and **2b**). The ^1H Me resonances of ^iPr groups are shown, and the cross peaks in the contour plot are characteristic for exchange. The pulse sequence was $\pi/2-t_1-\pi/4-t_m-\pi/4-t_2$; the mixing time $\tau_m = 0.5$ s was used.

3, and similar spectra were obtained for tin compounds such as **7c** in the presence of an excess of B^iPr_3. The cross peaks between the ^1H (Me) resonances support the proposed exchange between ^iPr groups in **7** or **8** and in B^iPr_3

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Table I. ^{13}C, ^{119}Sn, and ^{207}Pb NMR Data[a,b] for the Alkene Derivatives 3, 7, 8, 13, 14, and 15

	compd			δ(^{13}C)						
no.	L$_n$M	R^1	R	M—C=	B—C=	L$_n$M	R$_2$B	=C—R^1	=C—R	δ(M)
7a	Me$_3$Sn	H	Et	125.0 [503.0]	172.0 [br]	−8.4 [336.5]	21.8, 9.0 [br]	*c*	32.8, 13.5 [94.0, 10.6]	−55.2
8a	Me$_3$Pb	H	Et	130.7 [434.1]	170.6 [br]	−2.1 [244.7]	21.7, 9.0 [br]	*d*	33.0, 13.6 [152.1, 9.0]	−101.7
7b	Me$_3$Sn	Me	Et	133.6 [540.0]	163.2[e] [br]	−8.6 [317.9]	22.0, 9.1 [br]	19.8 [80.1]	23.2, 13.5 [83.9, 18.0]	−48.4
8b	Me$_3$Pb	Me	Et	140.9 [534.6]	160.8[e] [br]	−1.5 [194.0]	22.1, 9.2 [br]	22.3 [129.7]	24.0, 14.2 [141.7, 15.8]	−65.6
3	Me$_3$Si	Me	Et[f]	130.4 [70.9]	161.7	−0.8	21.3, 9.5	15.4	22.5, 12.9	−6.0 (^{29}Si)
7c	Me$_3$Sn	Me	^{i}Pr	131.2 [536.4]	165.0 [br]	−8.6 [317.1]	26.2, 19.7 [br]	20.9 [63.8]	31.1, 22.5 [87.2, 6.6]	−54.2
8c	Me$_3$Pb	Me	^{i}Pr	137.8 [545.0]	162.6 [br]	−1.3 [184.7]	26.2, 19.6 [br]	23.4 [130.8]	31.6, 22.8 [150.4, 11.0]	−76.5
7d	Me$_3$Sn	^{t}Bu	Et	150.0 [545.0]	162.6 [br]	−3.5 [307.4]	22.3, 9.5 [br]	40.3, 33.4 [59.4, 25.6]	25.5, 14.3 [107.4, 12.0]	−54.6
8d	Me$_3$Pb	^{t}Bu	Et[g]	157.0 [574.3]	159.6 [br]	3.5 [158.0]	22.4, 9.7 [br]	42.3, 33.7 [109.0, 48.0]	26.8, 14.8 [194.5, 18.5]	−92.8
7e	Me$_3$Sn	Ph	Et	141.8 [486.1]	163.7 [br]	−8.0 [328.1]	22.6, 9.3 [br]	146.4[h] [42.0]	25.8, 14.5 [70.3, 10.5]	−49.1
8e	Me$_3$Pb	Ph	Et	147.2 [436.0]	161.5 [br]	−0.2 [207.1]	22.5, 9.2 [br]	147.0[i] [83.4]	26.5, 14.7 [115.5, 13.1]	−65.3
7f	Me$_3$Sn	Ph	^{i}Pr[j]	140.0 [481.7]	165.9 [br]	−8.3 [328.1]	26.8, 19.6 [br]	147.3[k] [38.7]	33.3, 23.4 [74.7, 7.0]	−53.5
8f	Me$_3$Pb	Ph	^{i}Pr[l]	144.9 [438.7]	163.0 [br]	−0.2 [198.9]	26.6, 19.5 [br]	147.6[m] [81.2]	33.9, 23.5 [122.1, 8.7]	−76.9
7g	Et$_3$Sn	Me	Et	133.2 [462.0]	163.5 [br]	1.5[n] [321.0]	21.6, 8.8 [br]	20.4 [56.2]	22.9, 13.6 [75.0, 9.9]	−41.3
8g	Et$_3$Pb	Me	Et	143.5 [329.2]	161.5 [br]	12.9[o] [195.6]	22.0, 9.1 [br]	23.1 [104.1]	24.2, 14.4 [116.6, 14.1]	−2.1
8h	Et$_3$Pb	Me	^{i}Pr	141.2 [339.5]	162.3[p] [br]	13.0[q] [186.9]	26.3, 19.3 [br]	24.2 [105.2]	32.0, 22.7 [123.7, 9.3]	−15.6
8i	Et$_3$Pb	^{t}Bu	Et	159.9 [359.1]	160.3 [br]	16.6[r] [164.0]	22.1, 9.4 [br]	41.4, 33.6 [94.8, 39.3]	26.9, 14.5 [160.7, 15.3]	−3.7
8j	Ph$_3$Pb	Me	Et[s]	140.9 [640.0]	165.3 [br]	155.7[t] [338.0]	22.1, 9.0 [br]	23.3 [136.6]	24.6, 14.2 [171.0, 17.0]	−204.8[u]
8k	Ph$_3$Pb	Me	^{i}Pr	141.3 [630.0]	167.3[v] [123.2]	153.0[w] [324.2]	26.6, 19.4 [br]	24.6 [133.0]	32.7, 22.7 [176.6, 12.0]	−182.7
13b	Me$_2$EtPb	Me	Et	144.1 [435.0]	162.7 [br]	−1.9 (Me) [148.6] 13.5[x] [231.3]		23.0 [119.7]	24.2, 14.6 [129.3, 16.1]	−32.7
13d	Me$_2$EtPb	^{t}Bu	Et Me	160.3 [493.2]	161.8 [br]	2.6 (Me) [112.8] 17.7[y] [261.0]	24.3, 10.0 [br] 14.5 (Me) [br]	42.0, 33.5 [103.0, 45.8]	27.1, 15.3 [176.0, 17.4]	−48.3
13d′	MeEt$_2$Pb	^{t}Bu	Et Me	162.7 [415.8]	163.1 [br]	1.9 (Me) [73.0] 17.5[z] [213.6]	16.9 (Me) [br]	41.6, 33.4 [97.5, 42.5]	27.4, 15.3 [161.9, 16.3]	−18.2
14b	Me$_3$Sn	Me	Et	132.7 [493.5]	163.6 [br]	−8.3 [320.1]	22.9, 8.7 [br]	24.1 [70.8]	31.2, 15.0 [70.8, 9.8]	−55.6
15i	Et$_3$Pb	Bu	Et	164.4 [296.5]	153.1 [br]	15.7[aa] [175.5]	21.3, 10.3 [br]	40.4, 31.9 [96.5, 31.6]	31.4, 14.9 [130.8, 15.0]	−8.9

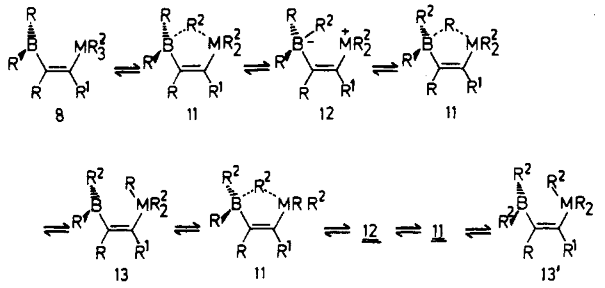
[a] Solutions (5–15%) in C_6D_6 or C_7D_8 in 5-mm (o.d.) tubes, measured at 27–28 °C, if not noted otherwise; data from the literature for **3**,[2b] **7a**, **7b**, and **14b**,[21a] and **7e**.[20a] [b] $\delta(^{13}C)$ values are given with respect to Me_4Si ($\delta(^{13}C)_{C_6D_6} = 128.0$, $\delta(^{13}C)_{C_6D_5CD_3} = 20.4$, $\delta(^{13}C)_{CD_2Cl_2} = 53.8$); $\delta(^{29}Si)$, $\delta(^{119}Sn)$, and $\delta(^{207}Pb)$ values are relative to external Me_4M, with use of the absolute frequencies $\Xi(^{29}Si) = 19\,867\,184$ Hz, $\Xi(^{119}Sn) = 37\,290\,665$ Hz, and $\Xi(^{207}Pb) = 20\,920\,597$ Hz. Coupling constants $^nJ(M^{13}C)$ (Hz) are given in brackets, and br denotes the broad ^{13}C resonances of carbon atoms linked to boron (partially relaxed scalar coupling $^1J(^{13}C^{11}B)$). [c] $^2J(^{119}Sn^1H) = 91.6$ Hz; $^1J(=^{13}C^1H) = 138.0$ Hz. [d] $^2J(^{207}Pb^1H) = 225.4$ Hz; $^1J(=^{13}C^1H) = 134.9$ Hz. [e] $^2J(^{119}Sn^{13}C) = 68.1$ Hz; $^2J(^{207}Pb^{13}C) = 117.0$ Hz (both at −50 °C in CD_2Cl_2). [f] Data from ref 2b. [g] In CD_2Cl_2 at −15 °C. [h] $\delta(^{13}C)$ for other phenyl carbon atoms: 127.4 [17.5] (o), 128.5 [8.0] (m), 125.0 [10.3] (p). [i] $\delta(^{13}C)$ for other phenyl carbon atoms: 128.4 [15.3] (o), 127.4 [31.6] (m), 125.2 [19.6] (p). [j] In CD_2Cl_2; barrier to rotation about the B—C= bond with $\Delta G^*(10\ °C) = 63.7 \pm 2$ kJ/mol, as determined from the coalescence of the B^iPr_2 Me resonances in the ^{13}C NMR spectrum (see also Figure 2 for **8f**). [k] $\delta(^{13}C)$ for other phenyl carbon atoms: 128.1 [17.4] (o), 128.3 [7.6] (m), 124.9 [10.3] (p). [l] In CD_2Cl_2; barrier to rotation about the B—C=bond with $\Delta G^*(5\ °C) = 57.7 \pm 2$ kJ/mol, as determined from the coalescence of the B^iPr_2 Me resonances in the ^{13}C NMR spectrum (see Figure 2). [m] $\delta(^{13}C)$ for other phenyl carbon atoms: 128.2 [15.3] (o), 127.5 [32.7] (m), 125.1 [22.9] (p). [n] $\delta(^{13}C)_{SnCH_2CH_3}$: 11.0 [23.1]. [o] $\delta(^{13}C)_{PbCH_2CH_3}$: 13.9 [30.0]. [p] $^2J(^{207}Pb^{13}C=) \approx 85 \pm 3$ Hz. [q] $\delta(^{13}C)_{PbCH_2CH_3}$: 14.0 [30.5]. [r] $\delta(^{13}C)_{PbCH_2CH_3}$: 13.6 [28.3]. [s] In CD_2Cl_2 at −30 °C. [t] $\delta(^{13}C)$ for other Pb–phenyl carbon atoms: 138.1 [62.5] (o), 129.2 [68.9] (m), 128.6 [16.2] (p). [u] At room temperature **8j** decomposes rapidly into a mixture of various products, including **13j** ($\delta(^{207}Pb)$ − 177.0) and **13j′** ($\delta(^{207}Pb)$ − 127.5). [v] Broadened ^{13}C resonance; owing to the large molecular weight efficient "quadrupolar decoupling" of the ^{11}B nuclei takes place. [w] $\delta(^{13}C)$ for other Pb–phenyl carbon atoms: 138.1 [61.1] (o), 129.2 [68.7] (m), 128.4 [15.2] (p). [x] $\delta(^{13}C)_{PbCH_2CH_3}$: 13.9 [31.5]. [y] $\delta(^{13}C)_{PbCH_2CH_3}$: 13.8 [31.1]. [z] $\delta(^{13}C)_{PbCH_2CH_3}$: 13.6 [28.3]. [aa] $\delta(^{13}C)_{PbCH_2CH_3}$: 14.0 [30.5].

(**2b**) and, therefore, prove that the organoboration (eq 1) is readily reversible. Since the methyl groups belong to different molecules, NOE and *J* coupling cannot be responsible for the cross peaks, leaving the exchange as the only explanation.

A further alternative to check on the reversibility of the organoboration is provided by crossover experiments. ^{1}H, ^{13}C, and ^{207}Pb NMR spectra of reaction solutions show that the treatment of **8c** (R = ^{i}Pr) with **2a** (R = Et) gives a mixture of **8b** and **8c** after several days.

We propose that the preferred structure **10** is an important prerequisite for the deorganoboration (eq 1). That particular conformation of the boryl group allows maximum interaction between the formally empty boron p$_z$

Scheme I. Intramolecular R^2/R Exchange between the Metal and the Three-Coordinate Boron Atom[a]



[a] For M = Pb, the products 13 and 13′, can be characterized by ^1H, ^{13}C, and ^{207}Pb NMR spectra (see Figure 4) in mixtures (see Table I) with the corresponding compounds 8.

orbital and the σ orbital of the =C—R bond. This causes a weakening of that bond, leading finally to re-formation of the alkynylmetal compound and the triorganoboranes via the intermediate 4. MO calculations, on the basis of the geometry of 10, support these arguments.[16] Clearly, the strength of the M—C= bond is important as well: for $L_nM = Me_3Si$ and R = Et the alkenes of type 3 have to be heated up to >140 °C to induce partial deorganoboration.[9] On the other hand, the organoboration of alkynylsilanes requires rather severe reaction conditions and is never complete under these conditions.[2] This can be explained by considering the equilibrium in eq 1.

Exchange of Groups R^2 and R between Tin, Lead, and Boron in 7 and 8. If one substituent R^2 in 7 and 8 functions as a Lewis base (e.g., $R^2 = NEt_2$,[17] OR[18]), the intramolecular coordination to the boron atom is well established. If one substituent R^2 is an alkynyl group (R^2 = C≡C—R^1), spectroscopic (M = Sn,[19] Pb[4]) and direct structural proof (M = Pb[4]) has been obtained that the alkynyl group is transferred from the metal to the boron atom, leading to an alkynylborate structure (such as 4) before further reactions take place.

For organyl groups R^2 = alkyl, phenyl as in 7 and 8, intermediates with tetracoordinate boron (11) are not sufficiently stable for NMR spectroscopic detection. However, there is indirect proof for bridging of the type M—R^2—B or M—R—B (11) if products such as 13 (Scheme I) can be characterized by NMR spectroscopy. Again the lead compounds 8 should be potential candidates for this objective, owing to the rather weak Pb-C bonds. R^2/R exchange in compounds of type 7 has been observed only when there were basic sites in R^1 that would stabilize a cationic metal fragment (e.g., in 12).[20] One decomposition pathway of the lead compounds leads to trialkylboranes BR_2R^2 and BRR^2_2, together with lead, Me_4Pb, and the alkyne R—C≡C—R^1. This suggests that the zwitterionic structure 12 not only serves to explain the exchange mechanism but also represents a conceivable intermediate prior to decomposition.

The rate of the R^2/R exchange is not noticeably affected by concentration, which strongly supports the intramolecular mechanism (vide infra for the influence of R^1). The first step in the R^2/R exchange involves electrophilic attack of the three-coordinate boron atom at the M—R^2 bond. Therefore, the preference of structure 10 is also important for this reaction. If the three-coordinate boron atom is sterically shielded (e.g., R = ^{i}Pr)), R^2/R exchange is very slow or does not take place at all. For R^2 = Ph, the R^2/R exchange is much faster than for R^2 = alkyl, and it is accompanied by extensive decomposition (8j). Furthermore, the substituent R^1 in 8 exerts considerable influence on the rate of R^2/R exchange. It is observed that the Me/Et exchange is accelerated (~1 min at 25 °C; see Figure 4) for R^1 = ^{t}Bu (8d) (eq 2) with respect to that for

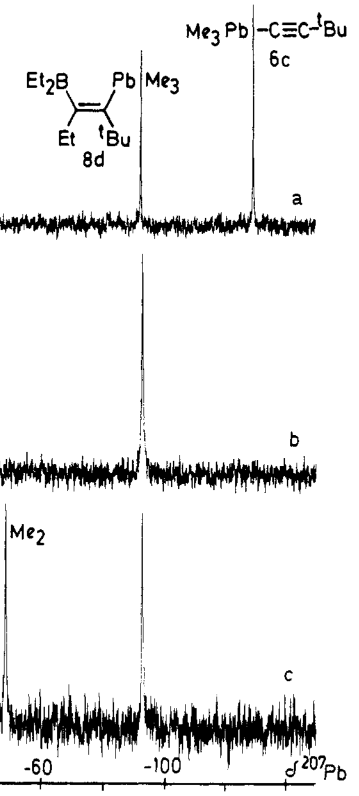
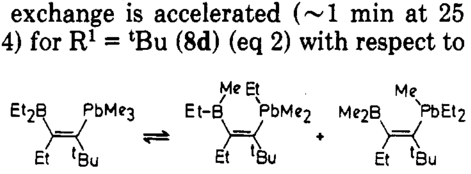


Figure 4. 62.8-MHz $^{207}Pb\{^1H\}$ NMR spectra for monitoring the formation of 8d and its rearrangement into 13d and 13d′: (a) spectrum taken at −50 °C, after mixing 6c and 2a at −78 °C in CD_2Cl_2, showing that 6c is still present; (b) spectrum taken after 10 min at −15 °C, showing that 6c is fully consumed and 8d is the only product; (c) spectrum taken at −15 °C immediately after warming the sample to 25 °C for 60 s, now showing a mixture of 8d, 13d, and 13d′ (note that the line widths of the ^{207}Pb resonances are very similar, as expected for an unchanged stereochemistry at the C=C double bond). If the mixture is left at 25 °C for 1 h, 8d is no longer detectable and 13d and 13d′ (ratio ~2:1) are the main products, together with a growing number of further unidentified products due to decomposition.



8d **13d** **13d′** (2)

R^1 = Me (8b) (several days!). It is conceivable that a more bulky substituent R^1 (which would kinetically stabilize 8 against intermolecular exchange processes) pushes the Me_3Pb group closer to the boryl group, where the boron atom—according to structure 10—is ready to attack one of the Pb—C bonds. For R^2 = Me and R = Et the R^2/R exchange leads to compounds 13 and 13′ with one and two *B*-methyl groups, respectively. These alkenes tend to be very unstable for M = Sn and, in particular, for M = Pb. Thus, many irreversible decomposition reactions of 8 follow

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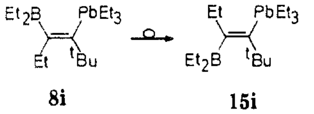
the reversible R^2/R exchange.

Cis/Trans Rearrangement of the Tin and Lead Derivatives 7 and 8. By UV irradiation or prolonged exposure to daylight, many tin compounds **7** isomerize to the derivatives **14** with the stannyl and the boryl groups in a trans position.[19] This has not been observed for the lead compounds **8**, which tend to undergo intramolecular exchange reactions (vide supra) and/or decompose in an uncontrolled manner. Even the fairly stable compound **8b** does not prefer cis/trans rearrangement to exchange and decomposition. However, in the case of **8i** ($R^1 = {}^tBu$ and $R = R^2 = Et$) cis/trans isomerization to **15i** (eq 3) does take place. Since $R = R^2$, the R^2/R exchange does not afford a new, less stable product (as in the case for $R^2 = Me$) that eventually decomposes and by this affects the equilibrium. On the other hand, the bulky substituents on the C=C double bond will favor deorganoboration. If the trans isomer **15i** is the thermodynamically stable product, it will eventually be formed via a large number of organoboration and deorganoboration steps.



8i **15i** (3)

NMR Parameters: Chemical Shifts and Coupling Constants. All $\delta(^{13}C)$ values for the alkenes (Table I) are found in the expected range. The ^{13}C resonances for the olefinic carbon atoms show the usual substituent-induced shifts exerted by R^1 and R, in addition to the effects of the organometallic substituents. Together with the conformational analysis for the boryl group (vide supra) the constancy of the $\delta(^{13}C)_{M-C=}$ and $\delta(^{13}C)_{B-C=}$ values (if corrected for other substituent effects) strongly suggests that all alkenes listed in Table I prefer structure **10** as far as the boryl group is concerned.

The $\delta(^{119}Sn)$ values cover a range of <20 ppm, whereas the range of the $\delta(^{207}Pb)$ values is ~100 ppm. The greater sensitivity of the ^{207}Pb nuclear shielding is expected, considering the ratio of the radial expansion terms $\langle r^{-3}\rangle_{6p}/\langle r^{-3}\rangle_{5p}$, which is >3 if relativistic corrections for the ^{207}Pb nucleus[22] are taken into account. However, the direction of substituent (R^2, R^1, R) induced changes of the $\delta(^{119}Sn)$ and $\delta(^{207}Pb)$ values is the same. The presence of the boryl group on the C=C double bond does not affect the δ(M) values in a particular way, as shown by comparison with δ(M) data for other alkenylstannanes[23] and -plumbanes.[24] Similarly, the δ(M) values are not particularly indicative of the boryl group in a position cis or trans to the $R^2{}_3M$ group (see **7b, 14b; 8i, 15i**), in strong contrast to the line width of the ^{119}Sn or ^{207}Pb resonances (vide infra).

Relationships between coupling constants $^1J(^{119}Sn^{13}C)$ and $^1J(^{207}Pb^{13}C)$ where the carbon atom is sp^3 or sp^2 hybridized have been discussed in detail,[25] and the trend for the data reported in this work is fully in agreement with that already reported. The usual pattern of the $|^3J(M^{13}C)|$ values across the C=C double bond is observed:[26] $|^3J(M^{13}C)|_{cis} < |^3J(M^{13}C)|_{trans}$ (see **7b, 14b; 8i, 15i**). This observation is very helpful for the discussion of the line width of the ^{119}Sn and ^{207}Pb resonances of **7, 8, 13, 14**, and **15**. The increase in the line width of the M resonances as a result of scalar relaxation of the second kind[27] is a function of the quadrupolar relaxation rate of the ^{11}B nucleus and the magnitude of the scalar coupling $|^3J(M^{11}B)|$. For **7** and **14** it has been shown that the sharper lines are always connected with a mutual cis position of stannyl and boryl groups.[21a] Accordingly, we find a fairly sharp ^{207}Pb resonance for **8i** ($h_{1/2} = 45$ Hz) and a much broader line for the trans isomer **15i** ($h_{1/2} = 85$ Hz). Therefore, it holds that $|^3J(^{207}Pb^{11}B)|_{cis} < |^3J(^{207}Pb^{11}B)|_{trans}$. The ^{207}Pb NMR spectrum of the mixture of **8d** with the rearrangement products **13d** and **13d′** (Figure 4) shows the same line width for the three ^{207}Pb resonances, indicating that the orginal cis arrangement of plumbyl and boryl groups is retained.

Experimental Section

The triorganoboranes **2** (**2a**,[30] **2b**[31]) and the alkynylstannanes (**5**[1b,32]) and -plumbanes (**6**[1b,33]) were prepared by following literature procedures. All reactions were carried out in pure, dry solvents under an N_2 atmosphere. Examples for many of the alkene derivatives **7** have been fully described previously.[3,10] The corresponding lead compounds **8** were prepared in the same way. Owing to their limited thermal stability they could not be stored (lead is deposited even at −20 °C after a few minutes) in solution or as pure compounds. Therefore, NMR spectra had to be measured immediately after the synthesis of **8**. Only **8b** could be distilled at 20 °C/10^{-4} Torr. All the other compounds **8, 13, 13′**, and **15** decomposed on attempted distillation into many products, one of which is the alkyne $R-C\equiv C-R^1$.

NMR spectra (see also Table I and Figures 1–4 for details) have been recorded by using a JEOL FX90Q and Bruker AC 200 and AC 300 spectrometers, all equipped with a multinuclear unit. ^{13}C NMR spectra have been assigned by using conventional techniques (*J* modulation, 2D $^{13}C/^1H$ shift correlations[34]). ^{119}Sn NMR spectra have been recorded with use of inverse gated decoupling (for suppression of the NOE, for quantitative information[23a]) or by the refocused INEPT pulse sequence.[35] At $B_0 = 7.05$ T the ^{207}Pb relaxation rate ($T_1(^{207}Pb)$) is rather fast, owing to significant contributions from chemical anisotropy relaxation.[24a,36] Therefore, the 62.5-MHz ^{207}Pb NMR spectra can be obtained within a short time (minutes) even for diluted solutions, with use of ca. 45–60° pulses and a short repetition time (ca. 0.3 s) (see Figure 4).

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