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Electrophilic Metal-Alkyl Bond Cleavage in Tetraorganosilicon and Tetraorganotin Compounds by Lead Tetracarboxylates and Aryllead Tricarboxylates

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Dedicated to the memory of Professor Sir Derek Barton

Abstract: Methyl-silicon bond cleavage of tetramethylsilane occurs with aryllead(IV) tricarboxylates in trifluoroacetic acid to produce aryl(methyl)lead(IV) bistrifluoroacetates in high yield. An extension of the study to tetraalkylstannanes has shown that alkyl-tin cleavage by lead(IV) carboxylates proceeds even in chloroform, while a detailed study of the reactions of lead tetraacetate with tetraalkylstannanes indicated the reaction to be an electrophilic cleavage rather than one involving an electron transfer mechanism.

Introduction

Some years ago we reported[1] the synthesis of a number of *m*- and *p*-halophenyllead triacetates by a new method, which involved the treatment of the corresponding aryltrimethylsilane with lead tetraacetate in trifluoroacetic acid, followed after a short time by addition of a large volume of acetic acid (Scheme 1). The reaction was unsuccessful with silanes containing more electron rich aromatic groups than these since conversion of the aryllead compound to the aryl trifluoroacetate, which occurs in trifluoroacetic acid,[2] was too rapid for it to be trapped as the relatively stable triacetate. With strong electron withdrawing groups such as NO_2 and CF_3 in the aromatic ring, the method was unsuccessful due to failure of the *ipso* electrophilic substitution by lead. In compounds of this type, cleavage of the silicon-methyl bond, which occurs to a minor extent with the p-halophenyltrimethylsilanes, becomes the

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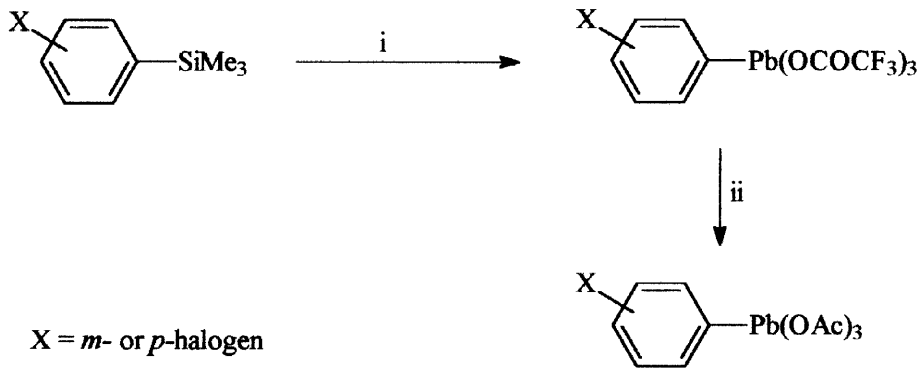
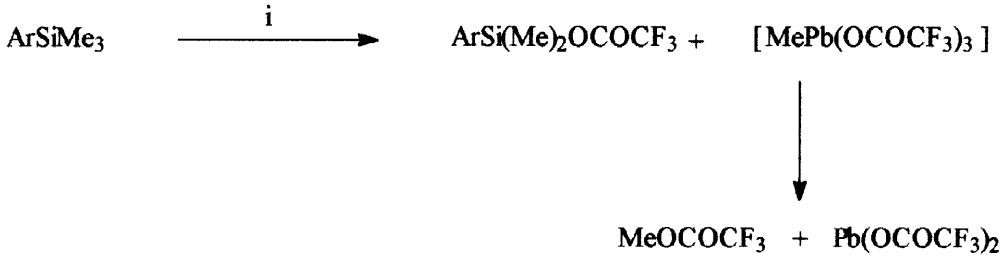
predominant reaction (Scheme 2).[1] A similar methyl cleavage occurs when tetramethylsilane is treated with lead tetrakistrifluoroacetate.[3]



Scheme 1 *Reagents:* i, $Pb(OAc)_4$, CF_3CO_2H; ii, CH_3CO_2H



Scheme 2 *Reagents:* i, $Pb(OAc)_4$, excess CF_3CO_2H

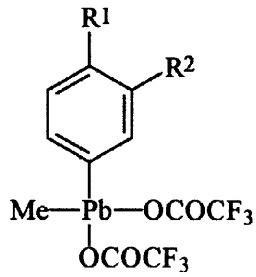
Results and Discussion

While recording the ^1H NMR spectra of aryllead tricarboxylates, we found that under certain conditions tetramethylsilane underwent a similar methyl cleavage to that noted in the last reaction above. Although the spectra of the aryllead compounds could be recorded in deuterochloroform with tetramethylsilane as internal standard, when an attempt was made to obtain spectra in trifluoroacetic acid, they reacted rapidly with the tetramethylsilane to give aryl(methyl)lead bistrifluoroacetates and trifluoroacetoxy(trimethyl)silane (Scheme 3). The reaction, which proceeds quantitatively, appears to be

quite general, and ^{1}H NMR parameters for the aryl(methyl)lead bistrifluoroacetates **1** - **7** generated in this way are given in Table 1. All showed a methyl proton resonance at δ 3.1 - 3.3 p.p.m. with a ^{207}Pb to CH_3 coupling constant of 135-140 Hz. Two of the compounds, **1** and **2**, were isolated and their analytic and spectroscopic data were in agreement with the proposed structures.

$$ArPb(OCOCF_3)_3 + Me_4Si \xrightarrow{TFA} Ar(Me)Pb(OCOCF_3)_2 + Me_3SiOCOCF_3$$

Scheme 3



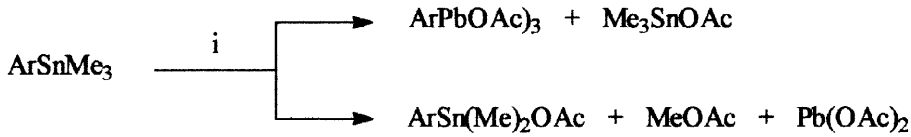
1 $R^1 = F$, $R^2 = H$
2 $R^1 = NHCOCF_3$, $R^2 = H$
3 $R^1 = Cl$, $R^2 = H$,
4 $R^1 = Br$, $R^2 = H$
5 $R^1 = CF_3$, $R^2 = H$
6 $R^1 = H$, $R^2 = F$
7 $R^1 = H$, $R^2 = Br$

The formation of aryl(methyl)lead(IV) compounds in the reactions of aryllead tristrifluoroacetates with tetramethylsilane would suggest that methyllead tristrifluoroacetate is probably an initial product in the reactions of aryl(trimethyl)silanes (Scheme 2) and tetramethylsilane with lead tetrakistrifluoroacetate. Since alkyllead tricarboxylates are known to be very unstable,[4] such a product would be expected to collapse to the observed products, methyl trifluoroacetate and lead(II) trifluoroacetate.

Table 1. ^{1}H NMR data for aryl(methyl)lead bistrifluoroacetates in trifluoroacetic acid.

Compound	Methyl resonance (ppm ex TMS)	^{207}Pb,Me Coupling (Hz)
1	3.12	137
2	3.19	138
3	3.17	136
4	3.20	136
5	3.24	138
6	3.24	135
7	3.22	137

In a previous paper[5] we reported that the treatment of aryl(trimethyl)stannanes with lead tetraacetate results in both aryl-tin and methyl-tin cleavage as shown in Scheme 4, and for *o*-methoxyphenyl(trimethyl)stannane it was found that the rates of the two reactions were comparable.

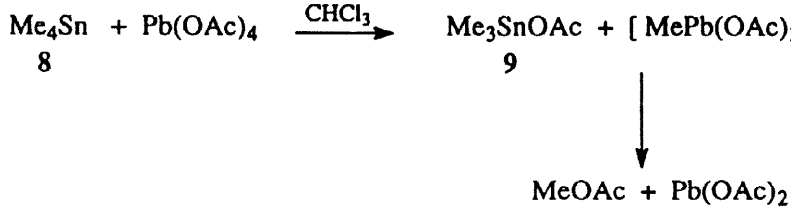


Scheme 4 *Reagent:* i, $Pb(OAc)_4$

However, in the case of aryl(tributyl)stannanes the alkyl-tin cleavage was considerably reduced, and the reaction of these compounds with lead tetraacetate has been developed as a convenient general route to aryllead triacetates.

Because the above results indicated a similarity in the reactions of silanes and stannanes with lead(IV) carboxylates, we extended our study to a number of tetraalkylstannanes. Tetramethyltin **8** was found to be considerably more reactive than the corresponding silane which underwent methyl cleavage with lead tetraacetate in trifluoroacetic acid but failed to react in acetic acid or chloroform. The stannane

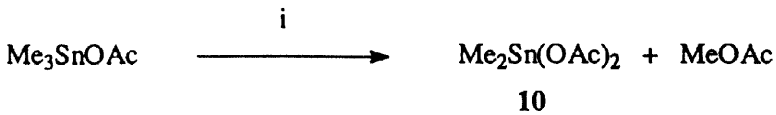
8 reacted with lead tetraacetate even in chloroform, and when the reaction was followed by ^{1}H NMR spectroscopy (28°C, 10% in $CDCl_3$) with a 50% excess of lead tetraacetate, there was no signal due to compound 8 after 3 h. The ^{1}H NMR spectrum showed resonances due to trimethyltin acetate 9 and methyl acetate, which were produced in over 90% yield, and when carried out on a preparative scale compound 9 was isolated in high yield. We believe that, as with the silanes the other products, methyl acetate and lead(II) acetate, arise from methyllead triacetate as shown in Scheme 5.



8 9

Scheme 5

A small amount (<2%) of dimethyltin diacetate 10 was also produced in the above NMR monitored reaction, and after 7 days a substantial amount of it had been produced. This slow methyl-tin cleavage of compound 9 by lead tetraacetate was examined by ^{1}H NMR spectroscopy, and it was found that with 90% excess lead tetraacetate approximately 10% of compound 9 had reacted after 4 h, while the reaction (Scheme 6) was complete within 5 days. Under these conditions the tin compound 10 was quite unreactive towards lead tetraacetate, and therefore it is readily isolated in good yield from preparative scale reactions.



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Scheme 6 *Reagents and conditions:* i, $Pb(OAc)_4$, $CHCl_3$, room temperature

To examine the generality of this lead tetraacetate cleavage of alkyltin compounds we carried out an ^{1}H NMR spectroscopic study of the reactions of tetraethyltin, tetrabutyltin and tetraisopropyltin in

chloroform as outlined under the conditions used above for tetramethyltin. Tetraethyltin was slightly slower to react than tetramethyltin **8**, giving triethyltin acetate and ethyl acetate in high yield after 4 h. There was no evidence for the formation of diethyltin diacetate in this reaction, and even after 3 days there had been only slight further reaction of the triethyltin acetate. Tetrabutyltin was considerably slower to react than the tetraethyl compound, 50% being unreacted after 4 h. Nevertheless, the reaction proceeded cleanly to give tributyltin acetate and butyl acetate in high yield within 71 h. There was no indication of further butyl-tin cleavage occurring in this case. Tetraisopropyltin showed no reactivity towards lead tetraacetate in chloroform, being unchanged after 3 days. Thus the reactivity for the cleavage of the alkyl group in tetraalkylstannanes by lead tetraacetate is Me>Et>Bu>>>i-Pr, which is the same as that observed for their cleavage by halogens,[6] and in keeping with the ordering expected for electrophilic cleavage rather than that suggesting a reaction involving an electron transfer mechanism.[7]

Experimental

General experimental procedures were described earlier.[8] Previously reported methods were used to obtain *p*-fluorophenyllead tristrifluoroacetate,[9,10] *p*-trifluoroacetamidophenyllead tristrifluoroacetate,[1] *p*-chlorophenyllead triacetate,[1] *p*-bromophenyllead triacetate,[1] *p*-trifluoromethylphenyllead tristrifluoroacetate,[1] *m*-fluorophenyllead triacetate[1] *m*-bromophenyllead triacetate[1] and tetraisopropyltin,[11] while tetrabutyltin and tetraethyltin were purchased from Sigma-Aldrich Pty Ltd. Trimethyltin acetate [δ_H (ppm) ($CDCl_3$) 0.54 (3H), 2.02 (3H) and a pair of ^{117}Sn and ^{119}Sn satellites, giving $J_{Me,Sn}$ of 56.5 and 59.0 Hz] was prepared by reaction of trimethyltin chloride with silver acetate in tetrahydrofuran and purified by sublimation. Lead tetraacetate was obtained from Merck, and was freed from acetic acid under high vacuum immediately prior to use.

Preparation of tetramethyltin

Trimethyltin chloride (47.0 g, 0.237 mol) in dry diethyl ether (50 mL) was added over 20 min to a solution of methylmagnesium iodide (1.15 equiv) in diethyl ether (100 mL) at reflux, and the mixture was heated for a further 30 min at reflux. Water (30 mL) was added dropwise to the mixture and the ether layer was then washed in turn with 3 M sulfuric acid (75 mL), saturated aqueous sodium bicarbonate (75 mL) and brine (75 mL). The solvent was evaporated and the residue was fractionated by distillation to yield tetramethyltin (15.1 g, 36%), b.p. 75-77°C/760 mmHg (lit.[12] 75-77°C/720 mm)

Reaction of p-*fluorophenyllead tristrifluoroacetate and tetramethylsilane in trifluoroacetic acid*

Polymeric *p*-fluorophenyllead tristrifluoroacetate[1] (1.55 g) was dissolved in trifluoroacetic acid (2 mL) and trifluoroacetic anhydride (0.5 mL) to generate a solution of the monomer [^{1}H NMR δ (ppm) 7.43 (2 H, dd, $J_{2,3}$ 9 Hz, $J_{3,F}$ 8 Hz, H3 and H5) and 7.96 (2 H, dd, $J_{2,3}$ 9 Hz, $J_{2,F}$ 4.5 Hz, H2 and H6), ^{207}Pb satellites gave $J_{2,Pb}$ 418 Hz and $J_{3,Pb}$ 168 Hz]. The addition of tetramethylsilane (300 mg) caused an exothermic reaction, and the ^{1}H NMR spectrum indicated that trimethylsilyl trifluoroacetate [δ_H (TFA) 0.45) and the diorganolead bistrifluoroacetate **1** [δ_H (TFA) 3.12 (3H, s), 7.42 (2H, dd, $J_{2,3}$ 9.0 Hz, $J_{3,F}$ 8.6 Hz, H3 and H5), 7.88 (2H, dd, $J_{2,3}$ 9.0 Hz, $J_{2,F}$ 5.1 Hz, H2 and H6), ^{207}Pb satellites gave $J_{Me,Pb}$ 137 Hz, $J_{2,Pb}$ 158 Hz, $J_{3,Pb}$ 51 Hz] were formed in stoichiometric quantities. p-*Fluorophenyl(methyl)lead bistrifluoroacetate* **1** (1.2 g, 55%), which separated from the solution, was obtained as colourless crystals, m.p. 160-162 °C (dec.) (from TFA) Anal. Found: C, 24.3; H, 1.1; F, 24.4. $C_{11}H_7O_4F_7Pb$. Calc.: C, 24.3; H, 1.3; F, 24.5%. IR (Nujol) 1690, 1670-1600, 1580, 1485 cm^{-1}. ^{1}H NMR (d_6-acetone) δ (ppm) 3.00 (3H, s), 7.47 (2H, dd, $J_{2,3}$ 9.0 Hz, $J_{3,F}$ 9.0 Hz, H3 and H5), 8.02 (2H, dd, $J_{2,3}$ 9.0 Hz, $J_{2,F}$ 5.5 Hz, H2 and H6), ^{207}Pb satellites gave $J_{Me,Pb}$ 164 Hz, $J_{2,Pb}$ 152 Hz, $J_{3,Pb}$ 50 Hz.

Reaction of p-*trifluoroacetamidophenyllead tristrifluoroacetate and tetramethylsilane in trifluoroacetic acid*

Polymeric *p*-trifluoroacetamidophenyllead trifluoroacetate[1] (1.00 g) was dissolved in trifluoroacetic acid (3.0 mL) to give a solution of the monomer [^{1}H NMR δ (ppm) 8.03 (4H, s) and 9.24 (1H, br s)]. The addition of tetramethylsilane at 37°C produced within 30 min a solution, which the ^{1}H NMR spectrum indicated to be a mixture of stoichiometric amounts of trimethylsilyl trifluoroacetate (δ_H 0.45) and the diorganolead bistrifluoroacetate **2** [δ_H 3.19 (3H, s), 7.98 (4H, s), ^{207}Pb satellites gave $J_{Me,Pb}$ 138 Hz]. *Methyl(*p-*trifluoroacetamidophenyl)lead bistrifluoroacetate* **2** (280 mg, 23%), which separated from the solution, was obtained as colourless crystals, m.p. 160°C (dec.) (from TFA), while a further quantity (730 mg, 59%) was obtained by concentration of the solution. Anal. Found: C, 24.6; H, 1.4; N, 2.3. $C_{13}H_8NO_5F_9Pb$. Calc.: C, 24.5; H, 1.3; N, 2.2%. IR (Nujol) 3280, 1710, 1680, 1625, 1550 cm^{-1}. UV (MeCN) λ_{max} 253 nm (ε 19300). ^{1}H NMR (d_6-acetone) δ (ppm) 2.94 (3H,s), 7.98 (2H, d, $J_{2,3}$ 9.0 Hz, H2 and H6), 8.02 (2H, d, $J_{2,3}$ 9.0 Hz, H3 and H5), 10.47 (1H, br s), ^{207}Pb satellites gave $J_{Me,Pb}$ 160 Hz, $J_{2,Pb}$ 161 Hz and $J_{3,Pb}$ 57 Hz. ^{19}F NMR ($CDCl_3$) δ (ppm ex C_6H_5F) -38.4 (3F, s), -39.2 (6F,s).

Reaction of various aryllead triacetates and tetramethylsilane in trifluoroacetic acid

Tetramethylsilane (*ca* 20 mg) was added to a freshly prepared solution of *p*-chlorophenyllead triacetate (*ca* 30 mg) in trifluoroacetic acid (0.4 mL). The ^{1}H NMR spectrum of the resulting solution showed only resonances due to trimethylsilyl trifluoroacetate, acetic acid and *p*-chlorophenyl(methyl)lead bistrifluoroacetate **3** [δ (ppm) 3.17 (3H, s), 7.72 and 7.78 (4H, AA'BB', H3 and H5, H2 and H6 respectively), ^{207}Pb satellites gave $J_{Me,Pb}$ 136 Hz, $J_{2,Pb}$ 160 Hz, $J_{3,Pb}$ 58 Hz]. The same method was used to prepare trifluoroacetic acid solutions of *p*-bromophenyl(methyl)lead bistrifluoroacetate **4** [δ (ppm) 3.20 (3H, s), 7.73 (2H, d, $J_{2,3}$ 9.0 Hz, H2 and H6), 7.91 (2H, d, $J_{2,3}$ 9.0, H3 and H5), ^{207}Pb satellites gave $J_{Me,Pb}$ 136 Hz, $J_{2,Pb}$ 164 Hz, $J_{3,Pb}$ 60 Hz], methyl(*p*-trifluoromethylphenyl)lead bistrifluoroacetate **5** [δ (ppm) 3.24 (3H, s), 8.05 (4H, s), ^{207}Pb satellites gave $J_{Me,Pb}$ 138 Hz, $J_{2,Pb}$ 162 Hz, $J_{3,Pb}$ 61 Hz], *m*-fluorophenyl(methyl)lead bistrifluoroacetate **6** [δ (ppm) 3.24 (3H,s), ^{207}Pb satellites gave $J_{Me,Pb}$ 135 Hz],

m-bromophenyl(methyl)lead bistrifluoroacetate 7 [δ (ppm) 3.22 (3H, s), 7.56-7.90 (3H, m, H4, H5 and H6), 8.02 (1H, br s, H2), ^{207}Pb satellites gave $J_{Me,Pb}$ 137 Hz]

Reaction of lead tetraacetate and tetraalkyltin compounds in chloroform

(a) Tetramethyltin (0.1 mmol) in dry chloroform (0.5 mL) was added by syringe to a dry nitrogen purged NMR tube fitted with a septum and containing an accurately weighed quantity of dibromomethane (1 drop) as an internal standard. The temperature was adjusted to 28°C (the probe temperature) and lead tetraacetate (0.15 mmol) in dry chloroform (0.33 mL) was added, and the tube contents were thoroughly mixed. ^{1}H NMR spectra were recorded at 20 min, 50 min, 1.5 h, 2.5 h and 3.0 h. Further spectra were recorded at the probe temperature up to 48 h, but beyond that time the reactions were kept at ambient temperature. The absolute and relative amounts of Me_4Sn, Me_3SnOAc, $Me_2Sn(OAc)_2$ and MeOAc were then calculated from the integrated spectra.

(b) The reactions of tetraethyltin, tetrabutyltin and tetraisopropyltin were performed as in (a) above, and the absolute and relative amounts of tetraalkyltin, trialkyltin acetate and alkyl acetate were calculated from the integrated spectra.

Reaction of trimethyltin acetate with lead tetraacetate in chloroform

Trimethyltin acetate (1.19 g, 5.34 mmol) and lead tetraacetate (4.74 g, 10.7 mmol) were stirred in dry chloroform (10 mL) at room temperature under nitrogen for 90 h when the ^{1}H NMR spectrum indicated that all the trimethyltin acetate had been consumed. The reaction mixture was stirred with dry light petroleum (30 mL) and the solid material was removed under anhydrous conditions. Evaporation of the solvent gave a cream coloured solid (1.20 g, 84%) which was shown by ^{1}H NMR spectroscopy to be $Me_2Sn(OAc)_2$ containing approximately 15% of the stannoxane, $(Me_2SnOAc)_2O$. The ^{1}H NMR data for both compounds were in agreement with those previously reported.[13] Crystallisation of the above material from aqueous methanol gave the pure stannoxane,m.p.237-238°C (lit.[13] 236°C).

ACKNOWLEDGEMENT

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