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Tri(*tert*-butyl) plumbyl derivatives of Group 14 elements Multinuclear magnetic resonance studies: determination of coupling signs [1]

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Abstract

A solution of tri(*tert*-butyl)plumbyl-lithium in THF (**2**) was prepared by the reaction of hexa(*tert*-butyl)diplumbane (**1**) with an excess of lithium. Treatment of this reagent with a variety of Group 14 electrophiles gave tetraorganolead compounds $^{t}Bu_3Pb{-}R$ (**3**, R = Me (**a**), Et (**b**), ^{n}Pr (**c**), ^{n}Bu (**d**), CH_2Ph (**e**), CH_2SiMe_3 (**f**)), plumbylsilanes $^{t}Bu_3Pb{-}SiR^1_2R^2$ (**4**, $R^1 = R^2 = Me$ (**a**), $R^1 = Me$, $R^2 = {}^{t}Bu$ (**b**), $R^1 = Me$, $R^2 = SiMe_3$ (**c**), $R^1 = Me$, $R^2 = Ph$ (**d**), $R^1 = R^2 = Ph$ (**e**)), one plumbylgermane $^{t}Bu_3Pb{-}GeMe_3$ (**5a**), plumbylstannanes $^{t}Bu_3Pb{-}SnR^3_3$ (**6**, $R^3 = Me$ (**a**), Et (**b**), ^{n}Bu (**c**), ^{t}Bu (**d**), Ph (**e**), 1,1′-ferrocenediyl (**f**)), and hexaorganodiplumbanes $^{t}Bu_3Pb{-}PbR^4_3$ (**7**, $R^4 = Me$ (**a**), Et (**b**), ^{i}Pr (**c**), ^{n}Hex (**d**), ^{c}Hex (**e**)], $^{i}Pr_3Pb{-}PbEt_3$ (**10**) and $^{t}Bu_2(Me)Pb{-}Pb(Me)^{t}Bu_2$ (**11**) as a side product. The plumbylstannanes $Et_3Pb{-}SnMe_3$ (**9a**) and $^{i}Pr_3Pb{-}SnMe_3$ (**9b**) were prepared for comparison of NMR data. All compounds were characterized by ^{1}H, ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb NMR data. Signs of coupling constants $^{n}J(^{207}Pb,^{13}C)$ ($n = 1, 2$), $^{1}J(^{207}Pb,^{29}Si)$, $^{1}J(^{207}Pb,^{119}Sn)$ and $^{1}J(^{207}Pb,^{207}Pb)$ were determined by appropriate 1D heteronuclear double resonance experiments and 2D heteronuclear shift correlations. The influence of the $^{t}Bu_3Pb$ group on the bonding situation is reflected by sign changes of several coupling constants when compared with analogous trimethyllead derivatives. © 1997 Published by Elsevier Science S.A.

Keywords: Silicon; Germanium; Tin; Lead; Multinuclear NMR; Coupling constant sign determination

1. Introduction

Organometallic compounds containing element–element bonds of Group 14 elements are of NMR spectroscopic interest, in particular for combinations involving the spin-1/2 nuclei ^{13}C, ^{29}Si, $^{117/119}Sn$ and ^{207}Pb. The NMR parameters (chemical shifts and coupling constants) of the heavier nuclei are attractive since they should sensitively reflect changes in the nature of element–element bonds. In contrast to the well known tetraorganolead compounds [1], only few examples of triorganoplumbyl-silanes [2,3], -germanes [4] and -stannanes [5,6] have been reported. Although numerous hexaorganodiplumbanes are known [7–9], derivatives containing two different triorganoplumbyl groups are rare [10]. It can be expected that bulky substituents at the lead atom help to stabilize compounds with lead–element bonds which otherwise tend to decompose readily. Among other substituents, *tert*-butyl groups can serve this purpose, and they have the advantage of NMR spectroscopic simplicity. In this paper, we report on the synthesis and NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si, ^{119}Sn, ^{207}Pb) of the tri(*tert*-butyl)plumbyl derivatives **3**–**7** of Group 14 elements, and of some similar compounds which were prepared for comparison.

2. Results and discussion

2.1. Syntheses

Hexa(*tert*-butyl)diplumbane (**1**) [11] was used as the starting material to generate tri(*tert*-butyl)plumbyl-lithium (**2**) in tetrahydrofuran (THF) according to Eq. (1). Attempts at the isolation of **2** led to decomposition, but the formation of **2** between −40 and −30 °C could be monitored in solution by ^{207}Pb NMR spectroscopy,

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[1] Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

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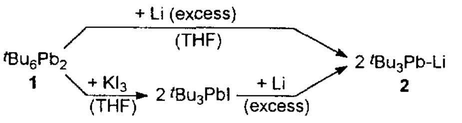
and these freshly prepared THF solutions were used for further reactions.



(1)

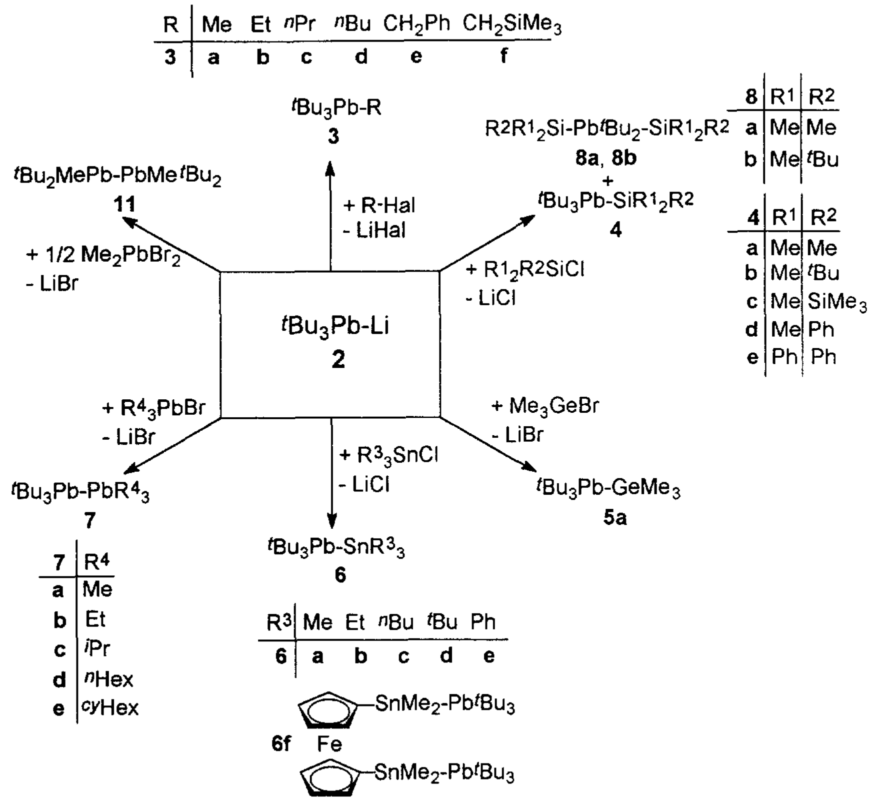
The results of the reaction of tri(*tert*-butyl)plumbyllithium in THF with various element halides are summarized in Scheme 1. Many of the compounds were isolated in the pure state, but several could not be obtained without impurities, some of which are unknown (e.g. **3c**, **4d**; **4a** and **4b** together with **8a** and **8b**; **6c** and **6d** as mixtures with **1** and Et_6Sn_2 or $^tBu_6Sn_2$). The compounds are colourless or yellowish oils or solids. They all decompose either on melting or, in general, by heating above room temperature up to 100 °C. They can be stored for a prolonged period of time in the refrigerator (−28 °C) in the dark. The C_6D_6 solutions of compounds **3**–**8** are stable in diffuse daylight at room temperature for several hours before slow decomposition to a variety of unknown compounds takes place.

Two other plumbylstannanes (**9a**,**9b**) and the

Table 1
^{13}C and ^{207}Pb NMR data [a] of tri(*tert*-butyl)organo-plumbanes **3a**–**f**

No.	$\delta^{207}Pb$	$\delta^{13}C$			
		$PbC(CH_3)_3$	$PbC(CH_3)_3$	R	
3a	101.1	48.4	33.4	−2.0 (C_1)	
		[+224.6]	[+10.4]	[104.4]	
3b	40.1	47.1	33.6	15.6 (C_1)	14.7 (C_2)
		[+190.2]	[+8.2]	[21.7]	[24.1]
3c	41.1	47.0	33.6	23.9 (C_1)	25.9 (C_2)
		[+191.3]	[+8.7]	[20.7]	[33.8]
				21.0 (C_3)	
				[64.3]	
3d	41.5	47.0	33.6	22.7 (C_1)	32.6 (C_2)
		[+191.0]	[+9.2]	[34.0]	[22.0]
				29.4 (C_3)	13.9 (C_4)
				61.4	[< 2]
3e	7.9	51.1	33.4	30.2 (CH_2)	146.0 (C_i)
		[+164.2]	[+9.2]	[132.5]	[35.9]
				128.8 (C_o)	128.2 (C_m)
				[17.1]	[15.3]
				123.1 (C_p)	
				[18.3]	
3f [b]	124.5	47.8	33.1	5.0 (CH_2)	
		[+202.7]	[+11.4]	[204.4]	

[a] In C_6D_6 (ca. 5–15%) at 25 ± 1 °C; coupling constants $^nJ(^{207}Pb,^{13}C)$ in brackets.
[b] $^tBu_3Pb{-}CH_2SiMe_3$: $\delta^{29}Si = 3.3$; $^2J(^{207}Pb^{29}Si) = +39.1$; $\delta^{13}C(SiMe_3) = 3.2$ [9.8].



Scheme 1.

diplumbane **10** were prepared, as shown in Eqs. (2) and (3) respectively, in order to collect NMR data for comparison.

$$R_3Pb{-}Li + Me_3SnCl \xrightarrow[(THF)]{-LiCl} R_3Pb{-}SnMe_3 \qquad (2)$$

9a: R = Et
9b: R = ^{i}Pr

$$Et_3Pb{-}Li + {}^{i}Pr_3PbBr \xrightarrow[(THF)]{-LiCl} Et_3Pb{-}Pb^{i}Pr_3 \qquad (3)$$

10

2.2. NMR spectroscopic results

The NMR data sets are fully in accord with the proposed structures. The ^{13}C and ^{207}Pb NMR data, together with ^{29}Si or ^{119}Sn NMR data are listed in Table 1 ($^{t}Bu_3Pb{-}R^1$ **3**, R^1 = organyl), Table 2 plumbylstannanes **4**, **8** and $^{t}Bu_3Pb{-}GeMe_3$ **5a**,), Table 3 plumbylstannanes **6**, **9**) and Table 4 (diplumbanes **7**, **10**, **11**). ^{1}H NMR data are given in Section 4. The assignment of the NMR signals is either straightforward on the basis of chemical shifts, relative intensities and/or coupling constants, or it has been achieved by various 2D ^{13}C/^{1}H, ^{207}Pb/^{1}H, ^{29}Si/^{1}H or ^{119}Sn/^{1}H heteronuclear shift correlations (HETCOR).

The main points of interest concern the mutual influence of the $^{t}Bu_3Pb$ group and of organyl, silyl, stannyl and plumbyl groups on the respective NMR parameters. If the influence of the $^{t}Bu_3Pb$ group is considered, a comparison with the effect exerted by the Me_3Pb group (Table 5) or the Et_3Pb group is helpful.

2.2.1. Chemical shifts $\delta^{13}C$, $\delta^{29}Si$, $\delta^{119}Sn$, $\delta^{207}Pb$

The δ^{13}C values for the $^{t}Bu_3Pb$ group show little variation within a range between $\delta \cong 47$ and $\cong 57$ for the quaternary carbon atom and $\delta \cong 33$ and $\cong 36$ for the methyl groups. In the series of the compound **3**, the ^{13}C resonances of carbon atoms attached to the lead atom become slightly deshielded (up to 5 ppm) when compared with data for the analogous trimethyllead derivatives.

The ^{29}Si, ^{119}Sn and ^{207}Pb nuclear shielding decreases significantly when the $PbMe_3$ group is replaced by the $^{t}Bu_3Pb$ group (Table 5). The relative decrease corresponds approximately to the respective ratios of the

Table 2
^{13}C, ^{29}Si and ^{207}Pb NMR data [a] of tri(*tert*-butyl)plumbyl-silanes **4a–e**, bis(silyl)plumbanes **8a,b** and tri(*tert*-butyl)plumbyl-trimethylgermane **5a**

No.	δ^{207}Pb	$^1J(^{207}Pb^{29}Si)$	δ^{13}C				δ^{29}Si
			PbC(CH$_3$)$_3$	PbC(CH$_3$)$_3$	PbSiR^1_2R$_2$	PbSiR$^1_2$$R_2$	
4a	−47.4	−207.6	44.3 [+118.3]	34.3 [+15.3]	4.7 (Me) [+45.8]		19.0
4b	−32.0	102.5	44.9 [+103.2]	34.5 [+16.5]	1.3 (Me) [+49.4]	21.0 (C) [32.7] 28.7 (CH$_3$) [4.7]	34.7
4c [b]	18.7	57.9	45.6 [+106.8]	34.4 [+15.9]	0.1 (SiMe$_2$) [20.1]	−0.9 (SiMe$_3$) [8.2]	−12.2
4d	−65.1	151.4	45.7 [+118.3]	34.3 [+14.0]	2.6 (Me) [49.1]	142.7 (C$_i$) [42.1] 134.2 (C$_o$) [9.8] 128.9 (C$_m$) 129.6 (C$_p$)	13.3
4e	−67.2		47.8 [+125.7]	34.3 [+12.8]	137.2 (C$_i$) [7.1] 137.0 (C$_o$) [6.8] 128.4 (C$_m$) 129.6 (C$_p$)		16.2
8a	−264.8	180.0	37.0 [+140.7]	35.9 [+21.3]	4.9 (Me) [+46.5]		12.9
8b	−252.7	80.6	37.9 [+102.6]	36.1 [+22.6]	1.5 (Me) [+47.4]	21.0 (C) [32.7] 28.7 (CH$_3$) [4.7]	30.2
5a	21.0		46.3 [+120.9]	34.3 [+15.9]	4.6 (Me) [27.5]		

[a] In C_6D_6 (ca. 5–15%) at 25 ± 1 °C; coupling constants $^{n}J(^{207}Pb,^{13}C)$ in brackets.
[b] $^{t}Bu_3Pb{-}SiMe_2\mathit{Si}Me_3$: $\delta^{29}Si = -11.3$; $^2J(^{207}Pb^{29}Si) = 6.0$.

Table 3
^{13}C, ^{119}Sn and ^{207}Pb NMR data [a] of tri(*tert*-butyl)plumbyl-stannanes **6a–f** and triethyl- and triisopropylplumbyl-trimetylstannanes **9a,b**

No.	δ^{207}Pb	$^1J(^{207}\mathrm{Pb}^{119}\mathrm{Sn})$	δ^{13}C				δ^{119}Sn
			$\mathrm{Pb}\mathit{C}(\mathrm{CH}_3)_3$	$\mathrm{PbC}(\mathit{C}\mathrm{H}_3)_3$	R^3		
6a	110.5	+1637	47.5 [+105.2] (−56.7)	34.7 [+19.1] (4.9)	−6.0 (C_1) [+20.2] (−198.4)		21.0
6b	131.7	+2504	46.9 [+88.3] (−46.9)	34.6 [+21.8] (3.0)	4.4 (C_1) [21.6] (−207.2)	12.2 (C_2) [5.9] (21.3)	31.9
6c	120.9	+2441	46.9 [+84.6] (−46.2)	34.6 [+21.6] (< 3)	12.9 (C_1) [21.4] (−203.3) 28.1 (C_3) [4.7] (57.8)	30.8 (C_2) [5.5] (17.8) 13.8 (C_4)	20.5
6d	158.0	+6685	55.0 [+92.3] (−39.9)	35.0 [+18.5] (4.4)	31.6 (C_1) [11.4] (−267.0)	32.0 (C_2) [3.9] (99.6)	137.0
6e	135.7	+3581	50.7 [+120.9] (−57.0)	34.6 [+16.7] (4.1)	143.7 (C_i) [17.6] (−301.9) 128.6 (C_m) (59.5)	137.8 (C_o) (40.8) 128.9 (C_p)	−33.0
6f [b]	105.0	+1985	48.4 [+102.1] (−55.6)	34.6 [+18.7] (< 3)	77.8 (C_1) [46.9] (−293.6)	−5.7 (CH_3) [26.9] (−206.4)	7.8
9a [c]	−135.2	−1398					−36.2
9b [d]	12.9	+303					−7.5

[a] In C_6D_6 (ca. 5–15%) at 25 ± 1 °C; coupling constants $^nJ(^{207}\mathrm{Pb},^{13}\mathrm{C})$ in brackets and $^nJ(^{207}\mathrm{Pb},^{13}\mathrm{C})$ in parentheses.

[b] Additional ^{13}C NMR data: $C_{2/5}$ 74.2 (49.6); $C_{3/4}$ 71.0 (34.4).

[c] ^{13}C NMR data: SnMe −6.8 [+57.6] (−222.8); PbEt 8.6 [+87.9] (−61.7) (CH_2), 15.6 [−20.1] (6.1) (CH_3).

[d] ^{13}C NMR data: SnMe −6.4 [+35.4] (−208.7); Pb^{i}Pr 27.8 [+105.1] (−56.6) (CH), 26.1 [< 3].

Table 4
^{13}C and ^{207}Pb NMR data [a] of hexaorganodiplumbanes **1**, **7a–e**, **10** and **11**

No.	δ^{207}Pb(Pb^{t}Bu)	$^1J(^{207}\mathrm{Pb}^{207}\mathrm{Pb})$	δ^{13}C				δ^{207}Pb(PbR$_3$)
			$\mathrm{Pb}\mathit{C}(\mathrm{CH}_3)_3$	$\mathrm{PbC}(\mathit{C}\mathrm{H}_3)_3$	PbR^4		
7a	213.6	−7380	51.7 [+81.7] [< 1.5]	34.2 [+20.7] [9.1]	−4.1 (C_1) [74.1] [4.1]		0.4
7b	261.2	−8126	51.6 [+52.5] [+55.8]	34.6 [+24.6] [6.7]	12.0 (C_1) [27.8] [10.5]	15.0 (C_2) [−18.2] [4.9]	83.0
7c	309.1	−9114	51.4 [+23.6] [36.0]	34.7 [+27.2] [5.4]	31.7 (C_1) [−8.2] [14.7]	26.0 (C_2) [−1.4]	164.8
1	335.1		52.5 [−16.4] [18.2]	35.1 [+28.4] [4.3]			
7d	302.3	−9200	51.2 [34.8] [15.9]	34.9 [+27.5] [5.5]	31.8 (C_1) [70.2]	44.1(C_6) [14.8]	75.4
7e	132.6	−8911					23.6
10 [b]	166.0	−6836					61.0
11	201.0		45.3 [+130.0] [42.1]	34.1 [+31.1] [3.8]	1.9 [221.0] [10.4]		

[a] In C_6D_6 (ca. 5–15%) at 25 ± 1 °C; coupling constants $^nJ(^{207}\mathrm{Pb},^{13}\mathrm{C})$ in brackets.

[b] ^{13}C NMR data: Et 12.3 [55.4] [32.5] (CH_2), 15.5 [16.9] [8.2] (CH_3); ^{i}Pr 31.4 [53.4] [6.6] (CH), 25.0 [13.0] [< 3] (CH_3).

Table 5
Comparison of NMR parameters of some $^{t}Bu_3Pb$ derivatives with those of the corresponding Me_3Pb compounds [a]

	$^{t}Bu_3Pb–SiMe_3$ **4a**	$^{t}Bu_3Pb–SnMe_3$ **6a**	$^{t}Bu_3Pb–PbMe_3$ **7a**
$\delta^{207}Pb(^{t}Bu_3Pb)$	-47.4	$+110.5$	$+213.6$
$[^1J(^{207}Pb,M)]$	$[-207.6]$ (^{29}Si)	$[+1637]$ (^{119}Sn)	$[-7380]$ (^{207}Pb)
$\delta^{29}Si/\delta^{119}Sn/\delta^{207}Pb$	$+19.0$	$+21.0$	$+0.4$
	$Me_3Pb–SiMe_3$ [b]	$Me_3Pb–SnMe_3$ [c]	$Me_3Pb–PbMe_3$ [d]
$\delta^{207}Pb(Me_3Pb)$	-298.2	-324	-281
$[^1J(^{207}Pb,M)]$	$[-764.2]$ (^{29}Si)	$[-3570]$ (^{119}Sn)	$[+290]$ (^{207}Pb)
$\delta^{29}Si/\delta^{119}Sn/\delta^{207}Pb$	$+6.8$	-57.0	-281

[a] In C_6D_6 at 25 ± 1 °C.
[b] Ref. [2].
[c] Ref. [5].
[d] Ref. [9].

radial expansion terms $\langle r^{-3} \rangle_{np}$ for ^{29}Si, ^{119}Sn and ^{207}Pb [12] which indicates that the substituent-induced changes in the character of the Pb–M bond (M = Si, Sn, Pb) are regular.

Branched alkyl groups (Me, Et, Pr to ^{t}Bu) lead to a decrease in ^{207}Pb nuclear shielding [8] which is fairly regular in the series of **7a**, **7b**, **7c** to **1** in C_6D_6 solution. On the other hand, a particularly large deshielding is observed for **2** in THF solution compared with $Li[PbMe_3]$, $Li[PbEt_3]$ and $Li[Pb^{i}Pr_3]$ (Fig. 1). For all THF solutions of trialkylplumbyl-lithium compounds the presence of solvent-separated ion pairs must be assumed since the ^{207}Pb NMR spectra do not show scalar $Pb–^{7}Li$ interactions even at −80 °C. The strong deshielding effect of the ^{t}Bu groups in **2** can be the result of steric repulsion which leads on average to wider bond angles C–Pb–C in **2** compared with other anions $[PbR_3]^-$.

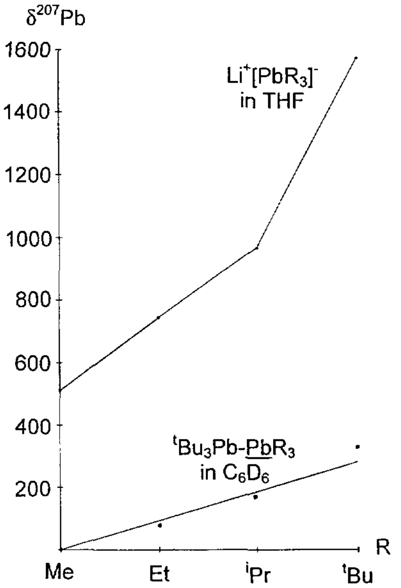


Fig. 1. Dependence of $\delta^{207}Pb$ values for $Li^+[PbR_3]^-$ and $^{t}Bu_3Pb–\mathit{Pb}R_3$ on branching in R.

The influence of Me_3Si, Me_3Ge, Me_3Sn and Me_3Pb groups on ^{207}Pb nuclear shielding in the series of the $^{t}Bu_3Pb$ derivatives **4a**–**7a** differs from that of the corresponding Me_3Pb compounds (Table 5). In the latter series, there are no regular changes (this is reminiscent of the irregular changes in $\delta^{13}C$ of Me_4Si, Me_4Ge, Me_4Sn and Me_4Pb), whereas in the case of **4a**, **5a**, **6a** and **7a** the $\delta^{207}Pb$ values change from δ −47.4, +21.0, +110.5 to +213.6.

2.2.2. *Coupling constants* $J(^{207}Pb,^{13}C)$, $J(^{207}Pb,^{29}Si)$, $^1J(^{207}Pb,^{119}Sn)$ *and* $^1J(^{207}Pb,^{207}Pb)$

Although coupling constants between ^{207}Pb and other nuclei can, in general, easily be measured (see Fig. 2 as an example for $^1J(^{207}Pb,^{207}Pb)$), their diagnostic value depends on the knowledge of the sign. Frequently, the sign is readily apparent if a series of compounds is studied and the sign is known for one example. This is the case for geminal and vicinal coupling constants $^2J(^{207}Pb,^1H)$ (in many cases < 0 [13,14]) and $^3J(^{207}Pb,^1H)$ (large and > 0 [13,14]) in MePb groups (^2J) or across two aliphatic carbon atoms (^3J) as in EtPb, $^{i}PrPb$ or $^{t}BuPb$ groups. However, for $J(^{207}Pb,^{13}C)$ as well as for $J(^{207}Pb,M)$ (M = ^{29}Si, ^{119}Sn, ^{207}Pb), the absolute value of the coupling constant may be misleading [14–16] and, therefore, experimental sign determination is required for a meaningful discussion. The most convenient way to determine the coupling sign involves heteronuclear double resonance experiments in which the resonances of two active spins are either observed or irradiated and the signs of their spin–spin coupling with a third, so-called passive spin are compared (important combinations here are ^1H and ^{13}C as active spins and ^{207}Pb as the passive spin, i.e. $^{13}C\{^1H(^{207}Pb)\}$, or ^1H and ^{207}Pb as active spins and M = ^{29}Si or ^{119}Sn or another ^{207}Pb nucleus as the passive spin, i.e. $^1H\{^{207}Pb(M)\}$). These experiments can be carried out either as 2D

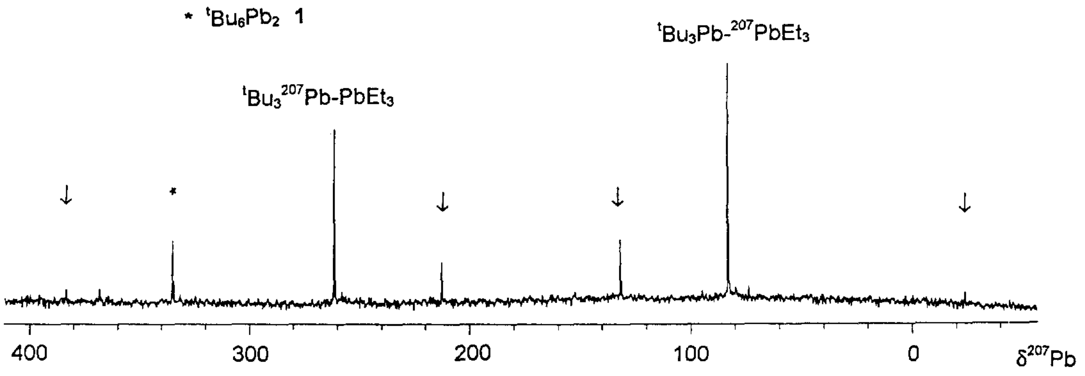


Fig. 2. 52.37 MHz ^{207}Pb{^{1}H} NMR spectrum of ^{t}Bu$_3$Pb–PbEt$_3$ (**7b**) in C_6D_6 at 25 ± 1 °C. The signals of the AB spin system of the isotopomer containing two ^{207}Pb nuclei are marked by arrows ($^1J(^{207}Pb,^{207}Pb) = 8126$ Hz).

HETCOR [14] or as selective 1D heteronuclear double resonance experiments adapted from techniques used previously for CW experiments [17].

2D ^{13}C/^{1}H HETCOR experiments, based on $^1J(^{13}C,^1H)$, establish the positive sign of $^2J(^{207}Pb,^{13}C)$ for the ^{t}Bu$_3$Pb group in all compounds studied, as shown in Fig. 3 for **7a**. However, in Et$_3$Pb and ^{i}Pr$_3$Pb groups, the signs of $^2J(^{207}Pb,^{13}C)$ are negative (see Fig. 4). If the 2D ^{13}C/^{1}H HETCOR experiments are based on $^2J(^{13}C,^1H)$, the signs of $^3J(^{207}Pb,^1H)$ (known to be > 0) and $^1J(^{207}Pb,^{13}C)$ can be compared. The results are shown in the Figs. 5 and 6 for ^{t}Bu$_3$Pb or ^{i}Pr$_3$Pb groups. In the case of the diplumbanes, the experiments also reveal which of the satellites belong to $^1J(^{207}Pb,^{13}C)$ or to $^2J(^{207}Pb,^{13}C)$ across the Pb–Pb bond. For the ^{t}Bu$_3$Pb group it turns out that the sign of $^1J(^{207}Pb,^{13}C)$ is always positive except in **1**, and that $^1J(^{207}Pb,^{13}C_{PbMe}) > 0$ in **7a**, whereas the coupling constants $^1J(^{207}Pb,^{13}C_{PbEt})$ in **7b** and $^1J(^{207}Pb,^{13}C_{Pb^iPr})$ in **7c** possess a negative sign.

Observation of differential effects on the M satellites (M = ^{29}Si, ^{119}Sn, ^{207}Pb) of the ^{1}H(Me$_3$M) signals of ^{t}Bu$_3$Pb–MMe$_3$ upon selective irradiation of appropriate ^{207}Pb(^{t}Bu$_3$Pb) transitions allows the comparison of the signs of $^1J(^{207}Pb,M)$ and $^2J(M,^1H_{Me})$. This reveals that $^1J(^{207}Pb,^{29}Si)$ is negative in **4a** ($\gamma^{29}Si < 0$; reduced coupling constant $^1K(^{207}Pb,^{29}Si) > 0$), $^1J(^{207}Pb,^{119}Sn)$ is positive in **6a** ($\gamma^{119}Sn < 0$; reduced coupling constant

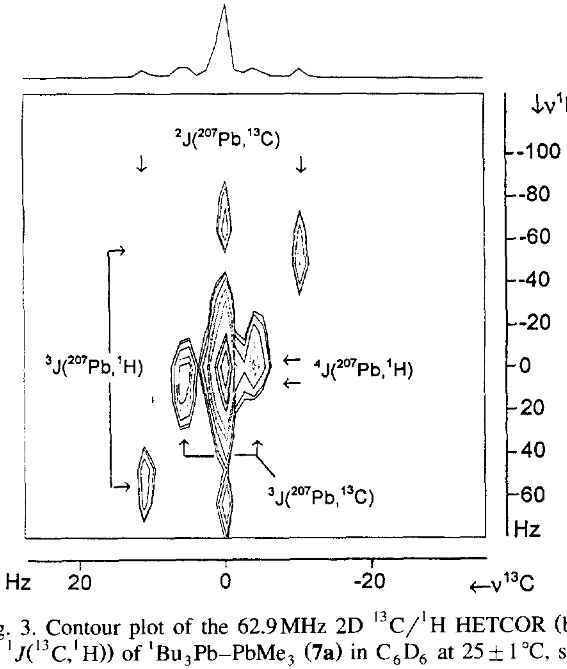


Fig. 3. Contour plot of the 62.9 MHz 2D ^{13}C/^{1}H HETCOR (based on $^1J(^{13}C,^1H)$) of ^{t}Bu$_3$Pb–PbMe$_3$ (**7a**) in C_6D_6 at 25 ± 1 °C, showing the region of the methyl group of the *tert*-butyl units. The coupling constants are indicated, and the positive tilt of the cross-peaks shows that $^3J(^{207}Pb,^1H)$ (> 0) and $^2J(^{207}Pb,^{13}C)$ have alike signs. This is also true for $^4J(^{207}Pb,Pb,C,C,^1H)$ and $^3J(^{207}Pb,Pb,C,^{13}C)$.

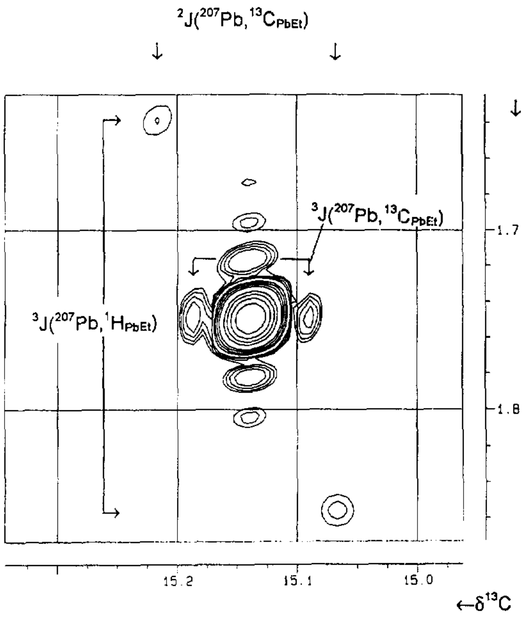


Fig. 4. Contour plot of the 62.9 MHz 2D ^{13}C/^{1}H HETCOR (based on $^1J(^{13}C,^1H)$) of ^{t}Bu$_3$Pb–PbEt$_3$ (**7b**) in C_6D_6 at 25 ± 1 °C, showing the region of the methyl group of the ethyl units. The coupling constants are indicated, and the negative tilt of the relevant cross-peaks shows that the signs of $^3J(^{207}Pb,^1H)$ and $^2J(^{207}Pb,^{13}C)$ are opposite.

${}^1K({}^{207}\mathrm{Pb},{}^{119}\mathrm{Sn}) < 0$), and ${}^1J({}^{207}\mathrm{Pb},{}^{207}\mathrm{Pb})$ is negative in **7a** ($\gamma^{207}\mathrm{Pb} > 0$; reduced coupling constant ${}^1K({}^{207}\mathrm{Pb},{}^{207}\mathrm{Pb}) < 0$). This confirms the trend which is already evident for other one-bond ${}^{207}\mathrm{Pb}$–${}^{119}\mathrm{Sn}$ and ${}^{207}\mathrm{Pb}$–${}^{207}\mathrm{Pb}$ couplings [5,9]. The high polarizability of the lead atom causes a small s overlap, and together with the influence of relativistic effects [18], this enforces the inversion of signs of coupling constants involving the ${}^{207}\mathrm{Pb}$ nucleus and other nuclei with an open shell valence electron configuration. In this respect the ${}^{207}\mathrm{Pb}$ nucleus plays a special role among the Group 14 elements, and the effects are much more emphasized by the ${}^t\mathrm{Bu}_3\mathrm{Pb}$ group compared to other $\mathrm{R}_3\mathrm{Pb}$ groups. There appears to be an approximately linear relationship between ${}^1J({}^{207}\mathrm{Pb},{}^{119}\mathrm{Sn})$ and ${}^1J({}^{207}\mathrm{Pb},{}^{207}\mathrm{Pb})$, (${}^1J({}^{207}\mathrm{Pb},{}^{119}\mathrm{Sn}) = -0.682\ {}^1J({}^{207}\mathrm{Pb},{}^{207}\mathrm{Pb}) - 3402$).

In the cases of ${}^t\mathrm{Bu}_3\mathrm{Pb}$–$\mathrm{CH}_2\mathrm{SiMe}_3$ (**3f**) and of $\mathrm{Me}_3\mathrm{Pb}$–$\mathrm{CH}_2\mathrm{SiMe}_3$ [16], it was of interest to compare the values ${}^2J({}^{207}\mathrm{Pb},{}^{29}\mathrm{Si})$ (**3f**: 39.1 and $\mathrm{Me}_3\mathrm{Pb}$–$\mathrm{CH}_2\mathrm{SiMe}_3$: +42.1 Hz [16]). Therefore, the sign was determined by the ${}^{29}\mathrm{Si}/{}^1\mathrm{H}$ HETCOR experiment, based on ${}^2J({}^{29}\mathrm{Si},{}^1\mathrm{H})$. As shown in Fig. 7, the signs of the reduced coupling constants ($\gamma^{29}\mathrm{Si} < 0$) ${}^2K({}^{207}\mathrm{Pb},{}^{29}\mathrm{Si})$ and ${}^2K({}^{207}\mathrm{Pb},{}^1\mathrm{H}_{\mathrm{CH}_2})$ (< 0), are alike, which means ${}^2K({}^{207}\mathrm{Pb},{}^{29}\mathrm{Si}) < 0$ and ${}^2J({}^{207}\mathrm{Pb},{}^{29}\mathrm{Si}) > 0$, the same sign as in $\mathrm{Me}_3\mathrm{Pb}$–$\mathrm{CH}_2\mathrm{SiMe}_3$.

3. Conclusions

The first study of the reactivity of tri(*tert*-butyl)plumbyl-lithium in THF solution has shown that this new reagent possesses considerable synthetic potential. The characterization of the new organolead compounds by multinuclear magnetic resonance proved to be straightforward. The change of signs of various coupling constants involving the ${}^{207}\mathrm{Pb}$ nucleus was established by 1D heteronuclear double resonance experiments and also by 2D HETCOR. In all cases studied here, the presence of the ${}^t\mathrm{Bu}_3\mathrm{Pb}$ group emphasizes effects which have been noted previously for trimethyl- and triethyllead compounds: (i) deshielding influence on the neighbour nucleus; (ii) large negative contributions to the coupling mechanism for one-bond coupling constants. These effects can be attributed to the great polarizability of the ${}^{207}\mathrm{Pb}$ nucleus in the ${}^t\mathrm{Bu}_3\mathrm{Pb}$ group,

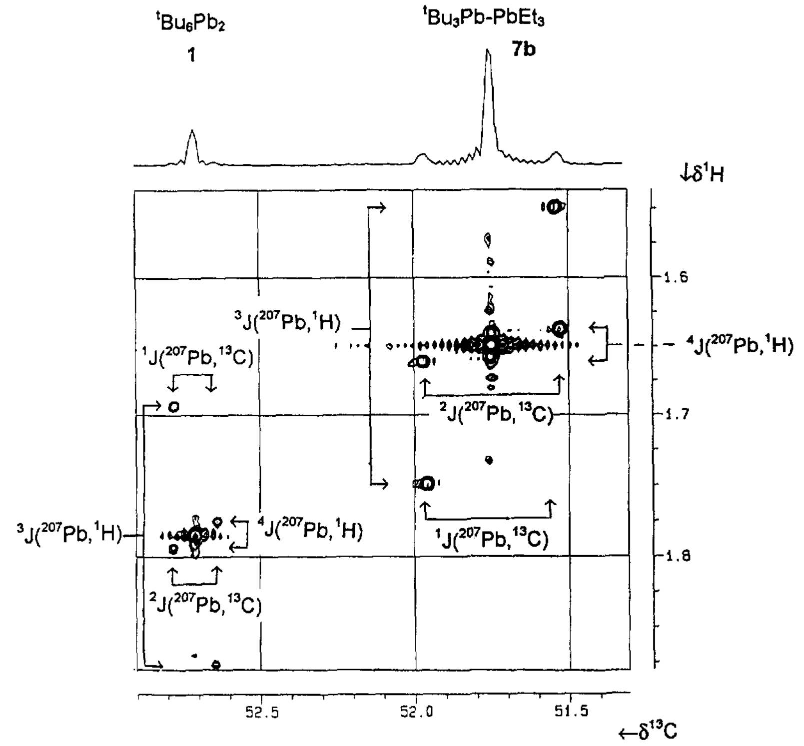


Fig. 5. Contour plot of the 125.8 MHz 2D ${}^{13}\mathrm{C}/{}^1\mathrm{H}$ HETCOR (based on ${}^2J({}^{13}\mathrm{C},{}^1\mathrm{H})$) of a mixture of ${}^t\mathrm{Bu}_3\mathrm{Pb}$–$\mathrm{Pb}{}^t\mathrm{Bu}_3$ (**1**) and ${}^t\mathrm{Bu}_3\mathrm{Pb}$–$\mathrm{PbEt}_3$ (**7b**) in $\mathrm{C}_6\mathrm{D}_6$ at 25 ± 1 °C, showing the region of the quaternary carbon atoms. In the case of ${}^t\mathrm{Bu}_3\mathrm{Pb}$–$\mathrm{Pb}{}^t\mathrm{Bu}_3$ (**1**), the negative tilt of the relevant cross-peaks indicates that the signs of ${}^3J({}^{207}\mathrm{Pb},{}^1\mathrm{H})$ (> 0) and ${}^1J({}^{207}\mathrm{Pb},{}^{13}\mathrm{C})$ are opposite, whereas in ${}^t\mathrm{Bu}_3\mathrm{Pb}$–$\mathrm{PbEt}_3$ (**7b**) the same coupling constants possess alike signs. The positive tilt of the cross-peaks belonging to ${}^4J({}^{207}\mathrm{Pb},\mathrm{Pb},\mathrm{C},\mathrm{C},{}^1\mathrm{H})$ and ${}^2J({}^{207}\mathrm{Pb},\mathrm{Pb},{}^{13}\mathrm{C})$ proves that these coupling constants have the same sign both in **1** and **7b**. Note that the assignment of the coupling constants ${}^1J({}^{207}\mathrm{Pb},{}^{13}\mathrm{C})$ and ${}^2J({}^{207}\mathrm{Pb},\mathrm{Pb},{}^{13}\mathrm{C})$ is straightforward only in the 2D spectra.

together with the influence of relativistic effects typical of heavy nuclei.

4. Experimental

All preparative work and the handling of the samples was carried out under argon atmosphere, using dry solvents. All educts were commercial products or prepared following literature procedures. EI-MS spectra (70 eV) were measured on a Finnigan MAT 8500 spectrometer. NMR spectra were recorded at 25 °C (if not stated otherwise) using 5 mm tubes with samples dissolved in C_6D_6 on Jeol FX 90 Q, Bruker ARX 250, AC 300 and DRX 500 spectrometers. Chemical shifts are given with respect to Me_4Si (δ^1H (C_6D_5H) 7.15; $\delta^{13}C$ (C_6D_6) 128.0; $\delta^{29}Si$: $\Xi(^{29}Si) = 19.867184$ MHz), Me_4Sn ($\delta^{119}Sn$: $\Xi(^{119}Sn) = 37.290665$ MHz) and Me_4Pb ($\delta^{207}Pb$: $\Xi(^{207}Pb) = 20.920597$ MHz).

4.1. Hexa(tert-butyl)diplumbane (1)

Compound **1** was prepared from $PbCl_2$ and the *tert*-butyl Grignard as described [11]. **1**: orange-red solid; yield: 29%; dec. 137 °C; EI-MS: m/z (%) 699 (8) $[M^+ - {}^tBu]$, 379 (29) $[{}^tBu_3Pb^+]$, 57 (100) $[C_4H_9^+]$; ^1H NMR: δ^1H $[^nJ(^{207}Pb^1H)] = 1.78$ [91.7] [9.4].

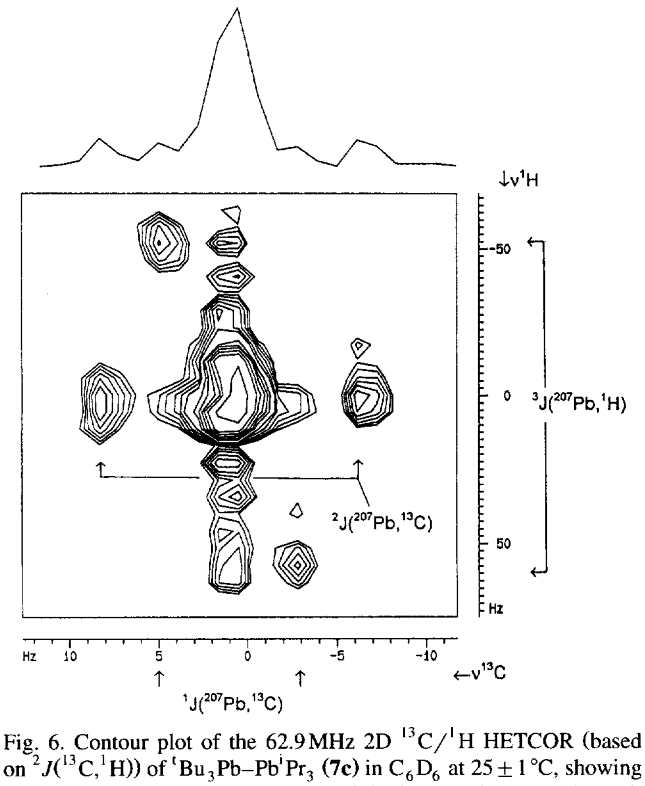


Fig. 6. Contour plot of the 62.9 MHz 2D $^{13}C/^1H$ HETCOR (based on $^2J(^{13}C,^1H)$) of $^tBu_3Pb{-}Pb^iPr_3$ (**7c**) in C_6D_6 at 25 ± 1 °C, showing the region of the CH carbon atoms of the isopropyl groups. According to the negative tilt of the relevant cross-peaks, the signs of $^3J(^{207}Pb,^1H)$ (> 0) and $^1J(^{207}Pb,^{13}C)$ are opposite. As shown also in Fig. 5, $^1J(^{207}Pb,^{13}C)$ and $^2J(^{207}Pb,Pb,^{13}C)$ can be clearly distinguished which is not possible in the 1D ^{13}C NMR spectra.

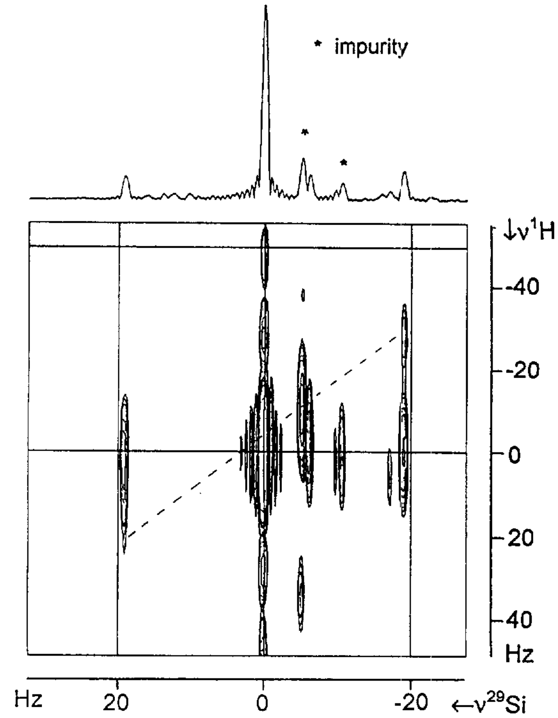


Fig. 7. Contour plot of the 49.7 MHz 2D $^{29}Si/^1H$ HETCOR (based on $^2J(^{29}Si,^1H)$) of $^tBu_3Pb{-}CH_2SiMe_3$ (**3f**) in C_6D_6 at 25 ± 1 °C. The positive tilt of the relevant cross-peaks (Pb–CH_2–Si group), connected by a broken line, indicates alike signs of $^2K(^{207}Pb,^1H)$ (< 0) and $^2K(^{207}Pb,^{29}Si)$; therefore ($\gamma^{29}Si < 0$) $^2J(^{207}Pb,^{29}Si) > 0$.

4.2. Tri(tert-butyl)plumbyl-lithium (2)

A solution of 0.38 g (0.5 mmol) **1** in 30 ml of THF was cooled to −50 °C and an excess of lithium metal (0.35 g, 50 mmol) was added. The mixture was stirred for 5 h at −40 to −30 °C. The reaction is complete when the colour of the solution has changed to bordeaux-red ($\delta^{207}Pb = 1573.8$). After decanting the THF solution of **2** into another flask, kept at −40 °C, the reagent is ready for further reactions.

4.3. Tri(tert-butyl)(alkyl)plumbanes (3)

A solution of **2** (1 mmol) in 30 ml of THF was treated with a stoichiometric amount of alkylhalide (1 mmol) at −30 °C. The mixture was stirred for 2 h at −30 °C, warmed to room temperature, the solvent was removed in vacuo, and the residue was taken up in hexane. After filtration over glass-wool the hexane was removed and the compounds **3** were left as yellow solids.

3a: tri(*tert*-butyl)(methyl)plumbane; yield: 81%; dec. 71 °C; EI-MS: m/z (%) = 337 (5) $[M^+ - 57]$, 57 (100) $[C_4H_9^+]$; ^1H NMR (C_6D_6): δ^1H $[^nJ(^{207}Pb^1H)] = 1.46$

[105.5] (s, 27H, ^{t}Bu), 0.46 [21.9] (s, 3H, Me).**3b**: tri(*tert*-butyl)(ethyl)plumbane; yield: 80%; dec. 73 °C; EI-MS: *m/z* (%) = 407 (2) [M$^+$], 57 (100) [$C_4H_9^+$]; ^{1}H NMR (C_6D_6): δ^1H = 1.50 [97.7] (s, 27H, ^{t}Bu), 1.55 (q, 2H, CH_2), 1.44 (t, 3H, CH_3).

3d: tri(*tert*-butyl)(^{n}butyl)plumbane; yield: 74%; dec. 75 °C; EI-MS: *m/z* (%) = 435 (10) [M$^+$], 265 (100) [BuPb$^+$]; ^{1}H NMR (C_6D_6): δ^1H = 1.51 [100.1] (s, 27H, ^{t}Bu), 1.90–0.90 (m, 9H, ^{n}Bu).

3e: tri(*tert*-butyl)(benzyl)plumbane; yield: 81%; dec. 91 °C, EI-MS: *m/z* (%) = 470 (1) [M$^+$], 299 (100) [$C_7H_7Pb^+$]; ^{1}H NMR (C_6D_6): δ^1H = 1.44 [104.8] (s, 27H, ^{t}Bu), 1.32 [122.1] (s, 2H, CH_2), 7.15–6.60 (m, 5H, Ph).

The compounds **3c** and **3f** were prepared in the same way. They were isolated with impurities.

3c: tri(*tert*-butyl)(^{n}propyl)plumbane; yield 75%; ^{1}H NMR (C_6D_6): δ^1H = 1.49 [100.1] (s, 27H, ^{t}Bu), 1.86–1.20 (m, 7H, ^{n}Pr).

3f: tri(*tert*-butyl)(trimethylsilylmethyl)plumbane; yield: 61%; ^{1}H NMR (C_6D_6): δ^1H [$^nJ(^{207}Pb^1H)$] ($^nJ(^{29}Si^1H)$) = 1.48 [106.2] (s, 27H, ^{t}Bu), 1.43 [125.9] (s, 2H, CH_2), 0.17 [17.8] (6.4) (s, 9H, $SiMe_3$).

4.4. Tri(*tert*-butyl)(trialkylsilyl)plumbanes (4)

A stoichiometric amount of trialkylchlorosilane (1 mmol) was added dropwise to a solution of **2** (1 mmol) in 30 ml of THF at −30 °C. At once the colour of the solution changed from bordeaux-red to green. The mixture was warmed up to room temperature and stirred for 2 h. The solvent THF was removed in vacuo, the residue was dissolved in hexane and the solvent was evaporated in vacuo after filtration over glass-wool. The products **4** were left as yellow solids. In the case of the compounds **4a** and **4b**, side products $(R'R_2Si)_2Pb^tBu_2$ **8a**, **8b** were formed (ca. 10%). Compounds **4d** and **4f** were isolated with impurities.

4a: tri(*tert*-butyl)(trimethylsilyl)plumbane; yield: 67%, EI-MS: *m/z* (%) = 395 (15) [M$^+$ − 57], 57 (100) [$C_4H_9^+$]; ^{1}H NMR (C_8D_8): δ^1H [$^nJ(^{207}Pb^1H)$] ($^nJ(^{29}Si^1H)$) = 1.49 [88.4] (s, 27H, ^{t}Bu), 0.34 [31.2] (6.8) (s, 9H, Me).

8a: di(*tert*-butyl)bis(trimethylsilyl)plumbane; ^{1}H NMR (C_6D_6): δ^1H [$^nJ(^{207}Pb^1H)$] ($^nJ(^{29}Si^1H)$) = 1.56 [88.1] (s, 18H, ^{t}Bu), 0.39 [30.5] (6.8) (s, 18H, Me).

4b: tri(*tert*-butyl)(*tert*-butyldimethylsilyl)plumbane; yellow solid; yield: 63%; EI-MS: *m/z* (%) 495 (5) [M +], 73 (100) [Me_3Si^+]; ^{1}H NMR (C_6D_6): δ^1H 1.59 [87.4] (s, 27H, Pb^{t}Bu), 1.01 [3.8] (s, 9H, Si^{t}Bu), 0.37 [32.4] (6.4) (s, 6H, Me).

8b: di(*tert*-butyl)bis(*tert*-butyldimethylsilyl)plumbane; ^{1}H NMR (C_6D_6): δ^1H = 1.64 [85.8] (s, 18H, ^{t}BuPb), 1.02 [3.2] (s, 9H, ^{t}BuSi), 0.42 [30.2] (6.4) (s, 12H, Me).

4c: tri(*tert*-butyl)(pentamethyldisilyl)plumbane; yield: 70%; dec. 53 °C; EI-MS: *m/z* (%) = 452 (34) [M$^+$ − 57], 131 (100) [$Me_5Si_2^+$]; ^{1}H NMR (C_6D_6): δ^1H = 1.68 [89.9] (s, 27H, ^{t}Bu), 0.59 [37.5] (6.4) (s, 6H, $SiMe_2$), 0.27 [7.2] (6.5) (s, 9H, $SiMe_3$).

4d: tri(*tert*-butyl)(dimethylphenylsilyl)plumbane; yield: 87%, EI-MS: *m/z* (%) = 457 (18) [M$^+$ − 57], 135 (100) [Me_2PhSi^+]; ^{1}H NMR (C_6D_6): δ^1H = 1.49 [90.3] (s, 27H, ^{t}Bu), 0.64 [28.6] (7.0) (s, 6H, Me), 7.90 (m, 1H, Ph), 7.53–7.49 (m, 2H, Ph), 7.20–7.13 (m, 2H, Ph).

4e: tri(*tert*-butyl)(triphenylsilyl)plumbane; yield: 75%, dec. 88 °C, EI-MS: *m/z* (%) = 581(35) [M$^+$ − 57], 259 (100) [Ph_3Si^+]; ^{1}H NMR (C_6D_6): δ^1H = 1.55 [95.1] (s, 27H, ^{t}Bu), 7.78–7.74 (dd, 6H, Ph), 7.56–7.53 (m, 3H, Ph), 7.12–7.08 (m, 6H, Ph).

4.5. Tri(*tert*-butyl)(trimethylgermyl)plumbane (5a)

Compound **5a** was prepared using the same procedure as described for **4**. **5a**: yellow solid; yield: 79%; dec. 79 °C; EI-MS: *m/z* (%) = 501 (10) [M$^+$], 57 (100) [$C_4H_9^+$]; ^{1}H NMR (C_6D_6): δ^1H [$^nJ(^{207}Pb^1H)$] = 1.49 [94.5] (s, 27H, ^{t}Bu), 0.48 [24.9] (s, 9H, Me).

4.6. Tri(*tert*-butyl)(trialkylstannyl)plumbanes (6)

A stoichiometric amount of trialkylstannylchloride (1 mmol) was given in one portion to a solution of **2** (1 mmol) in THF at −30 °C. The mixture was stirred for 2 h at that temperature and the solvent was removed in vacuo. The residue was dissolved in hexane, was filtrated over glass-wool, and the hexane was removed in vacuo. The products **6** were left as yellow solids. In the cases of **6b** and **6c**, Et_6Sn_2 and $^tBu_6Sn_2$ respectively, and **1** were formed as side products (ca. 15%).

6a: tri(*tert*-butyl)(trimethylstannyl)plumbane; yield: 79%; dec. 72 °C; EI-MS: *m/z* (%) = 543 (4) [M$^+$], 57 (100) [$C_4H_9^+$]; ^{1}H NMR (C_6D_6): δ^1H [$^nJ(^{207}Pb^1H)$] ($^nJ(^{119}Sn^1H)$) = 1.57 [98.2] (7.7) (s, 27H, ^{t}Bu), 0.40 [13.7] (45.7) (s, 9H, Me).

6b: tri(*tert*-butyl)(triethylstannyl)plumbane; yield: 83%; EI-MS: *m/z* (%) = 585 (15) [M$^+$], 379 (100) [$^tBu_3Pb^+$]; ^{1}H NMR (C_6D_6): δ^1H = 1.59 [96.4] (6.9) (s, 27H, ^{t}Bu), 1.02 (q, 6H, CH_2), 1.27 (t, 9H, CH_3).

6c: tri(*tert*-butyl)(tri^{n}butylstannyl)plumbane; yield: 76%; dec. 80 °C; ^{1}H NMR (C_6D_6): δ^1H = 1.59 [95.7] (7.2) (s, 27H, ^{t}Bu), 1.70–0.81 (m, 27H, ^{n}Bu).

6d: tri(*tert*-butyl)(tri-*tert*-butylstannyl)plumbane; yield: 81%; ^{1}H NMR (C_6D_6): δ^1H = 1.72 [107.8] (9.5) (s, 27H, ^{t}BuPb), 1.45 [5.4] (76.0) (s, 27H, ^{t}BuSn).

6e: tri(*tert*-butyl)(triphenylstannyl)plumbane; yield: 79%; dec. 112 °C; ^{1}H NMR (C_6D_6): δ^1H = 1.60 [106.3] (9.1) (s, 27H, ^{t}Bu), 7.21–7.02 (m, 9H, Ph), 7.77–7.74 (dd, 6H, Ph).

6f: 1,1′-bis-[tri(*tert*-butyl)plumbyl-dimethylstannyl]-ferrocene; yield: 80%; dec. 102 °C, ^{1}H NMR (C_6D_6):

δ^1H = 1.57 [99.0] (8.0) (s, 27H, ${}^tBu$), 0.66 [11.5] (45.7) (s, 6H, Me), 4.33 (3.8) (t, 2H, $H_{3/4}$), 4.11 (7.1) (t, 2H, $H_{2/5}$).

4.7. Tri(tert-butyl)tri(alkyl)diplumbanes (7)

The same procedure as for tin compounds **6** was used; **7c**–**7e** were isolated together with unidentified impurities.

7a: tri(*tert*-butyl)tri(methyl)diplumbane; yellow solid; yield: 89%, dec. 92 °C, EI-MS: m/z (%) = 615 (33) [$M^+ - 15$], 57 (100) [$C_4H_9^+$]; ${}^1H$ NMR (C_6D_6): δ^1H [${}^nJ({}^{207}Pb^1H)$] 1.54 [104.1] [14.3] (s, 27H, ${}^tBu$), 1.04 [28.2] [9.8] (s, 9H, Me).

7b: tri(*tert*-butyl)tri(ethyl)diplumbane; yellow solid; yield: 90%; dec. 109 °C; EI-MS: m/z (%) = 644 (2) [$M^+ - 29$], 615 (8) [$M^+ - 57$], 379 (100) [$Pb^tBu_3^+$]; ${}^1H$ NMR (C_6D_6): δ^1H = 1.64 [100.2] [12.1] (s, 27H, ${}^tBu$), 1.78 (q, 6H, CH_2), 1.74 [195.7] (t, 9H, CH_3); $C_{24}H_{42}Pb_2$ calc. (found): C, 32.13 (32.26); H, 6.29 (6.27); Pb, 61.58% (59.7%).

7c: tri(*tert*-butyl)tri(isopropyl)plumbane; yellow-orange solid; yield: 71%; ${}^1H$ NMR (C_6D_6): δ^1H = 1.68 [96.9] [10.3] (s, 27H, ${}^tBu$), 2.26 (sept, 3H, CH); 1.80 [102.3] [9.2] (d, 18H, CH_3).

7d: tri(*tert*-butyl)tri(^{n}hexyl)diplumbane; orange-red solid; yield: 78%; EI-MS: m/z (%) = 777 (22) [$M^+ - C_4H_9$], 457 (100) [Hex_3Pb^+]; ${}^1H$ NMR (C_6D_6): δ^1H = 1.73 [95.9] [10.2] (s, 27H, ${}^tBu$), 2.48–1.23 (m, 39H, Hex).

7e: tri(*tert*-butyl)tri(cyclohexyl)diplumbane; red solid; ${}^1H$ NMR (C_6D_6): δ^1H = 1.74 [91.6] [8.9] (s, 27H, ${}^tBu$), 2.51–1.20 (m, 33H, ${}^cHex$).

4.8. Organoplumbyl compounds with groups other than tert-butyl

*4.8.1. **9** triorgano(trimethylstannyl)plumbanes*

Solutions of Li[PbR_3] were prepared as described before at temperatures of −50 °C and then treated with chlorotrimethylstannane. The same procedure as for compounds **6** gave the products **9**.

9a: triethyl(trimethylstannyl)plumbane; colourless liquid; yield 92%; ${}^1H$ NMR (C_6D_6): δ^1H = 1.67 [27.9] (4.2) (6H, $PbCHCH_3$), 1.61 [108.6] (9H, $PbCH_2CH_3$), 0.37 [23.2] (49.0) (9H, $SnMe_3$).

9b: tri(isopropyl)(trimethylstannyl)plumbane; yellow solid; yield 84%; dec. 64 °C; ${}^1H$ NMR (C_6D_6): δ^1H = 2.18 (sept, 3H, $PbCH(CH_3)_2$), 1.65 [111.7] (7.0) (d, 18H, $PbCH(CH_3)_2$), 0.40 [17.5] (47.5) (s, 9H, $SnMe_3$).

*4.8.2. **10**: tri(isopropyl)tri(ethyl)diplumbane*

The same procedure as for compounds **7**. Side products were $PbEt_4$, Pb_2Et_6, Pb^iPr_4 and $Pb_2{}^iPr_6$.

*4.8.3. **11**: tetra(tert-butyl)di(methyl)diplumbane*

A solution of **2** (2 mmol) in 50 ml THF was treated with 1 mmol of dichlorodimethylplumbane at a temperature of −30 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed in vacuo, and the residue was taken up in hexane. After filtration the hexane was removed and compound **11** was left as an orange solid. Yield 72%; dec. 104 °C; EI-MS: m/z (%) 657 (18) [$M^+ - Me$], 615 (33) [$M^+ - C_4H_9$], 337 (95) [$Pb^tBu_2Me^+$], 57 (100) [$C_4H_9^+$], ${}^1H$ NMR (C_6D_6): δ^1H = 1.59 [114.0] [12.8] (s, 18H, ${}^tBu$), 0.76 [17.9] [10.7] (s, 3H, Me).

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