^{1}H NMR evidence for the formation of vinyllead triacetates. The reactions of vinylmercury, vinyltin, and vinylboronic acids with lead tetraacetate

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Abstract

Vinylmercury compounds, vinylboronic acids and vinylstannanes undergo rapid metal–lead exchange with lead tetraacetate in deuterochloroform to generate vinyllead triacetates, which have been characterised by their ^{1}H–^{1}H and ^{207}Pb–^{1}H coupling constants. In addition, a number of divinyl and mixed aryl-vinyllead dicarboxylates have been prepared via boron–lead exchange.

Keywords: Lead; Mercury; Tin; Boron; Boronic acid; Nuclear magnetic resonance

1. Introduction

Vinyllead triacetates were first proposed as reactive intermediates by Corey and Wollenberg [1] in 1974 in the reaction of vinylstannanes with lead tetraacetate (LTA), a reaction which ultimately yielded acetylenes (Scheme 1). Successful C-vinylation of β-dicarbonyl compounds by use of reagents derived in situ via mercury–lead and tin–lead exchange reactions of divinylmercury compounds and vinylstannanes with lead tetraacetate [2] prompted a more detailed spectroscopic analysis of these reactive intermediates. In that work, it was shown that both bis[(E)-styryl]mercury (1) and tributyl-(E)-styrylstannane (2) gave rise to a styryllead intermediate (3) which decomposed with time and gave the usual vinylated products when treated with β-keto-ester (4) (Scheme 2).

Unlike aryllead triacetates [3], which were the subject

of earlier work, these styryllead intermediates were extremely unstable compounds that generally decomposed via vinyl cation pathways [4,5] to yield either enol acetates or acetylenes, depending on substitution and the precursor. Additional evidence that vinyllead triacetates were the reactive intermediates was obtained when cyclopentenyltributylstannane (6) was reacted with lead tetraacetate to give a relatively stable lead intermediate (7), which could be isolated and subsequently used for vinylation reactions (Scheme 3). In earlier work [6] it had been shown that the intermediate, which could be observed by ^{1}H NMR spectroscopy, decomposed at about the same rate as that at which the final products were formed.

We now report that by following the Sn–Pb, Hg–Pb and also B–Pb metal–lead exchange reactions by high resolution NMR spectroscopy, it is possible to observe several of these vinyllead triacetate intermediates, which can be identified from the ^{207}Pb satellites about the vinylic signals in their ^{1}H NMR spectra.

2. Results and discussion

Cawley and Danyluk [7] reported the satellite spectral data for tetravinyllead (9) in 1968 (Table 1), but
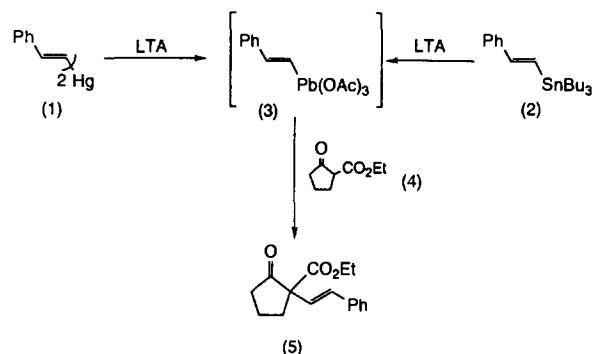
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Scheme 1.

Scheme 2.

(6)   (7)
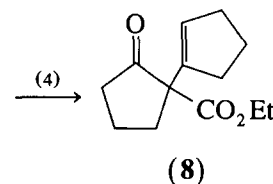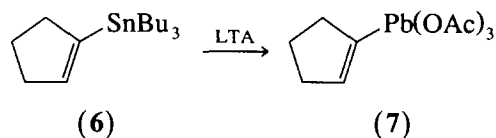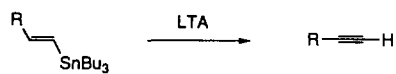
Scheme 3.

there have been very few other reports of vinyllead $^{207}Pb-^1H$ couplings in the literature [8,9]. In this early work it was found that $J_{Pb, H_{trans}} > J_{Pb, H_{gem}} > J_{Pb, H_{cis}}$.

Table 1
Proton–proton [8] and ^{207}Pb–proton [7] coupling constants for tetravinyllead (9)

$J_{Pb,H_{(gem)}}$	$J_{Pb,H_{(cis)}}$	$J_{Pb,H_{(trans)}}$	$J_{H,H_{(gem)}}$	$J_{H,H_{(cis)}}$	$J_{H,H_{(trans)}}$
212.4 Hz	161.7 Hz	330.1 Hz	2.02 Hz	12.13 Hz	19.57 Hz

Table 2
^1H NMR spectroscopic data (obtained at 200 MHz, unless otherwise indicated) for the vinylic protons of vinyllead triacetates (CDCl$_3$)

Compound	J(Hz)		
	H_{gem} to Pb	H_{cis} to Pb	H_{trans} to Pb
(3) [a,f]	7.50, $J_{H,H}$ 15.21	7.342, $J_{H,H}$ 15.21	
	$J_{Pb,H}$ 821.3	$J_{Pb,H}$ 691.7	
(10) [b,f]	7.37, $J_{H,H}$ 15.00	7.25, $J_{H,H}$ 15.00	
	$J_{Pb,H}$ 831.3	$J_{Pb,H}$ 692.5	
(11) [c,f]	7.72, $J_{H,H}$ 14.00	7.44, $J_{H,H}$ 14.00	
	$J_{Pb,H}$ 926.5	$J_{Pb,H}$ 761.0	
(E-12) [c,f]	7.39, $J_{H,H}$ 14.41	7.59, $J_{H,H}$ 14.41	
	$J_{Pb,H}$ 866.7	$J_{Pb,H}$ 708.1	
(Z-12) [c,f]	7.17, $J_{H,H}$ 6.48		7.88, $J_{H,H}$ 6.48
	$J_{Pb,H}$ 871.0		$J_{Pb,H}$ 1599.0
(E-13) [a]	6.89, $J_{Pb,H}$ 864.8		
(Z-13) [c]	6.83, $J_{Pb,H}$ 854.8,	$J_{CH3,H}$ 1.60	
(14) [d]	7.33, $J_{Pb,H}$ 819.0		
(15) [a,f]	6.37, $J_{Pb,H}$ 924.2		
(16) [c]	7.42, $J_{H,H}$ 14.79	7.27, $J_{H,H}$ 14.79	
	$J_{Pb,H}$ 860.0	$J_{Pb,H}$ 704.0	
(17) [e,f]		6.17, $J_{Pb,H}$ 729.8	
(18) [c]	7.03, $J_{Pb,H}$ 900.0		
(7) [c]		6.37, $J_{Pb,H}$ 293.9	
(E-19) [c]	7.84, $J_{H,H}$ 14.20	7.50, $J_{H,H}$ 14.20	
	$J_{Pb,H}$ 931.0	$J_{Pb,H}$ 689.5	
(Z-19) [c]	7.74, $J_{H,H}$ 6.10		7.77, $J_{H,H}$ 6.10
	$J_{Pb,H}$ 924.0		$J_{Pb,H}$ 1667.5
(20) [c]	7.25, $J_{H,H}$ 15.49	6.17, $J_{H,H}$ 15.49	6.29, $J_{H,H}$ 7.10
	$J_{H,H}$ 7.10	$J_{H,H}$ 4.80	$J_{H,H}$ 4.80
	$J_{Pb,H}$ 952.5	$J_{Pb,H}$ 812.8	$J_{Pb,H}$ 1671.9

[a] Prepared from divinylmercury compound and tributylstannane.
[b] Prepared from tributylstannane, and trimethylstannane.
[c] Prepared from tributylstannane.
[d] Prepared from divinylmercury compound.
[e] Prepared from divinylmercury compound, tributylstannane and vinylmercury bromide.
[f] Obtained at 400 MHz.

The first compound studied in this work, (E)-styryl-lead triacetate (3) shows two vinylic signals at δ 7.50 and δ 7.32 with $^3J_{H, H}$ 15.21 Hz, and ^{207}Pb couplings of 821.3 and 691.7 Hz respectively. From the trend observed for tetravinyllead [7], it appears that the larger of these two couplings belongs to the proton geminal to the lead group and the smaller to the proton cis to the lead. Of relevance to much of the earlier work was the finding that the same lead compound was formed whether it was derived from the stannane, the vinyl-boronic acid or the mercurial. In many other cases it was possible to show that the same lead compound was formed from both tin and mercury precursors (Table 2). The exchange reaction was essentially quantitative in all cases studied. No starting stannane or mercurial was recovered or observed by NMR spectroscopy
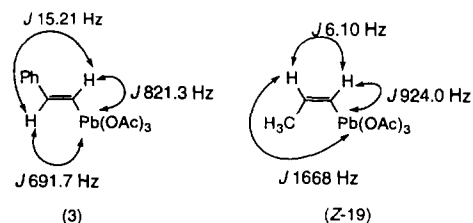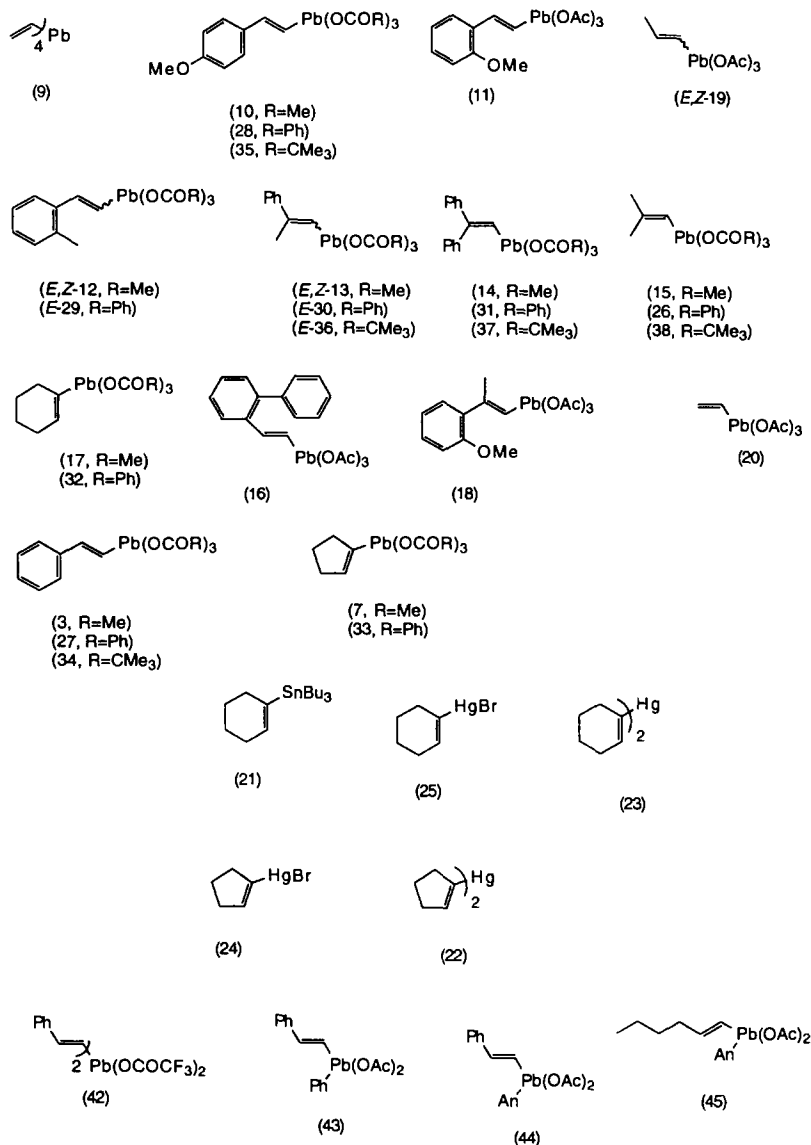

Fig. 1. Comparison of sample Pb–H and H–H coupling constants in cis and trans vinyllead triacetates.

The size of the proton–proton coupling constant in (3) (15.21 Hz) is clearly in the range normally associated with trans double bonds, and later results removed

any doubts about the double-bond configuration, since two cis-lead compounds were observed, and these were found to have normal cis H–H couplings in the range 6–7 Hz, and ^{207}Pb–H$_{trans}$ coupling constants of approximately 1600 Hz (Fig. 1, Table 2). The ^{207}Pb–H couplings are also considerably larger than those for tetravinyllead. This effect has been noted before [10], and is due to the stronger electron withdrawal by the triacetoxyplumbyl group.

The lead compound (20) is of particular interest, because it is the simplest vinyllead triacetate, and all three possible lead–proton coupling constants are observed. Firstly, it can be seen (Table 2) that the largest coupling constant (1671.9 Hz) is that to the proton trans to lead and the smallest (812.8 Hz) that to the proton cis to lead. This is in agreement with the assignments made above for the simple styryllead triacetate (3). The simple derivatives of styryllead triacetate, (10)–(14), (16) and (18), display couplings in the same range as the parent compound (Table 2). Of special note are the isomers of β-methylstyryllead triacetate, (E-13) and (Z-13), which have only one vinylic proton which is geminal to the lead. These also show couplings in the same range as that observed in the other cases, confirming the original assignment.

It is apparent from the results outlined in Table 2, that substituents at the β-position have a large effect on the size of the coupling constant. The largest effect is that on the Pb–H$_{gem}$ coupling constant. Starting with vinyllead triacetate (20), which has a coupling constant of 952.5 Hz, it can be seen that the addition of a methyl group β to lead, as in (E-19), decreases the coupling constant to 931.0 Hz (924.0 Hz in the Z isomer). Addition of a second methyl group in the β-position, as in compound (15), lowers the coupling constant further to 924.1 Hz, whilst replacing the methyl group with a phenyl group has an even greater effect, as in compound (3), resulting in a reduction to 821.3 Hz. When two phenyl groups occupy both β-positions, as in compound (14), then the coupling constant is reduced even more (819.0 Hz). The introduction of one methyl group and one phenyl group, as in the isomers (E-13) and (Z-13), has an intermediate effect. The effect of groups at the ortho-position in the styryl derivatives is also pronounced. The introduction of an ortho-methoxy sub

stituent, as in compound (11), raises the coupling constant to 926.5 Hz, whilst ortho-methyl (E, Z-12) and ortho-phenyl (16) groups have a significant, if somewhat smaller effect. In contrast, the coupling constant for the para-methoxystyryl compound (10) does not differ significantly from those for the simple styryl compound.

Cyclohexen-1-yllead triacetate (17) has a ^3J coupling constant that is approximately the same as the $J_{Pb, H_{cis}}$ coupling constants in the styryl compounds. However, compound (7) has a very much lower ^3J coupling constant (293.9 Hz). This is thought to be due to the ring strain in the five-membered ring. The same effect is observed for the parent stannanes (6) and (21), divinylmercury compounds (22) [6] and (23), and vinylmercury bromides (24) [6] and (25) (Table 3), and also for simple cyclopentenes (5–7 Hz) and cyclohexenes (8.5–11 Hz) [11].

In addition to the above vinyllead triacetates, it was also possible to observe a number of vinyllead triben

Table 4
NMR spectroscopic data for vinyllead tribenzoates (200 MHz)

Compound	J (Hz)		
	H$_{gem}$ to Pb	H$_{cis}$ to Pb	H$_{trans}$ to Pb
(26) [a]	6.58	$J_{Pb,H}$ 933.3	
(27) [b]	7.68, $J_{H,H}$ 14.79	7.51, $J_{H,H}$ 14.79	
	$J_{Pb,H}$ 819.8	$J_{Pb,H}$ 689.0	
(28) [c]	7.57, $J_{H,H}$ 14.46	7.45, $J_{H,H}$ 14.46	
	$J_{Pb,H}$ 829.5	$J_{Pb,H}$ 696.5	
(29) [a]	7.58, $J_{H,H}$ 14.40	7.78, $J_{H,H}$ 14.40	
	$J_{Pb,H}$ 869.4	$J_{Pb,H}$ 707.6	
(30) [d]	7.10, $J_{Pb,H}$ 871.9		
(31) [b]	7.60, $J_{Pb,H}$ 829.5		
(32) [d]		6.34, $J_{Pb,H}$ 732.4	
(33) [a]		6.54, $J_{Pb,H}$ 295.9	

[a] Prepared from tirbutylstannane.
[b] Prepared from divinylmercurcy compound.
[c] Prepared from tributylstannane and trimethylstannane.
[d] Prepared from tributylstannane and divinylmercury compound.

Table 3
$^3J_{X,H}$ coupling constants of metal-substituted cyclopentenes and cyclohexenes

Compound	$J_{X,H}$ (Hz)
(6)	$J_{119Sn,H}$ 35.89, $J_{117Sn,H}$ 34.21
(21)	$J_{119Sn,H}$ 70.74, $J_{117Sn,H}$ 66.99
(22)	$J_{199Hg,H}$ 79
(23)	$J_{199Hg,H}$ 136.21
(24)	$J_{199Hg,H}$ 150
(25)	$J_{199Hg,H}$ 298.31

Table 5
NMR spectroscopic data for vinyllead tripivalates (run at 200 MHz, unless otherwise indicated)

Compound	J (Hz)		
	H$_{gem}$ to Pb	H$_{cis}$ to Pb	H$_{trans}$ to Pb
(34) [a]	7.42, $J_{H,H}$ 14.89	7.26, $J_{H,H}$ 14.89	
	$J_{Pb,H}$ 795.6	$J_{Pb,H}$ 696.5	
(35) [b]	7.28, $J_{H,H}$ 14.86	7.19, $J_{H,H}$ 14.86	
	$J_{Pb,H}$ 799.4	$J_{Pb,H}$ 662.2	
(36) [c]	6.89, $J_{Pb,H}$ 834.7		
(37) [a]	7.34, $J_{Pb,H}$ 789.7		
(38) [d]	6.28, $J_{Pb,H}$ 879.0		

[a] Prepared from divinylmercury compound.
[b] Prepared from tirbutylstannane.
[c] Prepared from tributylstannane and divinylmercury compound.
[d] Prepared from tributylstannane (obtained at 90 MHz).

zoates and tripivalates by monitoring the exchange reactions of the corresponding lead reagents, lead tetrabenzoate and lead tetrapivalate. The results obtained differ only slightly from those obtained for the vinyllead triacetate series (Tables 4 and 5). It can be clearly seen that there is little change in the magnitudes of the Pb–H coupling constants, with only a slight increase for the tribenzoate series, and with a slight decrease in the tripivalate series. There is also a small but consistent downfield shift of the vinylic proton resonances for the tribenzoate series, accompanied by a small, but less consistent, upfield shift for the tripivalate series. These trends are easily accounted for, as they reflect the order of electron-withdrawing ability, with the tribenzoyloxy-plumbyl group the most electron withdrawing, and tripivaloyloxyplumbyl the least electron withdrawing.

As mentioned earlier, compared with aryllead triacetates vinyllead triacetates are extremely unstable species. It had been noted previously [12] that the reaction of (E)-styrylboronic acid (39) gave rise to bis-(E)-styryllead diacetate (40) on boron–lead exchange. Only in the presence of mercury(II) salts, such as mercury(II) acetate, does the boronic acid react normally to give the vinyllead triacetate (3), which then decomposes to the enol acetate (41) (Scheme 4).

Bis-(E)-styryllead diacetate (40) displays Pb–H coupling constants with values between those for tetravinyllead and vinyllead triacetates. This is once again consistent with the known effect of adding successive electron-withdrawing groups to the lead atom [10]. Also of note is the fact that the proton–proton coupling constant (16.21 Hz) is not as small as in the case of all the above styryllead triacetates. In view of the stability of this lead compound the synthesis of a number of divinyl and mixed aryl-vinyllead diacetates was attempted, and a representative number of these are listed in Table 6, along with their ^{1}H–^{1}H and ^{207}Pb–^{1}H coupling constants. Bis-(E)-styryllead bistrifluoroacetate (42) was readily obtained from bis-(E)-styryllead diacetate (40) by treatment with trifluoroacetic acid.

Diaryllead diacetates with equivalent aryl residues are well known [13] and have been used in organic synthesis [14], but mixed or unsymmetrical diorganolead
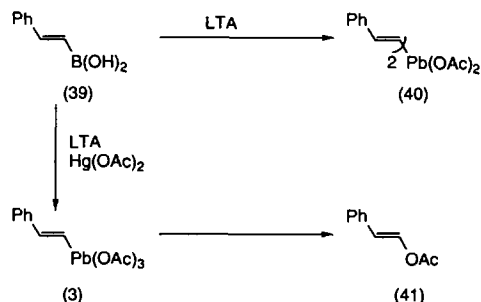
Table 6
^{1}H NMR spectroscopic data (obtained at 400 MHz, unless otherwise indicated) for the vinylic protons of diorganolead dicarboxylates

Compound	J (Hz)		
	H_{gem} to Pb	H_{cis} to Pb	H_{trans} to Pb
(40) [a]	7.59, $J_{H,H}$ 16.21	7.43, $J_{H,H}$ 16.21	
	$J_{Pb,H}$ 433.1	$J_{Pb,H}$ 339.9	
(42)	7.82, $J_{H,H}$ 16.00	7.62, $J_{H,H}$ 16.00	
	$J_{Pb,H}$ 430.0	$J_{Pb,H}$ 340.0	
(43)	7.55, $J_{H,H}$ 16.20	7.46, $J_{H,H}$ 16.20	
	$J_{Pb,H}$ 428.0	$J_{Pb,H}$ 380.0	
(44)	7.66, $J_{H,H}$ 16.00	7.44, $J_{H,H}$ 16.00	
	$J_{Pb,H}$ 430.0	$J_{Pb,H}$ 340.0	
(45)	6.82, $J_{H,H}$ 15.80	6.59, $J_{H,H}$ 15.80	
	$J_{Pb,H}$ 500.0	$J_{Pb,H}$ 320.0	

[a] Obtained at 200 MHz.

diacetates were previously unknown. We had shown that arylboronic acids were useful precursors of diaryllead diacetates [12,15], and the aryllead triacetate was clearly an intermediate in their formation. It appeared likely that treatment of an isolated aryllead triacetate with a vinylboronic acid would produce a mixed aryl(vinyl)lead diacetate, and this was indeed found to be the case, with the compounds (43), (44) and (45) being readily made in this way. The yields were generally good, and the products relatively stable.

It can be seen that the magnitude of the ^{207}Pb–^{1}H and ^{1}H–^{1}H coupling constants does not vary much for the series, except in the case of the aliphatic substituted compound (45). This increase in the size of the ^{207}Pb–^{1}H$_{gem}$ coupling constant is analogous to that observed for the vinyllead triacetates described above.

3. Experimental

The following compounds were prepared as described earlier [2,4–6,16] Tributyl-(E)-styrylstannane [2], tributyl-(E)-p-methoxystyrylstannane [2], tributyl-(E)-o-methoxystyrylstannane [4], tributyl-(E,Z)-methylstyrylstannane [4], tributyl(2-methylpropen-1-yl)stannane [4], tributylcyclohexen-1-ylstannane (21) [4], tributylcyclopenten-1-ylstannane (6) [2], tributyl-(E,Z)-propen-1-ylstannane [4], tributyl-(E)-o-phenyl-styrylstannane [5], tributyl-[(E)-α-methyl-o-methoxy-styryl]stannane [5], bis-(E)-styrylmercury (1) [2], bis-(E)-α-methylstyrylmercury [2], bis-(E)-α-phenylstyryl-mercury [2], bis(2-methylpropen-1-yl)mercury [2], cyclohexen-1-ylmercury bromide [6], phenyllead triacetate [3a], and methoxyphenyllead triacetate [16].

General experimental procedures were described earlier [2]. Deuterochloroform, used for mercury–lead and tin–lead exchange reactions, was passed through a short column of basic alumina and stored over type 4 Å

Scheme 4.

molecular seives. Lead tetraacetate was obtained from Merck, and freed from acetic acid under high vacuum immediately prior to use. Lead tetrabenzoate and lead tetrapivalate were prepared by the general method described by Hey et al. [17]. In addition to the NMR spectrometers listed previously [2], a Bruker AC-200F spectrometer was used for some of the ^{1}H NMR spectra.

3.1. Preparation of (Z)-1-bromo-2-(o-methylphenyl)ethene

A solution of N,N-dimethylformamide (27 ml, 0.350 mol) in dry ether (200 ml) was added dropwise during 20 min to the Grignard reagent prepared from o-bromotoluene (40 ml, 0.333 mol) and magnesium turnings (9.7 g, 0.399 mol) in dry ether (400 ml). The solution was refluxed for 1 h, cooled and quenched with hydrochloric acid (3 M, 400 ml). The ethereal layer was separated, washed with water (400 ml) and brine (100 ml), dried (Na$_2$SO$_4$), and filtered and the solvent was removed by distillation. The residue was fractionally distilled to yield o-methylbenzaldehyde (24.51 g, 61%) as a colourless oil, b.p. 110 °C/40 mmHg (lit. value [18] 199–200 °C).

A solution of malonic acid (53.07 g, 0.51 mol) and o-methylbenzaldehyde (24.51 g, 0.20 mol) in a mixture of pyridine (100 ml) and piperidine (5 ml) was refluxed for 3 h, then poured onto a mixture of ice (200 g) and hydrochloric acid (10 M, 300 ml). The mixture was stirred at 0 °C for 30 min and the solid was collected and dried at the pump, then recrystallized from ethanol to yield o-methylcinnamic acid (23.7 g, 73%) as colourless needles, m.p. 173 °C (lit. value [19] 174–175 °C). ^{1}H NMR (90 MHz, CDCl3 + DMSO-d$_6$): 2.56 (s, CH$_3$), 6.25 (d, J 15.8 Hz, H2), 7.02–7.25 (m, 3H, ArH), 7.49 (m, 1H, ArH), 7.77 (d, J 15.8 Hz, H3), 9.8 (bs, COOH).

To a stirred solution of o-methylcinnamic acid (1.40 g, 8.6 mmol) in dry chloroform (10 ml) was added during 30 min a solution of bromine (0.5 ml, 9.7 mmol) in dry chloroform (3 ml). The mixture was stirred at room temperature for 4 h, washed with sodium bisulfite solution (5%, 50 ml) and brine (20 ml), dried (Na$_2$SO$_4$), filtered, and the solvent was removed to yield 2,3-dibromo-3-(o-methylphenyl)propanoic acid (2.53 g, 91%) as a pale yellow solid, m.p. 157–159 °C. Anal.: Calc. for C$_{10}$H$_{10}$Br$_2$O$_2$: C, 37.3; H, 3.1. Found: C, 37.5; H, 3.1%. UV (ethanol) 279(sh), 272(sh), 238, 202 nm (1223, 1654, 4350, 21183). IR (chloroform) 1729 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$ + DMSO-d$_6$): 2.44 (s, CH$_3$), 4.99 (d, J 11.70 Hz, H2), 5.65 (d, J 11.70 Hz, H3), 7.11–7.30 (m, 3H, ArH), 7.45 (m, 1H, ArH), 9.11 (bs, COOH). The sample contained 13% of the other diastereomer (doublet at 5.50, J 10.33 Hz, the other peak was under H2 of the major diastereomer, methyl group at 2.43). ^{13}C NMR (50 MHz, CDCl$_3$): 19.78 (CH$_3$), 45.78 (2 × CHBr), 126.94 (ArCH), 127.11 (ArCH), 129.23 (ArCH), 130.90 (ArCH), 135.00 (ArC), 137.22 (ArC), 172.26 (CO$_2$H). (m/z) 324(M + + 4, < 1%), 322(M$^+$ +2, 1%), 320(M$^+$, < 1%).

A mixture of 2,3-dibromo-3-(o-methylphenyl)propanoic acid (1.5 g, 4.7 mmol) and potassium carbonate (1.6 g, 11.6 mmol) in acetone (20 ml) was refluxed for 3 h, and the solvent was then removed. The residue was shaken with a mixture of water (30 ml) and ether (30 ml) and the ethereal layer was separated, washed with brine (10 ml), dried (Na$_2$SO$_4$), and filtered, and the solvent was removed. The residue was distilled (Kugelrohr) to yield (Z)-1-bromo-2-(o-methylphenyl)ethene (0.69 g, 75%) as a pale yellow oil, b.p. 53 °C/0.8 mmHg. Anal.: Calc. for C$_9$H$_9$Br: C, 54.9; H,4.6. Found: C, 54.9; H, 4.6%. UV (ethanol) 247, 206 nm (10097, 20945). IR (liquid film) 1674 (C=C) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): 2.23 (s, CH$_3$), 6.46 (d, J 7.90 Hz, =CHBr), 7.09 (d, J 7.90 Hz, ArCH=), 7.08–7.29 (m, 3H, ArH), 7.54 (m, 1H, ArH). ^{13}C NMR (50 MHz, CDCl$_3$): 19.97 (CH$_3$), 108.62 (=CHBr), 125.61 (ArCH), 128.44 (ArCH), 128.86 (ArCH), 130.15 (ArCH), 132.19 (ArCH=), 135.66 (ArC), 136.33 (ArC). (m/z) 198(M$^+$ +2, 22%), 196(M$^+$, 24).

3.2. Synthesis of tributylvinylstannanes

The following compounds were prepared by the general procedure described previously [2].

(i) Tributyl[(Z)-o-methylstyryl]stannane was prepared in 86% yield as a pale yellow oil, b.p. 180 °C/0.6 mmHg. Anal.: Calc. for C$_{21}$H$_{36}$Sn: C, 61.9; H, 8.9. Found: C, 62.1; H, 8.8%. UV (ethanol) 248, 202 nm (7460, 24073). IR (liquid film) 1566 (C=C) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): 0.70 (t, J 8.29 Hz, 3 × SnCH$_2$–), 0.83 (t, J 7.11 Hz, 3 × CH$_3$), 1.15–1.26 (m, 3 × CH$_2$), 1.26–1.42 (m, 3 × CH$_2$), 2.26 (s, ArCH$_3$), 6.23 (d, J 13.50 Hz, =CHSn), 7.07–7.19 (m, 3H, ArH), 7.47 (bd, J 7.59 Hz, ArH), 7.65 (d, J 13.50 Hz, $J_{119Sn, CH}$ 136.70 Hz, $J_{117Sn, CH}$ 131.10 Hz (relative area, 16%), ArCH=). ^{13}C NMR (50 MHz, CDCl$_3$): 9.80 (C4), 12.77 (C1), 18.74 (ArCH$_3$), 26.38 (C2 or C3), 28.13 (C2 or C3), 124.81 (ArCH), 126.38 (ArCH), 126.58 (ArCH), 128.54 (ArCH), 132.29 (C5), 134.85 (C7 or C8), 140.56 (C7 or C8), 146.16 (C). (m/z) 408(M$^+$, 0.2%). This sample contained 22% of the E-isomer as shown by ^{1}H NMR (400 MHz, CDCl$_3$): 0.91 (t, J 7.11 Hz, 3 × CH$_3$), 0.97 (t, J 8.29 Hz, 3 × SnCH$_2$–), 1.26–1.42 (m, 3 × CH$_2$), 1.49–1.64 (m, 3 × CH$_2$), 2.36 (s, ArCH$_3$), 6.71 (d, J 19.50 Hz, =CHSn), 7.07–7.19 (m, 5H, ArH + ArCH=). ^{13}C NMR (50 MHz, CDCl$_3$): 8.79 (C4), 12.83 (C1), 18.74 (ArCH3), 26.38 (C2 or C3), 28.28 (C2 or C3), 124.33 (ArCH), 125.16 (ArCH), 126.40

(ArCH), 129.30 (ArCH), 130.34 (C5), 133.78 (C7 or C8), 137.55 (C7 or C8), 143.30 (C6).

(ii) (E)-p-methoxystyryltrimethylstannane was prepared in 86% yield as a colourless oil, b.p. 120 °C/0.9 mmHg (lit. value [20] m.p. 34–5 °C, b.p. 104 °C/0.6 mmHg). ^{1}H NMR (200 MHz, CDCl$_3$): 0.10 (s, SnMe$_3$), 3.68 (s, OCH$_3$), 6.60 (d, J 19.40 Hz, H1), 6.74 (d, J 19.40 Hz, H2), AA'BB' system: 6.75 (d, $J_{AB} + J_{AB'}$ 8.80 Hz, ArH), 7.25 (d, $J_{AB} + J_{AB'}$ 8.80 Hz, ArH).

3.3. Preparation of tributyl(ethenyl)stannane

To a stirred solution of tri-n-butyltin chloride (3 g, 9.2 mmol) in dry tetrahydrofuran (10 ml) under nitrogen at 0 °C was added a solution of vinylmagnesium bromide in tetrahydrofuran (1.0 M, 18 ml, 18 mmol). The mixture was warmed to room temperature, refluxed for 18 h then cooled to 0 °C. Ammonium chloride (1 g, 19 mmol) was added and the mixture was stirred for 30 min. The solution was diluted with light petroleum (30 ml) and filtered through Celite. The solvent was removed and the residue distilled (Kugelrohr) to yield tributyl(ethenyl)stannane (2.07 g, 71%) as a colourless oil, b.p. 105 °C/2 mmHg (lit. value [21] 95 °C/1.5 mmHg). ^{1}H NMR (200 MHz, CDCl$_3$): 0.71–1.69 (m, 3 × Bu), 5.65 (dd, J 20.69 Hz, J 3.75 Hz, =CH–), 6.15 (dd, J 14.10 Hz, J 3.75 Hz, =CH–), 6.47 (dd, J 20.69 Hz, J 14.10 Hz, =CH–Sn).

3.4. Preparation of vinylboronic acids

(E)-Styrylboronic acid and (E)-1-hexenylboronic acid were prepared via the reaction of phenylacetylene and 1-hexyne with catechol borane in 71% and 62% overall yields respectively by the method of Brown [22].

3.5. Preparation of diorganolead dicarboxylates

3.5.1. Bis-(E)-styryllead diacetate (40)

(E)-Styrylboronic acid (591 mg, 4.00 mmol) was added to a stirred solution of lead tetraacetate (887 mg, 2.00 mmol) in chloroform (8 ml) at room temperature. The solution was stirred at room temperature for 1 h then filtered through Celite. The filtrate was concentrated to 2 ml, diluted with light petroleum (50 ml) and cooled to 0 °C. The title compound (828 mg, 78%) was collected at the pump as a white solid, m.p. 196–198 °C (dec.). Anal.: Calc. for C$_{20}$H$_{20}$O$_4$Pb: C, 45.2; H, 3.8. Found: C, 44.9; H, 3.7%. UV (CH$_3$CN) 265 (47300). IR (CHCl$_3$) 1570 (C=C) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): 2.08 (s, 2 × OAc), 7.18 (4H, m, ArH), 7.22–7.29, 6H, m, ArH), 7.43 (2H, d, J 16.20 Hz, JPb, H 339.9 Hz, 2 × CH=CHPb), 7.59 (2H, d, J 16.20 Hz, J_{Pb}, H 433.1 Hz, 2 × CH=CHPb). ^{13}C NMR (100 MHz, CDCl$_3$): 23.0 (2 × OCOCH$_3$), 127.3 (4 × ArCH),

128.7 (4 × ArCH), 129.7 (2 × CH=CHPb), 135.4 (2 × ArC), 146.4 (2 × ArCH), 148.6 (2 × CH=CHPb), 181.9 (2 × OCOCH$_3$)

3.5.2. Bis-(E)-styryllead bistrifluoroacetate (42)

Trifluoroacetic acid (285 mg, 2.50 mmol) was added to a solution of bis-(E)-styryllead diacetate (530 mg, 1.00 mmol) in chloroform (5 ml) at room temperature. The solution was cooled to 0 °C and the title compound (580 mg, 91%) was collected at the pump as a white solid, m.p. 219–222 °C (dec.). This material was unstable unless kept under nitrogen or argon and underwent protodemetallation rapidly in the presence of moisture. ^{1}H NMR (400 MHz, CDCl$_3$ + DMSO-d$_6$): 7.33–7.41 (6H, m, ArH), 7.45–7.49, 4H, m, ArH), 7.62 (2H, d, J 16.00 Hz, J_{Pb}, H 340.0 Hz, 2 × CH=CHPb), 7.82 (2H, d, J 16.00 Hz, J_{Pb}, H 430.0 Hz, 2 × CH=CHPb). ^{13}C NMR (100 MHz, CDCl$_3$ + DMSO-d$_6$): 120.8 (2 × OCOCF$_3$), 127.4 (4 × ArCH), 128.8 (4 × ArCH), 129.7 (2 × CH=CHPb), 135.4 (2 × ArC), 145.4 (2 × ArCH), 152.5 (2 × CH=CHPb), 163.0 (2 × OCOCF$_3$).

3.5.3. (E)-Styryl(phenyl)lead diacetate (43)

(E)-Styrylboronic acid (359 mg, 2.43 mmol) was added to a solution of phenyllead triacetate (1.018 g, 2.21 mmol) in chloroform (30 ml). The solution was stirred at room temperature for 18 h, filtered through Celite, concentrated to 5 ml and diluted with light petroleum (50 ml). The solution was kept at 0 °C for 24 h. The title compound (912 mg, 82%) was collected at the pump as cream needles, m.p. 183–185.5 °C. Anal.: Calc. for C$_{18}$H$_{18}$O$_4$Pb: C, 43.0; H, 3.7. Found: C, 42.8; H, 3.6%. IR (CHCl$_3$) 1574 (C=C) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): 2.05 (s, 2 × OCOCH$_3$), 7.30–7.45 (8H, m, ArH), 7.46 (d, J 16.20 Hz, J_{Pb}, H 380.0 Hz, CH=CHPb), 7.55 (d, J 16.20 Hz, J_{Pb}, H 428.0 Hz, CH=CHPb), 7.72 (2H, d, J 7.00 Hz, 2 × ArH ortho to Pb). ^{13}C NMR (100 MHz, CDCl$_3$): 22.8 (2 × OCOCH$_3$), 127.4 (2 × ArCH), 128.6 (2 × ArCH), 129.7 (CH=CHPb), 130.7 (2 × ArCH), 130.8 (2 × ArCH), 133.8 (ArCH), 135.8 (ArCH), 146.9 (ArC), 148.7 (CH=CHPb), 161.7 (ArC–Pb), 181.9 (2 × OCOCH$_3$).

3.5.4. Preparation of (E)-styryl(p-methoxyphenyl)lead diacetate (44)

(E)-Styrylboronic acid (400 mg, 2.68 mmol) was added to a solution of p-methoxyphenyllead triacetate (1.20 g, 2.44 mmol) in chloroform (12 ml) and the mixture was stirred at room temperature for 4 h. The solution was filtered through Celite and the filtrate concentrated to 2 ml. The residue was dispersed in light petroleum (50 ml) and the mixture kept at 4 °C for 40 h. The title compound was collected at the pump as a white solid, m.p. 205–208 °C (dec.). Anal.: Calc. for C$_{19}$H$_{20}$O$_5$Pb: C, 42.6; H, 3.8. Found: C, 42.3; H, 3.7%. IR (CHCl$_3$) 1572 (C=C) cm^{-1}. ^{1}H NMR (400 MHz,

CDCl$_3$): 1.98 (s, 2 × OCOCH$_3$), AA'BB' system: 7.04 (d, $J_{AB} + J_{AB'}$ 8.00 Hz, ArH ortho to OCH$_3$), 7.78 (d, $J_{AB} + J_{AB'}$ 8.00 Hz, ArH meta to OCH$_3$), 7.44 (d, J 16.00 Hz, J_{Pb}, H 340.0 Hz, CH=CHPb), 7.31–7.48 (5H, m, ArH), 7.66 (d, J 16.00 Hz, J_{Pb}, H 430.0 Hz, CH=CHPb). ^{13}C NMR (100 MHz, CDCl$_3$): 23.0 (2 × OCOCH$_3$), 55.1 (OCH$_3$), 115.2 (2 × ArCH), 127.0 (×xArCH), 128.6 (2 × ArCH), 129.0 (CH=CHPb), 134.2 (2 × ArCH), 135.9 (ArC), 143.3 (ArCH), 153.1 (CH=CHPb), 156.2 (ArC–OCH$_3$), 160.7 (ArC–Pb), 181.0 (2 × OCOCH$_3$).

3.5.5. Preparation of (E)-1-hexenyl(p-methoxyphenyl)-lead diacetate (45)

(E)-1-Hexenylboronic acid (486 mg, 3.80 mmol) was added to a stirred solution of p-methoxyphenyllead triacetate (1.70 g, 3.46 mmol) in chloroform (15 ml). The mixture was stirred at room temperature for 24 h then filtered through Celite, and the filtrate concentrated to 3 ml. The residual oil was diluted with light petroleum (60 ml) and the mixture kept at −20 °C for 24 h. The title compound (1.31 g, 74%) was collected at the pump as a slightly unstable white solid, m.p. 127–129 °C (dec.). Anal.: Calc. for C$_{17}$H$_{24}$O$_5$Pb: C, 39.6; H, 4.7. Found: C, 39.6; H, 4.7%. IR (CHCl$_3$) 1572 (C=C) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): 0.90 (t, J 6.80 Hz, CH$_3$), 1.34 (tq, J 7.20, J 6.80 Hz, CH$_2$CH$_3$), 1.43 (tt, J 7.60, J 7.20 Hz, CH$_2$CH$_2$CH$_3$), 2.02 (2 × OCOCH$_3$), 2.22 (ddt, J 6.90, J 1.50, J 7.60 Hz, CH$_2$–CH=CH), 3.80 (s, OCH$_3$), 6.59 (dt, J 15.80, J 6.9 Hz, J_{Pb}, H 320.0 Hz, CH=CHPb), 6.82 (dt, J 15.8, J 1.50 Hz, J_{Pb}, H 500.0 Hz, CH=CHPb), AA'BB' system: 7.02 (d, $J_{AB} + J_{AB'}$ 8.90 Hz, ArH ortho to OCH$_3$), 7.63 (d, $J_{AB} + J_{AB'}$ 8.90 Hz, ArH meta to OCH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): 13.7 (CH$_3$), 22.1 (CH$_2$), 22.7 (2 × OCOCH$_3$), 30.2 (CH$_2$), 35.3 (CH$_2$), 55.3 (OCH$_3$), 116.0 (2 × ArCH ortho to OCH$_3$), 135.4 (2 × ArCH meta to OCH$_3$), 148.4 (CH=CHPb), 151.5 (CH=CHPb), 152.8 (ArC–OCH$_3$), 161.5 (ArC–Pb), 181.9 (2 × OCOCH$_3$).

3.6. Analysis of vinyllead tricarboxylates by ^{1}H NMR spectroscopy

The exchange reactions were generally carried out with ca. 50 mg of the stannane or mercurial in dry deuterochloroform (0.4 ml). NMR spectra were recorded under conditions that gave a signal-to-noise ratio sufficient to allow clear observation of the tin or mercury satellites. When Fourier transform NMR spectrometers were used, this commonly involved about 64 scans. It was important to limit the sample size, otherwise the exchange reaction produced an almost solid sample, and the resolution was poorer. After the required parameters had been determined the sample was treated with a solution of the lead reagent in the minimum volume of solvent. Spectra were repeatedly recorded as rapidly as possible for the first 10 min, and after 1 h and 24 h. It was generally found that the resolution deteriorated immediately after the addition, but it recovered after a few minutes. Thus if the lead compound was relatively stable, it was possible to obtain very clean spectra. However, if the vinyllead compound was at all unstable, then the first spectrum obtained, generally of lower quality, had to be used.

References

[1] E.J. Corey and R.H. Wollenberg, J. Am. Chem. Soc., 96 (1974) 5581.
[2] M.G. Moloney and J.T. Pinhey, J. Chem. Soc. Perkin Trans. 1, 10 (1988) 2847.
[3] (a) R.P. Kozyrod, J. Morgan and J.T. Pinhey, Aust. J. Chem., 38 (1985) 1147; (b) R.P. Kozyrod, and J.T. Pinhey, Tetrahedron Lett., 24 (1984) 1301; (c) H.C. Bell, J.T. Pinhey and S. Sternhell, Aust. J. Chem., 32 (1979) 1551; (d) H.C. Bell, G.L. May, J.T. Pinhey and S. Sternhell, Tetrahedron Lett., 47 (1976) 4303; (e) J.T. Pinhey and B.A. Rowe, Aust. J. Chem., 32 (1979) 1561; (f) J.T. Pinhey and B.A. Rowe, Aust. J., (1984) 1245; (h) D.J. Ackland and J.T. Pinhey, J. Chem. Soc. Perkin Trans. 1, 12 (1987) 2695.
[4] M.G. Moloney, J.T. Pinhey and M.J. Stoermer, J. Chem. Soc. Perkin Trans. 1, 10 (1990) 2645.
[5] J.T. Pinhey and M.J. Stoermer J. Chem. Soc. Perkin Trans. 1, 10 (1991) 2455.
[6] M.G. Moloney, Ph.D. Thesis, 1985, University of Sydney.
[7] S. Cawley and S.S. Danyluk, J. Phys. Chem., 68 (1964) 1240.
[8] S. Cawley and S.S. Danyluk, Can. J. Chem., 46 (1968) 2373.
[9] P. Krebs and H. Dreeskamp, Spectrochim. Acta (A), 25 (1969) 1399.
[10] P. de Vos, H.O. van der Kooi, J. Wolters and A. van der Gen, Recl. Trav. Chim. Pays-Bas, 91 (1972) 1465.
[11] E. Pretsch, T. Clerc, J. Seibl and W. Simon, Spectral Data for Structure Determination of Organic Compounds, 2nd edn., Springer-Verlag, 1989.
[12] J. Morgan, M.Sc. Thesis, 1989, University of Sydney.
[13] D. de Vos, A.A. van Barneveld, D.C. van Beelen and J. Wolters, Recl. Trav. Chim. Pays-Bas, 98 (1979) 202.
[14] D.H.R. Barton, N.Y. Bhatnagar, J.-P. Finet and J. Khamsi, Tetrahedron Lett., 28 (1987) 3111.
[15] J. Morgan and J.T. Pinhey, J. Chem. Soc. Perkin Trans. 1, 3 (1990) 715.
[16] R.P. Kosyrod and J.T. Pinhey, Organic Syntheses, 62 (1984) 24.
[17] D.H. Hey, C.J.M. Stirling and G.H. Williams, J. Chem. Soc., (1954) 2747.
[18] E. Bornemann, Chem. Ber., 17 (1884) 1162.
[19] K. v. Auwers, Ann., 413 (1917) 265.
[20] A. Alvanipour, C. Eaborn and D.R.M. Walton, J. Organomet Chem., 201 (1980) 233.
[21] D. Seyferth and F.G. Stone, J. Am. Chem. Soc., 79 (1957) 515.
[22] H.C. Brown and S.K. Gupta, J. Am. Chem. Soc., 97 (1975) 5249.