

Tris(trimethylsilyl)methyl-lead(IV) Compounds

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PbMe₃[C(SiMe₃)₃] may be mono- or di-halogenated to PbXMe₂R or PbX₂MeR (R = (Me₃Si)₃C, X = Cl, Br) without cleavage of the R–Pb bond. Similarly electrophilic cleavage of one Pb–Me bond occurs selectively when PbMe₃R is treated with acetic or halosubstituted acetic acids yielding monoesters. The esters, PbMe₂R(OCOCX₃) slowly decomposed in solution to PbXMe₂R + CO₂ + CX₃. The formate ester PbMe₂R(OCHO) appeared to disproportionate in benzene solution to PbMe₃R and products derived from PbMeR(OCHO)₂ (viz. Pb + Pb(OCHO)₂ + CO₂ + RH + CH₄). Other esters also disproportionated to PbMe₃R when heated in aqueous dioxan.

Introduction

Earlier studies on tris(trimethylsilyl)methyl-metal compounds have shown that, for a wide range of metals including Ge, Sn, Hg, Au, Zn, Cd, the (Me₃Si)₃C group is extremely unreactive towards both nucleophiles and electrophiles because of the high steric requirement of this ligand [1–3]. For example, Me₃GeC(SiMe₃)₃ may be brominated to yield Me₂BrGeC(SiMe₃)₃, but under more forcing conditions brominative cleavage of SiMe bonds occurs rather than further Ge–C bond cleavage. Similar low reactivity is observed for [(Me₃Si)₃C]₂Hg which fails to react with HgCl₂ at 150 °C [2] and for [(Me₃Si)₃C]₂Zn which can be steam distilled without decomposition [3]. However, under some circumstances (Me₃Si)₃C–metal compounds show quite unexpectedly high reactivity and perhaps the most striking example is the cleavage of one Me₃Si group from 6-coordinate tin complexes with 8-hydroxyquinoline by heating in ethanol [4] (reaction 1)



Similarly [5] (Me₃Si)₃C(Ph)₂SiI rearranges on reaction with ICl to yield (Me₃Si)₂(Me₂SiCl)CSiMePh₂.

In this paper we describe the lead compound Me₃PbR (where R = (Me₃Si)₃C and its reactions with

halogens, SnCl₄, acetic and substituted acetic acids, the main objective being to determine whether the reactivity parallels that reported for the germanium [1] and tin [1, 4] analogues.

Experimental

PbMe₃R – PbClMe₃ (9.5 g, 33 mmol) in ether (50 ml) was added to a solution of RLi (prepared *in situ* from RH (10 g, 43 mmol) and LiMe (47 mmol) in THF (250 ml)) and the mixture refluxed for 15 h. Hydrolysis and normal work-up gave PbMe₃R as a white crystalline solid. Yield, 12.6 g (79%). (Found: C, 32.5; H, 7.8 C₁₃H₃₆PbSi₃ requires: C, 32.3; H, 7.5%).

Halogenation reactions

a) With SnCl₄

Dropwise addition of SnCl₄ (1.3 g, 4.8 mmol) to PbMe₃R (2.3 g, 4.7 mmol) in benzene (20 ml) gave after 5 h at 20 °C a pale yellow solution containing SnCl₃Me and PbClMe₂R. Vacuum sublimation gave first SnCl₃Me (60 °C/0.01 mm) and then PbClMe₂R (120 °C/5 × 10^{−4} mm) as a white solid (2.2 g).

b) With Cl₂

A solution of chlorine in benzene was slowly added to PbMe₃R in benzene until the solution remained pale yellow. Work up gave PbClMe₂R (Found: C, 28.4; H, 6.8; Cl, 7.3. C₁₂H₃₃ClPbSi₃ requires: C, 28.6; H, 6.6; Cl, 7.0%. Excess of chlorine produced PbCl₂, PbCl₂MeR and other unidentified products.

PbBrMe₂R and PbI Me₂R

Bromine (0.3 g) or iodine (0.5 g) was added to PbMe₃R (0.85 g) in benzene (10 ml) with stirring at 20 °C. PbBrMe₂R, formed a white solid (0.8 g) (Found: C, 26.2, H, 6.1; Br, 14.2. C₁₂H₃₃BrPbSi₃ requires: C, 26.3; H, 6.1; Br 14.6%); the iodide PbI Me₂R formed a pale yellow solid (Found: C,

TABLE I. Analytical Data on Esters.

		C	H	Cl/Br
PbMe ₂ R(OCOCCl ₃)	Found	26.6	5.4	17.0
	Calc.	26.6	5.3	16.9
PbMe ₂ R(OCOCBr ₃)	Found	22.3	4.4	31.7
	Calc.	22.0	4.4	31.4
PbMe ₂ R(OCOCHF ₂)	Found	30.0	6.1	
	Calc.	29.8	6.1	
PbMe ₂ R(OCOCHCl ₂)	Found	27.9	5.7	12.0
	Calc.	28.2	5.7	11.9
PbMe ₂ R(OCOCH ₂ F)	Found	31.3	6.6	
	Calc.	30.8	6.5	
PbMe ₂ R(OCOCH ₂ Cl)	Found	30.4	6.5	
	Calc.	29.9	6.3	
PbMe ₂ R(OCOCH ₂ Br)	Found	28.1	6.0	
	Calc.	27.7	5.8	
PbMe ₂ R(OCOCH ₂ I)	Found	24.9	5.1	
	Calc.	25.7	5.4	
PbMe ₂ R(OCOCH ₃)	Found	31.6	6.9	
	Calc.	31.9	6.9	
PbMe ₂ R(OCHO)	Found	30.5	6.8	
	Calc.	30.4	6.7	

25.1; H, 5.9. C₁₂H₃₃IPbSi₃ requires C, 24.2; H, 5.6%).

PbCl₂MeR

Dropwise addition of SnCl₄ (2.5 ml) to PbMe₃R (3.4 g) in benzene (25 ml) gave an exothermic reaction. After 1 h SnCl₃Me was separated by vacuum sublimation and the residue of PbCl₂MeR purified by crystallisation from benzene as a pale yellow solid, (3.4 g, 90%) (Found: C, 25.7; H, 6.0. C₁₁-H₃₀Cl₂PbSi₃ requires: C, 25.2; H, 5.8%).

PbBr₂MeR

PbBrMe₂R (0.2 g) with Br₂ (0.1 g) or SnBr₄ (0.2 g) in benzene (10 ml) at room temperature gave the dibromide (Found: C, 22.5; H, 5.0. C₁₁H₃₀Br₂PbSi₃ requires: C, 21.5; H, 4.9%). The reaction with Br₂ was fast whereas SnBr₄ reacted slowly.

Organolead esters (Table I)

PbMe₂R(OCOCF₃)

Treatment of PbMe₃R (1.0 g) in CHCl₃ or C₆H₆ (20 ml) with CF₃CO₂H (1.2 g) gave, after 2 h at 20 °C, the monoester as a white solid (1.13 g, 94%) (Found: C, 29.1; H, 5.6; C₁₄H₃₃F₃O₂PbSi₃ requires: C, 28.9; H, 5.7%).

Other haloesters were similarly prepared by refluxing a solution of PbMe₃R in benzene with a large excess of the acid followed by vacuum sublimation or distillation of the excess acid. Formation of the acetate required heating PbMe₃R with acetic acid and acetic anhydride in benzene at 100 °C

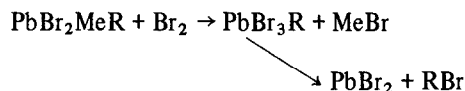
for 1 week in a sealed tube. Only the formate, PbMe₂-R(OCHO) couldn't be made by direct reaction: it was prepared by ester exchange between the acetate and formic acid at room temperature. When PbMe₃R was heated with excess formic acid in benzene at 100 °C white crystals of Pb(OCHO)₂ formed (Found: C, 8.2; H, 0.6. C₂H₂O₄Pb requires: C, 8.1; H, 0.7%) together with CO₂, CH₄ and (Me₃Si)₃CH.

Results and Discussion

Whereas PbClMe₃ readily reacts with RLi to form PbMe₃R attempts to bond more than one R group to lead using PbCl₂Me₂ and an excess of RLi produced the monochloride PbClMe₂R, presumably due to steric overcrowding. When PbCl₂ was reacted with RLi at 0 °C lead was deposited and no organolead(II) compound could be isolated.

Halogenolysis

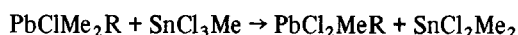
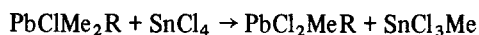
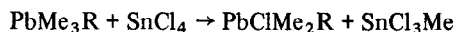
Equimolar ratios of PbMe₃R and chlorine, bromine or iodine reacted at 20 °C in benzene with selective cleavage of one methyl group. With an excess of chlorine or bromine a second-Pb-Me bond was slowly cleaved, but this is not a satisfactory route to the dihalides, PbMeRX₂, because much PbX₂ is formed under the conditions employed. Further bromination gave no direct evidence for PbBr₃R, though it is probably a reaction intermediate.



Thermal decomposition of PbBr₂MeR gave lead, methyl bromide and RBr.

Redistribution reactions with SnCl₄

This type of reaction, extensively studied in relation to tetraorgano-tin and -germanium compounds, has been little investigated for organolead compounds: both dichlorination to PbCl₂Me₂ and reduction to PbCl₂ have been reported in patent literature. The reaction of PbMe₃R with SnCl₄ is exothermic and may be taken to either the mono- or di-chloride stage. In the latter case SnCl₂Me₂ was also formed.



The pure dichloride slowly decomposed to PbCl₂ either in chloroform solution (1 week at 20 °C) or

TABLE II. Melting Point and IR Data (KBr) of Organolead Derivatives.

Compound	M.P. (°C)	ν Pb—CH ₃ (cm ⁻¹)	ν COO, ν CO (cm ⁻¹)
PbMe ₃ R	263–265	450(vs)	
PbClMe ₂ R	270–275(d)	455(m)	
PbCl ₂ MeR	>300	460(w)	
PbBrMe ₂ R	260–265(d)	450(m), 465(m)	
PbBr ₂ MeR	200(d)	457(w)	
PbI ₂ Me ₂ R	245(d)	453(m), 464(m)	
PbMe ₂ R(OCOCF ₃)	194–196(d)	470(s)	1700(vs), 1580(m)
PbMe ₂ R(OCOCCl ₃)	155–156	480(s)	1690(vs)
PbMe ₂ R(OCOCBr ₃)	145–147	452, 481(s)	1675(vs), 1610(m)
PbMe ₂ R(OCOCHF ₂)	232–236(d)	455(sh), 472(s)	1670(vs)
PbMe ₂ R(OCOCHCl ₂)	148–150	458, 478(s)	1650(vs)
PbMe ₂ R(OCOCH ₂ F)	222–225(d)	460, 475(s)	1655(vs)
PbMe ₂ R(OCOCH ₂ Cl)	250–260(d)	460(sh), 475(m) 495(sh)	1645(vs)
PbMe ₂ R(OCOCH ₂ Br)	268–272(d)	455(m), 475(sh)	1645(vs)
PbMe ₂ R(OCOCH ₂ I)	64–66	467(sh), 482(m)	1700(m), 1630(vs), 1590(s)
PbMe ₂ R(OCOCH ₃)	183–185	460(sh), 474(m)	1620(vs)
PbMe ₂ R(OCHO)	138–140(d)	462(m), 480(m)	1630(vs)

as the solid, and it could not be sublimed. The complexity of the organic products, examined by ¹H NMR spectroscopy, (multiplet, 3.7–4.4 δ) suggest that radical intermediates are formed rather than the expected product of reductive elimination, (Me₃Si)₃-CMe. The final solution also contained MeCl and RCl. Tin tetrabromide reacted in the same way as SnCl₄, but more slowly and the reaction could be controlled to yield either PbBrMe₂R or PbBr₂MeR.

Acetolysis Reactions

In earlier work [6] tetra-alkyllead compounds have been shown to react with acetic and substituted acetic acids to yield either mono- or di-esters, e.g. PbR₃'(OCOCF₃), PbR₂'(OCOCF₃)₂. The rate of reaction is a function of acid strength, and whereas mono esters are formed at room temperature conversion to diesters requires a temperature of 80–100 °C. Comprehensive studies on the kinetics of acetolysis of PbMe₄ and PbEt₄ have been reported [7, 8].

In the present work we have found that electrophilic cleavage of one Pb—Me bond occurs selectively when PbMe₃R is treated with acetic acid or halo-substituted acetic acids. Reactions were faster in chloroform than in benzene solution and qualitatively the rates followed the dissociation constants of the acids (CF₃CO₂H > CCl₃CO₂H > CBr₃CO₂H). The mono- and di-halo acids reacted quite rapidly at reflux temperature, but acetic acid required a higher

temperature for a long period. Diester formation was not observed for the lead compounds. For example, the monoester PbMe₂R(OCOCF₃) which readily formed at 20 °C, was unaffected by heating with excess CF₃CO₂H for 1 week at 100 °C. For the tin compound SnMe₂R(OCOCX₃) exchange of ester groups was feasible provided an excess of acid was used (e.g. SnMe₂R(OCOCF₃) + CH₃CO₂H $\rightleftharpoons$ SnMe₂-R(OCOCH₃) + CF₃CO₂H). By contrast for the analogous lead esters exchange only occurred to yield the ester derived from the stronger acid. This observation is unexpected and suggests that there may be a structural difference between SnMe₂R(OCOCX₃) and PbMe₂R(OCOCX₃) compounds. When PbMe₂R(OCOCBr₃) was prepared in chloroform solution it slowly decomposed to PbBrMe₂R and PbClMe₂R suggesting (as in the case of tin analogues) decarboxylation followed by carbene elimination and halide exchange: PbMe₂R(OCOCBr₃) $\rightarrow$ CO₂ + PbMe₂-RBr₃ $\rightarrow$ CBr₂ + PbBrMe₂R. The trichloroacetate behaved in the same way. Properties of the monoesters are listed in Table II.

The monoformate ester when heated with formic acid in benzene decomposed mainly by reductive elimination to Pb(OCHO)₂, though some lead was also formed, together with PbMe₄ and PbMe₃R. Carbon dioxide, methane and (Me₃Si)₃CH were also identified, and there were two minor unidentified volatile compounds produced which had

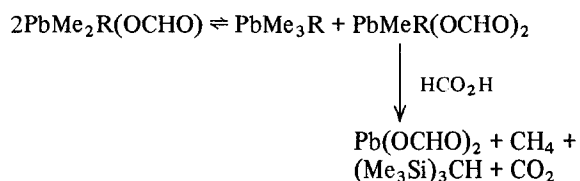
TABLE III. ^1H NMR Data (A in CDCl_3 , B in C_6D_6 at 35°C).^a

	$\delta(\text{SiMe})$	$\delta(\text{PbMe})$	$\delta(\text{CH}_n\text{X}_{3-n})$	$^2\text{J}(\text{PbH})$
PbMe_3R	A 0.17 B 0.23	0.91 0.91		53 53
PbClMe_2R	A 0.28 B 0.23	1.62 1.36		54 54
PbCl_2MeR	A 0.40 B 0.25	2.29 1.74		65 67
PbBrMe_2R	A 0.29 B 0.23	1.72 1.46		52 53
PbBr_2MeR	A 0.41 B 0.27	2.48 1.97		61 61
PbIMe_2R	A 0.30 B 0.23	1.86 1.62		50 50
$\text{PbMe}_2\text{R}(\text{OCOCF}_3)$	A 0.26 B 0.11	1.73 1.44		55 55
$\text{PbMe}_2\text{R}(\text{OCOCCH}_3)$	A 0.27 B 0.15	1.76 1.48		54 55
$\text{PbMe}_2\text{R}(\text{OCOCBr}_3)$	A 0.28 B 0.17	1.76 1.49		55 56
$\text{PbMe}_2\text{R}(\text{OCOCHF}_2)$	A 0.25 B 0.14	1.71 1.48	5.79t ^b 5.58t ^b	56 57
$\text{PbMe}_2\text{R}(\text{OCOCHCl}_2)$	A 0.25 B 0.17	1.70 1.48	5.87 5.78	56 57
$\text{PbMe}_2\text{R}(\text{OCOCH}_2\text{F})$	A 0.24 B 0.17	1.68 1.52	4.70d ^c 4.53d ^c	58 59
$\text{PbMe}_2\text{R}(\text{OCOCH}_2\text{Cl})$	A 0.24 B 0.18	1.66 1.49	4.01 3.79	58 59
$\text{PbMe}_2\text{R}(\text{OCOCH}_2\text{Br})$	A 0.24 B 0.18	1.65 1.50	3.83 3.58	58 59
$\text{PbMe}_2\text{R}(\text{OCOCH}_2\text{I})$	A 0.24 B 0.19	1.64 1.50	3.68 3.40	58 60
$\text{PbMe}_2\text{R}(\text{OCOCH}_3)$	A 0.23 B 0.22	1.59 1.53	1.97 1.97	60 62
$\text{PbMe}_2\text{R}(\text{OCHO})$	A 0.23 B 0.19	1.64 1.52	8.18 8.34	59 60

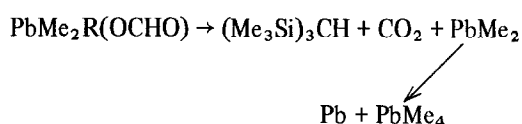
^ad = doublet, t = triplet. ^b $^2\text{J}(\text{HF}) = 55\text{ Hz}$. ^c $^2\text{J}(\text{HF}) = 48\text{ Hz}$.

longer g.l.c. retention times than $(\text{Me}_3\text{Si})_3\text{CH}$. We have attempted to rationalise these observations in terms of:

a) an initial redistribution reaction followed by reductive elimination of $\text{Pb}(\text{OCHO})_2$ in the presence of free formic acid



b) reductive elimination of $(\text{Me}_3\text{Si})_3\text{CH}$ and CO_2 with subsequent decomposition of PbMe_2



NMR Spectra

Proton and ^{13}C NMR spectra are listed in Tables III and IV. ^1H chemical shifts were quite strongly solvent dependent between deuteriochloroform and deuterobenzene, the differences being greatest for the trihalosubstituted esters. A downfield shift in $\delta(\text{PbMe})$ was observed on going from PbMe_3R to its derivatives in both solvents, with $^2\text{J}(^{209}\text{Pb}-^1\text{H})$ in the range 52–62 Hz, the largest coupling constant being observed for the acetate, $\text{PbMe}_2\text{R}(\text{OCOCH}_3)$. The MeSi proton shifts in C_6D_6 ($\delta = 0.23$ – 0.28 ppm) were little affected by the substituent, though successive substitution of F, Cl or Br in the series $\text{PbMe}_2\text{R}(\text{OCOCH}_n\text{X}_{3-n})$ ($n = 0$ – 3) gave a uniform upfield shift with increasing halide substitution. In CDCl_3 a small opposite trend was apparent.

In the ^{13}C NMR spectra $\delta(\text{PbMe})$ showed a large downfield shift between PbMe_3R and its derivatives whilst $^1\text{J}(\text{PbMe})$ values were lowest for the trifluoroacetate and highest for the acetate and dichloride.

TABLE IV. ^{13}C NMR Spectra in CDCl_3 at 35 °C.

	$\delta(\text{SiMe})$	$\delta(\text{PbMe})$	$\delta(\text{C}_{\text{quat.}})$	$\delta(\text{CHX})$	$\delta(\text{CO})$	$^1\text{J}(\text{PbMe})$	$^3\text{J}(\text{PbMe})$
PbMe_3R (60 °C)	5.4	6.0	8.6			201	51
PbClMe_2R	4.8	23.6	30.5			189	43
PbBrMe_2R	4.9	23.1	29.7 ^a			184	42
PbCl_2MeR	4.6	39.6	58.3			225	63
$\text{PbMe}_2\text{R}(\text{OCOCF}_3)$	4.6	25.4	33.0	114.9q ^b	161.4q	161	40
$\text{PbMe}_2\text{R}(\text{OCOCCl}_3)$ (50 °C)	4.7	25.5	33.1	92.0	165.3	164	40
$\text{PbMe}_2\text{R}(\text{OCOCBr}_3)$	4.7	25.4	32.7	128.2	165.9	167	39
$\text{PbMe}_2\text{R}(\text{OCOCHF}_2)$	4.6	24.8	31.3	107.3t ^c	167.1t ^c	176	39
$\text{PbMe}_2\text{R}(\text{OCOCHCl}_2)$	4.8	24.9	31.3 ^e	65.9	168.5	175	40
$\text{PbMe}_2\text{R}(\text{OCOCH}_2\text{F})$	4.7	24.3	29.6	77.7d ^f	172.6d ^f	198	39
$\text{PbMe}_2\text{R}(\text{OCOCH}_2\text{Cl})$	4.8	24.5	30.0	42.0 ^g	169.4	197	39
$\text{PbMe}_2\text{R}(\text{OCOCH}_2\text{Br})$	4.8	24.4	29.9	28.4	169.2	197	39
$\text{PbMe}_2\text{R}(\text{OCOCH}_3)$	4.8	23.5	28.0	22.2	164.4	225	38
$\text{PbMe}_2\text{R}(\text{OCOCH}_3)(\text{C}_6\text{D}_6)$	5.0	23.3	26.7	21.9	158.6	240	35
$\text{PbMe}_2\text{R}(\text{OCHO})$	4.9	24.3	29.4 ^h		166.8	208	39
$\text{PbMe}_2\text{R}(\text{OCHO})(\text{C}_6\text{D}_6)$	4.9	23.9	28.1		166.1	222	37

^a $^1\text{J}(\text{Pb C}_{\text{quat.}}) = 165$. ^b $^1\text{J}(\text{CF}) = 290$, $^2\text{J}(\text{CF}) = 38$. ^c $^1\text{J}(\text{CF}) = 250$, $^2\text{J}(\text{CF}) = 26$. ^e $^1\text{J}(\text{Pb C}_{\text{quat.}}) = 182$. ^f $^1\text{J}(\text{CF}) = 184$, $^2\text{J}(\text{CF}) = 21$. ^g $^3\text{J}(\text{PbCHCl}) = 34$. ^h $^1\text{J}(\text{Pb C}_{\text{quat.}}) = 166$.

Neither the $\text{SiMe } ^{13}\text{C}$ chemical shifts nor $^3\text{J}(\text{PbC})$ couplings were significantly affected by structural changes. The dichloro compound PbCl_2MeR gave the greatest $\delta(\text{PbMe})$ and $\delta(\text{C}_{\text{quaternary}})$ values, as expected.

Comparison of ^1H and ^{13}C NMR parameters of compounds MMe_3R , MClMe_2R and MBrMe_2R ($\text{M} = \text{Ge, Sn, Pb}$) shows large differences in $\delta(\text{MMe})$ in both ^1H and ^{13}C spectra ($\delta(\text{PbMe}) \gg \delta(\text{GeMe}) > \delta(\text{SnMe})$). There is a roughly linear relationship between $^1\text{J}(\text{PbC})$ and $^2\text{J}(\text{PbH})$ for the series of $\text{PbMe}_2\text{R}(\text{OCOCH}_n\text{X}_{3-n})$ ($\text{X} = \text{F, Cl}; n = 0-3$); extrapolation to $^1\text{J}(\text{PbC}) = 0$ gives a large intercept of 40 Hz for $^2\text{J}(\text{PbH})$, similar to observations by Singh [9].

Few of the compounds examined in this work showed parent ions in their mass spectra, but strong $(\text{p-Me})^+$ ions were present in most cases. Other lead containing ions commonly observed include PbMe_2R^+ , PbMeR^+ , $\text{PbCSi}_2\text{Me}_5^+$, $\text{PbCSi}_2\text{Me}_4^+$, PbMe^+ , Pb^+ . The spectra of $\text{PbMe}_2\text{R}(\text{OCOCF}_3)$, $\text{PbMeR}(\text{OCOCHF}_2)$ and $\text{PbMe}_2\text{R}(\text{OCOME})$ contained ions due to elimina-

tion of CO_2 from the parent and most spectra showed a metastable peak corresponding to the process: $\text{PbMe}_2\text{R}^+ \rightarrow \text{C}_2\text{H}_6 + \text{PbR}^+$.

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