

## $\alpha$ -METALLATED VINYL CARBANIONOIDS

### III \* . REACTIONS OF $\alpha$ -TRIORGANOSTANNYLVINYL LITHIUMS WITH GROUP IVB ORGANOMETALLIC HALIDES: FORMATION OF $\alpha$ -TRIMETHYLPLUMBYLVINYL LITHIUMS

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#### Summary

Reactions of  $\alpha$ -stannylvinyl lithiums  $RR'C=C(Li)SnMe_3$  with halides  $Me_3MCl$  ( $M = Si, Ge, Pb$ ) give the corresponding mixed bis(trimethylmetal)alkenes  $RR'C=C(SnMe_3)MMe_3$ . With two equivalents of methyl lithium and trimethyllead chloride,  $RR'C=C(SnMe_3)_2$  can be converted to  $RR'C=C(PbMe_3)_2$ . The latter, as well as  $RR'C=C(SnMe_3)PbMe_3$ , undergoes transmetallation with methyl lithium to give  $\alpha$ -plumbylvinyl lithiums  $RR'C=C(Li)PbMe_3$ , which are more stable and apparently less basic than the corresponding  $\alpha$ -stannyl anions.

Multinuclear NMR data for the anionic species are presented and discussed.

#### Introduction

While reactions of organotin-substituted vinyl lithiums  $RR'C=C(Li)SnMe_3$  with various electrophiles ( $D_2O$ ,  $Me_2SO_4$ , aldehydes, ketones) have already been investigated [1], reactions with "organometallic" electrophiles had (with the exception of two reactions of trimethylchlorosilane) not been carried out prior to this study. We thus felt it useful to react these organolithiums with halides  $Me_3MCl$  ( $M = Si, Ge, Pb$ ): such reactions should yield reagents with some synthetic potential, since the products  $RR'C=C(SnMe_3)MMe_3$  contain two organometallic residues with differing reactivities which can thus be replaced sequentially by organic groups. The products obtained from reactions of  $RR'C=C(Li)SnMe_3$  with  $Me_3PbCl$  are, as shown below, precursors for stable  $\alpha$ -trimethylplumbylvinyl lithiums  $RR'C=C(Li)PbMe_3$ .

\* For part II see ref. 3.

## Results and discussion

### 1. Replacement of lithium by germanium, tin or lead

Since the hydrostannylation of 1-trimethylsilyl-1-alkynes  $\text{RC}\equiv\text{CSiMe}_3$  is apparently much less regioselective than that of the corresponding stannylalkynes, we have previously prepared  $\text{RCH}=\text{C}(\text{SiMe}_3)\text{SnMe}_3$  ( $\text{R} = \text{Ph}, t\text{-Bu}$ ) by treating  $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$  with  $\text{Me}_3\text{SiCl}$  in THF [2].

The corresponding organolithiums of the type  $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$ , which are more readily formed and more stable [3], react more slowly with  $\text{Me}_3\text{SiCl}$  in THF, so that the side reaction of  $\text{Me}_3\text{SiCl}$  with methyllithium becomes important. This problem can be readily solved by replacing THF by dimethoxyethane. However, THF can be used in cases where the anion exhibits intramolecular chelation [3].

The regioselectivity of this transmetallation reaction apparently varies according to the alkyl groups attached to tin: thus while  $\text{PhCH}=\text{C}(\text{SnMe}_3)_2$  gives only (*E*)- $\text{PhCH}=\text{C}(\text{SiMe}_3)\text{SnMe}_3$  on lithiation/silylation, a temperature-dependent regioselectivity is observed for the reaction of  $\text{PhCH}=\text{C}(\text{SnBu}_3)_2$ . Lithiation of the latter at  $-78^\circ\text{C}$  followed by reaction with  $\text{Me}_3\text{SiCl}$  at that temperature gives a product with an *E/Z* ratio of 91/9, while the ratio when  $\text{Me}_3\text{SiCl}$  is added at room temperature is 8/92.

Several examples of reactions of  $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$  with  $\text{Me}_3\text{GeCl}$  have also been carried out successfully; details of reactions of  $\text{Me}_3\text{SiCl}$  and  $\text{Me}_3\text{GeCl}$  are given in Table 1.

Extension of these reactions to include  $\text{Me}_3\text{PbCl}$  was then investigated: somewhat to our surprise, we found that the products  $\text{RR}'\text{C}=\text{C}(\text{SnMe}_3)\text{PbMe}_3$  are distillable in vacuum without appreciable decomposition. As can be seen from Table 2, the *E/Z* ratios of the products vary widely, however.

A further unexpected observation was that the reaction of non-intramolecularly chelated anionoids requires the use of DME as solvent: if this is not used, large amounts of 1,1-diplumbyl-1-alkenes are produced in addition to the required product. This in turn requires the formation of  $\text{RR}'\text{C}=\text{C}(\text{Li})\text{PbMe}_3$  as a relatively stable species, a point to which we shall return below.

TABLE 1

ISOLATED YIELDS, BOILING POINTS AND ISOMER COMPOSITION FOR COMPOUNDS  $\text{RR}'\text{C}=\text{C}(\text{SnMe}_3)\text{MMe}_3$  ( $\text{M} = \text{Si}, \text{Ge}$ ) PREPARED FROM  $\text{RR}'\text{C}=\text{C}(\text{SnMe}_3)_2$

R	R'	M	Solvent <sup>b</sup>	Yield (%)	B.p. ( $^\circ\text{C}/\text{mmHg}$ ) <sup>f</sup>
Me	Me	Si	DME	46	105/12
Me	Me	Ge	THF	34	110/12
EtOCH <sub>2</sub>	Me	Si	THF	48 <sup>c</sup>	69/0.01
MeOCH <sub>2</sub>	MeOCH <sub>2</sub>	Si	THF	71	66/0.05
MeOCH <sub>2</sub>	MeOCH <sub>2</sub>	Ge	THF	67	71/0.003
Ph	Ph	Si	DME	73	(103) <sup>g</sup>
Ph	Ph	Ge	THF	85	(110) <sup>g</sup>
Ph	H	Ge	THF	65 <sup>d</sup>	87/0.04
MeO(C <sub>6</sub> H <sub>10</sub> ) <sup>a</sup>	H	Si	THF	68 <sup>e</sup>	89/0.08

<sup>a</sup> (1-Methoxy)-1-cyclohexyl. <sup>b</sup> DME = dimethoxyethane, THF = tetrahydrofuran. <sup>c</sup>  $\geq 95\%$  *E*. <sup>d</sup> 74% *E*. <sup>e</sup>  $\geq 95\%$  *E*. <sup>f</sup> Values in brackets are melting points. <sup>g</sup> After recrystallisation from hexane.

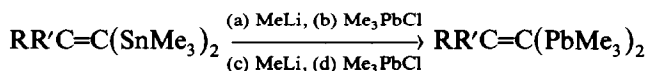
TABLE 2

ISOLATED YIELDS, BOILING POINTS AND ISOMER COMPOSITION FOR COMPOUNDS  $RR'C=C(SnMe_3)PbMe_3$  PREPARED FROM  $RR'C=C(SnMe_3)_2$ 

R	R'	Solvent	Yield (%)	B.p. (°C/mmHg)	E (%) <sup>d</sup>
H	H	DME	72	50/1	
n-Bu	H	DME	b	<sup>b</sup>	43
t-Bu	H	DME	66	71/0.08	13
MeO(C <sub>6</sub> H <sub>10</sub> ) <sup>a</sup>	H	THF	71	125/0.02	80
Ph	H	DME	58	106/0.05	16
Me	Me	DME	59	76/1.1	
EtOCH <sub>2</sub>	Me	THF	56	100/0.01	16
MeOCH <sub>2</sub> CH <sub>2</sub>	Me	THF	48	85/0.05	17
MeOCH <sub>2</sub>	MeOCH <sub>2</sub>	THF	67	105/0.01	
Ph	Me	DME	b	<sup>b</sup>	80
Ph	CF <sub>3</sub>	DME	b	<sup>b</sup>	≥ 95
Ph	Ph	DME	51	(124) <sup>c</sup>	

<sup>a</sup> (1-Methoxy)-1-cyclohexyl. <sup>b</sup> Not determined, product impure. <sup>c</sup> Melting point. <sup>d</sup> From proton NMR.

We next attempted to prepare 1,1-diplumbyl-1-alkenes directly by a double transmetallation:



We were indeed able to obtain these products in moderate to good (isolated) yields as colourless, high-boiling liquids ( $RR' = Ph_2$ , solid): for details see Table 3. They decompose on standing under the influence of light, and should be stored in a refrigerator.

TABLE 3

ISOLATED YIELDS AND BOILING POINTS FOR DIPLUMBYLALKENES OF THE TYPE  $RR'C=C(PbMe_3)_2$ 

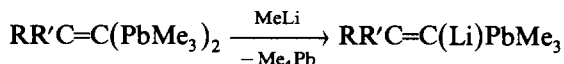
R	R'	Yield (%)	B.p. (°C/mmHg)
H	H	47	53–60/0.16
Me	H	41	58–62/0.01
n-Bu	H	52	92–100/0.005
c-Hex	H	55	123–130/0.02
t-Bu	H	38	78–81/0.005
Me <sub>2</sub> NCH <sub>2</sub>	H	37	95/0.005
MeO(c-C <sub>6</sub> H <sub>10</sub> ) <sup>a</sup>	H	65	135–143/0.02
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub>	H	60	85–90/0.005
Ph	H	64	130–150/0.005
Me	Me	41	95–105/0.05
EtOCH <sub>2</sub>	Me	42	106/0.005
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub>	Me	53	103/0.02
Ph	Me	40	160/0.01
Ph	CF <sub>3</sub>	< 10	<sup>b</sup>
Ph	Ph	73	(130) <sup>c</sup>
CH <sub>3</sub> OCH <sub>2</sub>	CH <sub>3</sub> OCH <sub>2</sub>	46	116–125/0.005

<sup>a</sup> (1-Methoxy)-1-cyclohexyl. <sup>b</sup> Not determined, product highly impure. <sup>c</sup> M.p. (after recrystallisation from hexane).

## 2. Formation of $\alpha$ -plumbylvinylolithiums

Not only the exchange of lithium for tin, but also that for lead is a process which has been known for many years [4]; recent examples have been provided by Kauffmann [5,6].

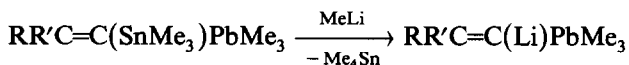
We thus studied the reaction:



Diethyl ether is not a suitable solvent, but THF can be used successfully: as can be seen from Table 4, the main product observed is generally the *E*-isomer.

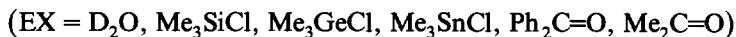
The  $\alpha$ -plumbylvinylolithiums are clearly thermally more stable than the corresponding stannyl compounds; some examples of their reactions will be given below.

The lithiodemetallation of stannylplumbylalkenes  $\text{RR}'\text{C}=\text{C}(\text{SnMe}_3)\text{PbMe}_3$  can in principle proceed with the replacement of tin or lead by lithium: in fact only the  $\alpha$ -plumbylvinylolithiums are observed as products of this reaction, reflecting at least in part their high thermal stability.



## 3. Reactions of $\alpha$ -plumbylvinylolithiums

While no detailed study of the reactions of  $\alpha$ -plumbylvinylolithiums has as yet been carried out, preliminary investigations of reactions with various electrophiles have been made:



Details are given in Table 5. Perhaps the most significant result is the following: the reaction of (*E*)- $\text{PhCH}=\text{C}(\text{Li})\text{PbMe}_3$  with acetone gives (after hydrolysis) 53% of the allylic alcohol (*E*)- $\text{PhCH}=\text{C}(\text{PbMe}_3)\text{CMe}_2\text{OH}$  and 47% (*E*)-trimethylstyryllead. The corresponding organotin reagent gives only (*E*)-trimethylstyryltin, the product of acetone enolisation; thus the lead reagent appears to be less basic than the tin reagent.

TABLE 4

ISOMERIC COMPOSITION (from  $^1\text{H}$  NMR at room temperature) OF  $\alpha$ -PLUMBYLVINYLLITHIUMS OF THE TYPE  $\text{RR}'\text{C}=\text{C}(\text{Li})\text{PbMe}_3$

R	R'	<i>E</i> -isomer (%)
n-Bu	H	39
c-Hex	H	53
t-Bu	H	≥ 95
Ph	H	≥ 95
$\text{Me}_2\text{NCH}_2$	H	≥ 95
$\text{MeO}(c\text{-C}_6\text{H}_{10})$	H	≥ 95
$\text{Me}_3\text{OCH}_2\text{CH}_2$	H	≥ 95
Ph	Me	77
$\text{EtOCH}_2$	Me	≥ 95

TABLE 5

PRODUCTS OF REACTIONS OF  $\alpha$ -PLUMBYLVINYLLITHIUMS  $RR'C=C(Li)PbMe_3$  WITH ELECTROPHILES EX

R	R'	EX	Isolated yield (%)	B.p. ( $^{\circ}C/mmHg$ )	E-Isomer (%) <sup>d</sup>
n-Bu	H	D <sub>2</sub> O	52	90-100/12	40
c-Hex	H	D <sub>2</sub> O	42	60/0.02	52
t-Bu	H	D <sub>2</sub> O	61	69-72/12	$\geq 95$
Me <sub>2</sub> NCH <sub>2</sub>	H	D <sub>2</sub> O	64	90/12	$\geq 95$
MeO(C <sub>6</sub> H <sub>10</sub> ) <sup>a</sup>	H	D <sub>2</sub> O	58	90-95/0.08	$\geq 95$
MeOCH <sub>2</sub> CH <sub>2</sub>	H	D <sub>2</sub> O	b	<sup>b</sup>	$\geq 95$
Ph	H	D <sub>2</sub> O	60	70/0.03	$\geq 95$
Me	Me	H <sub>2</sub> O	64	60/12	
H	H	Me <sub>3</sub> SiCl	61	75/0.65	
H	H	Me <sub>3</sub> GeCl	60	52/2.2	
MeOCH <sub>2</sub>	MeOCH <sub>2</sub>	Me <sub>3</sub> SiCl	56	60/0.01	
MeOCH <sub>2</sub>	MeOCH <sub>2</sub>	Me <sub>3</sub> GeCl	66	103/0.02	
Ph	Ph	Me <sub>3</sub> SiCl	82	(95) <sup>c</sup>	
Ph	Ph	Me <sub>3</sub> GeCl	84	(111) <sup>c</sup>	
Ph	H	Ph <sub>2</sub> C=O	56	(67) <sup>c</sup>	$\geq 95$
Ph	H	Me <sub>2</sub> C=O	53	<sup>b</sup>	$\geq 95$

<sup>a</sup> (1-Methoxy)-1-cyclohexyl. <sup>b</sup> Not determined, product impure. <sup>c</sup> Melting point. <sup>d</sup> From proton NMR.

#### 4. NMR investigations

(a) *1,1-Bis(trimethylmetal)-1-alkenes*. Full multinuclear NMR data for the new 1,1-bis(trimethylmetal)alkenes have been recorded, but only those <sup>1</sup>H and <sup>13</sup>C data relevant for structure determination are presented here (Table 6); the remaining data will be reported and discussed in a forthcoming paper.

In the case of compounds  $RCH=C(MMe_3)M'Me_3$  the geometry is indicated by the value of <sup>3</sup>J(M', H) (M' = Sn, Pb) observed for the vinylic proton. In compounds  $RR'C=C(MMe_3)M'Me_3$ , however, the geometry must be determined from the values of the three-bond coupling between M' and the " $\alpha$ -carbons" of the groups R and R'. In both cases the difference between the *cis* and *trans* couplings is sufficient to permit clear stereochemical assignments.

(b)  *$\alpha$ -Plumbylvinyl anionoids*. Multinuclear NMR studies (<sup>207</sup>Pb, <sup>13</sup>C, <sup>1</sup>H) for this new class of reagent have also been carried out; the results can be found in Tables 7-10. The lead chemical shifts (Table 7) cover a wide range (ca. 150 ppm) and appear at a first glance to show no clear trends. However, in 13 cases the <sup>119</sup>Sn chemical shifts for the corresponding  $\alpha$ -stannylvinyl anionoids have been recorded [3], and a regression analysis affords the following relation between the lead and tin shifts:

$$\delta(Pb) = 2.98 \delta(Sn) + 155.6, \quad |r| = 0.956$$

This corresponds quite well with the more general expression [7] previously obtained for lead and tin shifts, which is:

$$\delta(Pb) = 2.42 \delta(Sn) + 74.8 \quad (35 \text{ values})$$

The signal linewidths at room temperature vary between 5 and 50 Hz.

Tables 8 and 9 contain <sup>13</sup>C data. In contrast to the  $\alpha$ -stannylvinylolithiums, where the extreme width (often > 100 Hz) of the signal for C(1) (the vinyl carbon bonded

(Continued on p. 158)

TABLE 6  
STRUCTURE-RELEVANT PROTON AND  $^{13}\text{C}$  NMR DATA FOR COMPOUNDS OF THE TYPE  $\text{RR}'\text{C}=\text{C}(\text{MMe}_3)\text{M}'\text{Me}_3$  ( $\text{M} = \text{Si, Ge, Pb}$ ;  $\text{M}' = \text{Sn, Pb}$ ) ( $\delta$  in ppm vs. TMS,  $J$  in Hz)

M	M'	R	R'	E/Z	$\delta(\text{=CH})$	$^3J(\text{M}', \text{H})$		$^3J(\text{M}', \text{C})$		
						cis <sup>e</sup>	trans <sup>e</sup>	cis <sup>f</sup>	trans <sup>f</sup>	
Si	Sn	Me	Me					74.9	90.6	
		EtOCH <sub>2</sub>	Me	E				71.2	99.0	
		MeOCH <sub>2</sub>	MeOCH <sub>2</sub>					57.2	94.1	
	Pb	Ph	Ph					51.8	85.1	
		MeOC <sub>6</sub> H <sub>10</sub> <sup>b</sup>	H	E	6.5	137			87.7	
		Ph	H <sup>c</sup>	E	7.6	112			90.6	
Si	Pb	Ph	H <sup>c</sup>	Z	7.8		175	<sup>g</sup>		
		H	H		6.2, 6.7 <sup>d</sup>	230	374			
	Ge	MeOCH <sub>2</sub>	MeOCH <sub>2</sub>						117.1	148.1
		Ph	Ph						90.6	136.9
Ge	Sn	Me	Me					70.3	88.8	
		MeOCH <sub>2</sub>	MeOCH <sub>2</sub>					90.3	120.8	
	Pb	Ph	Ph	E	7.3	114		49.9	82.3	
		Ph	H	Z	7.3		182	51.4	98.5	
Ge	Pb	H	H		6.2, 6.5 <sup>d</sup>	215	364	111.0	144.3	
		MeOCH <sub>2</sub>	Ph					85.2	133.5	

Pb	Sn	H	H	6.4,6.6 <sup>d</sup>	110 (236)	198 (390)		
	t-Bu	H	H	6.7	(237)	212	<sup>g</sup>	<sup>g</sup>
	t-Bu	H	H	6.9	116	(438)		87.7 (154.4)
	MeOC <sub>6</sub> H <sub>10</sub> <sup>b</sup>	H	H	6.6	(244)	201	38.8	<sup>g</sup>
	MeOC <sub>6</sub> H <sub>10</sub> <sup>b</sup>	H	H	6.7	107	(407)	<sup>g</sup>	<sup>g</sup>
Pb	Sn	Ph	H	7.8	(222)	184	<sup>g</sup>	<sup>g</sup>
	Ph	H	H	8.0	102	(343)		<sup>g</sup>
	Me	Me						91.0(164.6)
	EtOCH <sub>2</sub>	Me	Z					94.2(157.9)
	MeOCH <sub>2</sub> CH <sub>2</sub>	Me	Z					83.1(161.1)
	Ph	Me	E					85.1(161.3)
	Ph	Ph						87.7(143.7)
	MeOCH <sub>2</sub>	MeOCH <sub>2</sub>						91.6(150.0)
Pb	Pb <sup>a</sup>	H	H	6.4	224	384		
	Me	H	H	6.8	202	355	138.7	175.7
	n-Bu	H	H	6.6	204	368	127.8	162.9
	c-Hex	H	H	6.3	204	360	122.1	154.9
	t-Bu	H	H	6.9	245	416	70.8	156.3
	Me <sub>2</sub> NCH <sub>2</sub>	H	H	6.8	207	363	127.6	170.2
	MeOC <sub>6</sub> H <sub>10</sub> <sup>a</sup>	H	H	6.7	223	385	71.9	149.3
	MeOCH <sub>2</sub> CH <sub>2</sub>	H	H	6.6	204	354	125.8	161.4
	Ph	H	H	7.9	204	339	91.6	170.3
	Me	Me						91.0
	MeOCH <sub>2</sub>	MeOCH <sub>2</sub>						50.9
	Ph	Ph						48.3

<sup>a</sup> No distinction made between M and M' in the following compounds. <sup>b</sup> (1-Methoxy)-1-cyclohexyl. <sup>c</sup> Tributylstannyl compound. <sup>d</sup> <sup>2</sup>J(H, H) 3 Hz. <sup>e</sup> Values in brackets are for <sup>3</sup>J(M, H). <sup>f</sup> Values in brackets are for <sup>3</sup>J(M, C). <sup>g</sup> Not determined.

TABLE 7

<sup>207</sup>Pb CHEMICAL SHIFTS (in ppm vs. internal Me<sub>4</sub>Pb) FOR α-PLUMBYLVINYLLITHIUMS OF THE TYPE RR'C=C(Li)PbMe<sub>3</sub> (Solvent THF, concentration ca. 2 mol/l.)

R	R'	δ(PbMe <sub>3</sub> )	
		E	Z
H	H		-14.9
n-Bu	H	-0.6	-118.8
t-Bu	H	33.9	<sup>b</sup>
Me <sub>2</sub> NCH <sub>2</sub>	H	13.5	<sup>b</sup>
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub>	H	15.1	<sup>b</sup>
MeO(c-C <sub>6</sub> H <sub>10</sub> ) <sup>a</sup>	H	27.5	<sup>b</sup>
Ph	H	26.5	<sup>b</sup>
Me <sup>c</sup>	Me		-102.1
EtOCH <sub>2</sub>	Me	-95.3	<sup>b</sup>
Ph	Ph		-83.3
CH <sub>3</sub> OCH <sub>2</sub>	CH <sub>3</sub> OCH <sub>2</sub>		-100.3
Ph	Me	-100.3	-89.9

<sup>a</sup> (1-Methoxy)-1-cyclohexyl. <sup>b</sup> Not observed.

to tin) prevented the determination of <sup>1</sup>J(Sn-C<sub>vin</sub>), this signal in the lead species is relatively sharp (linewidth 4–10 Hz): the values of <sup>1</sup>J(Pb, C) determined (in some cases an insufficient signal-to-noise ratio precluded determinations) lie between 850 and 1030 Hz, while those of the coupling to the second vinyl carbon lie between 205 and 260 Hz.

For compounds RCH=C(Li)PbMe<sub>3</sub>, the values of <sup>3</sup>J(Pb, C) and <sup>3</sup>J(Pb, H) can be used in combination to determine whether the *E*- or *Z*-isomer is present: however, as can be seen from Table 8, <sup>3</sup>J<sub>cis</sub>(Pb, C) and <sup>3</sup>J<sub>trans</sub>(Pb, C) can be of almost equal magnitudes (see the third and sixth entries). The data in Table 9 confirm that <sup>3</sup>J<sub>trans</sub> is abnormally low when intramolecular chelation of lithium by oxygen is present

TABLE 8

<sup>13</sup>C NMR DATA (δ in ppm vs. (CD<sub>3</sub>)<sub>2</sub>C=O 207 ppm, <sup>n</sup>J(<sup>207</sup>Pb, <sup>13</sup>C) (in brackets) in Hz) FOR α-PLUMBYLVINYLLITHIUMS OF THE TYPE RCH=C(Li)PbMe<sub>3</sub>

R	E/Z	δ(PbMe <sub>3</sub> )	δ(C(1))	δ(C(2))	δ(C(3))	δ(C(4))	δ(C(5))	δ(C(6))
H	-	-2.1 (250.0)	217.3 (918.4)	139.1 (264.5)				
n-Bu	<i>E</i>	-2.0 (276.1)	198.9 ( <sup>b</sup> )	153.9 ( <sup>b</sup> )	43.1 (653.9)	34.1 (21.8)	23.6 (10.2)	14.9
n-Bu	<i>Z</i>	-0.6 (225.6)	199.9 (970.0)	151.5 (251.4)	45.7 (476.7)	33.2 (27.6)	23.3	14.7
t-Bu	<i>E</i>	-1.1 (261.0)	<sup>b</sup>	<sup>b</sup>	38.9 (525.2)	31.1 (16.9)		
Me <sub>2</sub> NCH <sub>2</sub>	<i>E</i>	-1.4 (168.7)	209.1 ( <sup>b</sup> )	149.1 (205.6)	68.1 (559.0)	46.5		
MeO(c-C <sub>6</sub> H <sub>10</sub> ) <sup>a</sup>	<i>E</i>	-2.3 (177.6)	205.8 ( <sup>b</sup> )	152.0 (219.2)	82.3 (485.5)	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>
Ph	<i>E</i>	-1.8 (276.1)	225.3 (987.5)	150.1 (212.2)	147.4 (606.0)	126.1 (12.4)	127.9 (9.5)	124.4

<sup>a</sup> (1-Methoxy)-1-cyclohexyl. <sup>b</sup> Not observed. <sup>c</sup> Not assigned because of line overlap.



TABLE 9  
 $^{13}\text{C}$  NMR DATA ( $\delta$  in ppm vs. external  $(\text{CD}_3)_2\text{C}=\text{O}$  207 ppm,  $^2J(^{207}\text{Pb}, ^{13}\text{C})$  (in brackets) in Hz) FOR  $\alpha$ -PLUMBYLVINYLLITHIUMS OF THE TYPE  $\text{RR}'\text{C}=\text{C}(\text{L})\text{PbMe}_3$  (Solvent THF, Vinylithium concentration ca. 2 mol/l.)

R	R'	E/Z	$\delta(\text{PbMe}_3)$	$\delta(\text{C}(1))$	$\delta(\text{C}(2))$	$\delta(\text{C}(3))$	$\delta(\text{C}(3'))$	$\delta(\text{C}(4))$	$\delta(\text{C}(4'))$	$\delta(\text{C}(5))$	$\delta(\text{C}(5'))$
Me	Me		-0.4 (333.9)	197.2 (1030.4)	146.6 (258.5)	31.6 (689.3)	33.4 (472.1)				
EtOCH <sub>2</sub>	Me	E	-1.2 (204.6)	197.8 (847.3)	145.7 (215.4)	80.8 (477.5)	28.7 (445.2)	67.0		15.7	
CH <sub>3</sub> OCH <sub>2</sub>	CH <sub>3</sub> OCH <sub>2</sub>		-1.1 (175.8)	208.3 (856.0)	146.0 (216.5)	81.2 (462.1)	83.5 (454.9)	58.7 <sup>c</sup>	56.4 <sup>c</sup>		
Ph	Ph		0.2 (234.3)	227.8 (953.7)	159.7 (211.8)	150.1 (531.4)	152.5 (363.5)	128.1 <sup>c</sup>	127.4 <sup>c</sup>	129.9 <sup>a,c</sup>	128.9 <sup>b,c</sup>
Ph	Me	E	-0.3 (299.6)	216.1	153.4	151.8 (567.3)	32.3 (467.4)	127.3		127.5 <sup>d</sup>	

<sup>a</sup>  $\delta(\text{C}(6))$  124.8. <sup>b</sup>  $\delta(\text{C}(6'))$  124.7. <sup>c</sup> Assignment uncertain. <sup>d</sup>  $\delta(\text{C}(6))$  124.3 ppm.

TABLE 10

<sup>1</sup>H NMR DATA ( $\delta$  in ppm vs. TMS,  $^2J(^{207}\text{Pb}, ^1\text{H})$  in Hz) FOR  $\alpha$ -PLUMBYLVINYLLITHIUMS OF THE TYPE  $\text{RR}'\text{C}=\text{C}(\text{Li})\text{PbMe}_3$  (Solvent THF, vinyl lithium concentration ca. 0.5–1 mol/l.)

R	R'	E/Z	$\delta(\text{PbMe}_3)$	$^2J(\text{PbCH})$	$\delta(=\text{CH})$	$^3J_{\text{cis}}(\text{Pb,H})$	$^3J_{\text{trans}}(\text{Pb,H})$
H	H		-0.5	5	5.9,6.1	888	1228
n-Bu	H	E	-0.5	11	6.2	738	
n-Bu	H	Z	-0.3	10	6.5		1092
c-Hex	H	E	-0.4	8	5.9	768	
c-Hex	H	Z	-0.5	8	6.2		1130
t-Bu	H	E	-0.5	5	6.2	806	
Ph	H	E	-0.3	10	7.2	762	
Me <sub>2</sub> NCH <sub>2</sub>	H	E	-0.4	18	6.5	680	
MeO(C <sub>6</sub> H <sub>10</sub> ) <sup>a</sup>	H	E	-0.3	18	6.5	686	
MeOCH <sub>2</sub> CH <sub>2</sub>	H	E	-0.4	16	6.5	678	
Me	Me		-0.4	5			
Ph	Me	E	-0.3	8			
Ph	Me	Z	-0.6	b			
EtOCH <sub>2</sub>	Me	E	-0.3	16			
MeOCH <sub>2</sub>	MeOCH <sub>2</sub>		-0.4	18			
Ph	Ph		-0.6	13			

<sup>a</sup> (1-Methoxy)-1-cyclohexyl. <sup>b</sup> Not observed.

(see the second and third entries). Chelation is also accompanied by a decrease in the (presumably positive [8]) value of  $^1J(\text{Pb}-\text{CH}_3)$  and (Table 10) an increase in the numerical value of the (presumably negative [9]) coupling  $^2J(\text{Pb}-\text{CH}_3)$  (i.e. a decrease in the absolute value). The carbon chemical shifts are comparable to those of the corresponding tin species [3]. Table 10 contains only those <sup>1</sup>H data which provide direct evidence on the structure of the vinyl lithium species.

## Experimental

All manipulations involving organotin or organolithium compounds were carried out under argon. Starting materials were prepared as described previously [2,3]. All new compounds isolated (see Tables) were fully characterised by multinuclear NMR spectroscopy and gave satisfactory elemental analysis values. NMR spectra were recorded using Varian EM-360 (proton) and Bruker AM-300 (<sup>13</sup>C, <sup>29</sup>Si, <sup>119</sup>Sn, <sup>207</sup>Pb) spectrometers.

### Preparation of compounds $\text{RR}'\text{C}=\text{C}(\text{SnMe}_3)\text{MMe}_3$ ( $M = \text{Si}, \text{Ge}, \text{Pb}$ )

(a) *General procedure for M = Si, Ge.* Equimolar amounts (ca. 0.01 mol) of solutions of 1,1-distannyl-1-alkene and methyl lithium in the required solvent (ca. 5 and 20 ml respectively) (see Table 1) are mixed at  $-78^\circ\text{C}$  and stirred at that temperature for 1–2 h. An equimolar amount of  $\text{Me}_3\text{MCl}$  is then added dropwise with stirring. After a further hour the reaction mixture is allowed to warm to room temperature, water is added, the organic phase separated and dried, and the solvent removed. The crude liquid products are distilled in vacuo, solids are recrystallised from n-hexane.

(b) *General procedure for M = Pb.* The cold solution of the vinyl lithium reagent (ca. 0.01 mol) prepared as described above is transferred using a pipette to a flask

containing an equimolar amount of  $\text{Me}_3\text{PbCl}$  dissolved in ca. 20 ml of the same solvent (see Table 2) and cooled to  $-78^\circ\text{C}$ . The reaction mixture is stirred for 1 h, allowed to warm to room temperature and worked up as described under a).

(c) *Reaction for  $R,R' = \text{Me}$  and THF as solvent.*  $\text{Me}_3\text{PbCl}$  in THF is added dropwise to the vinylolithium reagent in THF at  $-78^\circ\text{C}$ , prepared as under (a). The mixture is stirred for 1 h, allowed to warm to room temperature, and worked up as described under (a).

The  $^{119}\text{Sn}$  NMR spectrum shows the presence of approximately equimolar amounts of distannylalkene, diplumbylalkene and stannylplumbylalkene.

#### *Preparation of compounds $\text{RR}'\text{C}=\text{C}(\text{PbMe}_3)_2$*

*General procedure.* An equimolar amount of 1,1-distannyl-1-alkene (ca. 0.01 mol) is added dropwise to a solution of methyllithium in THF (ca. 20 ml) at  $-78^\circ\text{C}$ . After stirring for 1 h, an equimolar amount of a solution of  $\text{Me}_3\text{PbCl}$  in THF (ca. 20 ml) is added dropwise. After 30 min the mixture is warmed rapidly to room temperature, cooled to  $-78^\circ\text{C}$  and treated with 1 equivalent of methyllithium solution followed by 1 equivalent  $\text{Me}_3\text{PbCl}$ . After a further 30 min this procedure is repeated with 0.3 equivalents each of methyllithium and  $\text{Me}_3\text{PbCl}$ . Workup is carried out as described above. For details of products see Table 3.

#### *Preparation of $\alpha$ -plumbylvinylolithiums*

To a solution of methyllithium in THF, precooled to  $-78^\circ\text{C}$ , is added an equimolar amount of either  $\text{RR}'\text{C}=\text{C}(\text{SnMe}_3)\text{PbMe}_3$  or  $\text{RR}'\text{C}=\text{C}(\text{PbMe}_3)_2$ ; the solution so obtained is subjected after 1 h to a proton NMR analysis (see Table 4).

#### *Reactions of $\alpha$ -plumbylvinylolithiums with electrophiles*

Solutions of  $\alpha$ -plumbylvinylolithiums in THF are treated at  $-78^\circ\text{C}$  with the relevant electrophile: in the case of  $\text{D}_2\text{O}$  two molar equivalents are used, in other cases one equivalent. Work-up is carried out as described above. For details of products see Table 5.

#### **Acknowledgement**

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