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Tris(trimethylsilyl)methyl-lead(IV) Compounds

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$PbMe_3[C(SiMe_3)_3]$ may be mono- or di-halogenated to $PbXMe_2R$ or PbX_2MeR ($R = (Me_3Si)_3C$, $X = Cl, Br$) without cleavage of the R–Pb bond. Similarly electrophilic cleavage of one Pb–Me bond occurs selectively when $PbMe_3R$ is treated with acetic or halosubstituted acetic acids yielding monoesters. The esters, $PbMe_2R(OCOCX_3)$ slowly decomposed in solution to $PbXMe_2R + CO_2 + CX_2$. The formate ester $PbMe_2R(OCHO)$ appeared to disproportionate in benzene solution to $PbMe_3R$ and products derived from $PbMeR(OCHO)_2$ (viz. $Pb + Pb(OCHO)_2 + CO_2 + RH + CH_4$). Other esters also disproportionated to $PbMe_3R$ 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 $(Me_3Si)_3C$ group is extremely unreactive towards both nucleophiles and electrophiles because of the high steric requirement of this ligand [1–3]. For example, $Me_3GeC(SiMe_3)_3$ may be brominated to yield $Me_2BrGeC(SiMe_3)_3$, but under more forcing conditions brominative cleavage of SiMe bonds occurs rather than further Ge–C bond cleavage. Similar low reactivity is observed for $[(Me_3Si)_3C]_2Hg$ which fails to react with $HgCl_2$ at 150 °C [2] and for $[(Me_3Si)_3C]_2Zn$ which can be steam distilled without decomposition [3]. However, under some circumstances $(Me_3Si)_3C$–metal compounds show quite unexpectedly high reactivity and perhaps the most striking example is the cleavage of one Me_3Si group from 6-coordinate tin complexes with 8-hydroxyquinoline by heating in ethanol [4] (reaction 1)

$$(Me_3Si)_3C(Me)Sn(C_9H_6NO)_2 + EtOH \rightarrow$$
$$(Me_3Si)_2CH(Me)Sn(C_9H_6NO)_2 + Me_3SiOEt \quad (1)$$

Similarly [5] $(Me_3Si)_3C(Ph)_2SiI$ rearranges on reaction with ICl to yield $(Me_3Si)_2(Me_2SiCl)CSiMePh_2$.

In this paper we describe the lead compound Me_3PbR (where $R = (Me_3Si)_3C$ and its reactions with halogens, $SnCl_4$, 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

$PbMe_3R$ – $PbClMe_3$ (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 $PbMe_3R$ as a white crystalline solid. Yield, 12.6 g (79%). (Found: C, 32.5; H, 7.8 $C_{13}H_{36}PbSi_3$ requires: C, 32.3; H, 7.5%).

Halogenation reactions

a) With $SnCl_4$

Dropwise addition of $SnCl_4$ (1.3 g, 4.8 mmol) to $PbMe_3R$ (2.3 g, 4.7 mmol) in benzene (20 ml) gave after 5 h at 20 °C a pale yellow solution containing $SnCl_3Me$ and $PbClMe_2R$. Vacuum sublimation gave first $SnCl_3Me$ (60 °C/0.01 mm) and then $PbClMe_2R$ (120 °C/5 × 10^{-4} mm) as a white solid (2.2 g).

b) With Cl_2

A solution of chlorine in benzene was slowly added to $PbMe_3R$ in benzene until the solution remained pale yellow. Work up gave $PbClMe_2R$ (Found: C, 28.4; H, 6.8; Cl, 7.3. $C_{12}H_{33}ClPbSi_3$ requires: C, 28.6; H, 6.6; Cl, 7.0%. Excess of chlorine produced $PbCl_2$, $PbCl_2MeR$ and other unidentified products.

$PbBrMe_2R$ and $PbIMe_2R$

Bromine (0.3 g) or iodine (0.5 g) was added to $PbMe_3R$ (0.85 g) in benzene (10 ml) with stirring at 20 °C. $PbBrMe_2R$, formed a white solid (0.8 g) (Found: C, 26.2, H, 6.1; Br, 14.2. $C_{12}H_{33}BrPbSi_3$ requires: C, 26.3; H, 6.1; Br 14.6%); the iodide $PbIMe_2R$ formed a pale yellow solid (Found: C,

TABLE I. Analytical Data on Esters.

		C	H	Cl/Br
$PbMe_2R(OCOCCl_3)$	Found	26.6	5.4	17.0
	Calc.	26.6	5.3	16.9
$PbMe_2R(OCOCBr_3)$	Found	22.3	4.4	31.7
	Calc.	22.0	4.4	31.4
$PbMe_2R(OCOCHF_2)$	Found	30.0	6.1	
	Calc.	29.8	6.1	
$PbMe_2R(OCOCHCl_2)$	Found	27.9	5.7	12.0
	Calc.	28.2	5.7	11.9
$PbMe_2R(OCOCH_2F)$	Found	31.3	6.6	
	Calc.	30.8	6.5	
$PbMe_2R(OCOCH_2Cl)$	Found	30.4	6.5	
	Calc.	29.9	6.3	
$PbMe_2R(OCOCH_2Br)$	Found	28.1	6.0	
	Calc.	27.7	5.8	
$PbMe_2R(OCOCH_2I)$	Found	24.9	5.1	
	Calc.	25.7	5.4	
$PbMe_2R(OCOCH_3)$	Found	31.6	6.9	
	Calc.	31.9	6.9	
$PbMe_2R(OCHO)$	Found	30.5	6.8	
	Calc.	30.4	6.7	

25.1; H, 5.9. $C_{12}H_{33}IPbSi_3$ requires C, 24.2; H, 5.6%).

$PbCl_2MeR$

Dropwise addition of $SnCl_4$ (2.5 ml) to $PbMe_3R$ (3.4 g) in benzene (25 ml) gave an exothermic reaction. After 1 h $SnCl_3Me$ was separated by vacuum sublimation and the residue of $PbCl_2MeR$ purified by crystallisation from benzene as a pale yellow solid, (3.4 g, 90%) (Found: C, 25.7; H, 6.0. $C_{11}H_{30}Cl_2PbSi_3$ requires: C, 25.2; H, 5.8%).

$PbBr_2MeR$

$PbBrMe_2R$ (0.2 g) with Br_2 (0.1 g) or $SnBr_4$ (0.2 g) in benzene (10 ml) at room temperature gave the dibromide (Found: C, 22.5; H, 5.0. $C_{11}H_{30}Br_2PbSi_3$ requires: C, 21.5; H,4.9%). The reaction with Br_2 was fast whereas $SnBr_4$ reacted slowly.

Organolead esters (Table I)

$PbMe_2R(OCOCF_3)$

Treatment of $PbMe_3R$ (1.0 g) in $CHCl_3$ or C_6H_6 (20 ml) with CF_3CO_2H (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; $C_{14}H_{33}F_3O_2PbSi_3$ requires: C, 28.9; H, 5.7%).

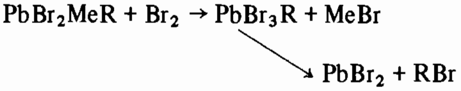
Other haloesters were similarly prepared by refluxing a solution of $PbMe_3R$ in benzene with a large excess of the acid followed by vacuum sublimation or distillation of the excess acid. Formation of the acetate required heating $PbMe_3R$ with acetic acid and acetic anhydride in benzene at 100 °C for 1 week in a sealed tube. Only the formate, $PbMe_2R(OCHO)$ couldn't be made by direct reaction: it was prepared by ester exchange between the acetate and formic acid at room temperature. When $PbMe_3R$ 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. $C_2H_2O_4Pb$ requires: C, 8.1; H, 0.7%) together with CO_2, CH_4 and $(Me_3Si)_3CH$.

Results and Discussion

Whereas $PbClMe_3$ readily reacts with RLi to form $PbMe_3R$ attempts to bond more than one R group to lead using $PbCl_2Me_2$ and an excess of RLi produced the monochloride $PbClMe_2R$, presumably due to steric overcrowding. When $PbCl_2$ was reacted with RLi at 0 °C lead was deposited and no organolead(II) compound could be isolated.

Halogenolysis

Equimolar ratios of $PbMe_3R$ 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, $PbMeRX_2$, because much PbX_2 is formed under the conditions employed. Further bromination gave no direct evidence for $PbBr_3R$, though it is probably a reaction intermediate.



$$PbBr_2MeR + Br_2 \rightarrow PbBr_3R + MeBr$$
$$\searrow PbBr_2 + RBr$$

Thermal decomposition of $PbBr_2MeR$ gave lead, methyl bromide and RBr.

Redistribution reactions with $SnCl_4$

This type of reaction, extensively studied in relation to tetraorgano-tin and -germanium compounds, has been little investigated for organolead compounds: both dichlorination to $PbCl_2Me_2$ and reduction to $PbCl_2$ have been reported in patent literature. The reaction of $PbMe_3R$ with $SnCl_4$ is exothermic and may be taken to either the mono- or di-chloride stage. In the latter case $SnCl_2Me_2$ was also formed.

$$PbMe_3R + SnCl_4 \rightarrow PbClMe_2R + SnCl_3Me$$

$$PbClMe_2R + SnCl_4 \rightarrow PbCl_2MeR + SnCl_3Me$$

$$PbClMe_2R + SnCl_3Me \rightarrow PbCl_2MeR + SnCl_2Me_2$$

The pure dichloride slowly decomposed to $PbCl_2$ 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})	νCOO, νCO (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)	
PbIMe$_2$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 ^{1}H NMR spectroscopy, (multiplet, 3.7–4.4 δ) suggest that radical intermediates are formed rather than the expected product of reductive elimination, (Me$_3$Si)$_3$-CMe. The final solution also contained MeCl and RCl. Tin tetrabromide reacted in the same way as SnCl$_4$, but more slowly and the reaction could be controlled to yield either PbBrMe$_2$R or PbBr$_2$MeR.

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.* PbR$'_3$(OCOCF$_3$), PbR$'_2$(OCOCF$_3$)$_2$. 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 PbMe$_4$ and PbEt$_4$ have been reported [7, 8].

In the present work we have found that electrophilic cleavage of one Pb–Me bond occurs selectively when PbMe$_3$R 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 (CF$_3$CO$_2$H > CCl$_3$CO$_2$H > CBr$_3$CO$_2$H). 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 PbMe$_2$R(OCOCF$_3$) which readily formed at 20 °C, was unaffected by heating with excess CF$_3$CO$_2$H for 1 week at 100 °C. For the tin compound SnMe$_2$R(OCOCX$_3$) exchange of ester groups was feasible provided an excess of acid was used (*e.g.* SnMe$_2$R(OCOCF$_3$) + CH$_3$CO$_2$H $\rightleftharpoons$ SnMe$_2$-R(OCOCH$_3$) + CF$_3$CO$_2$H). 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 SnMe$_2$R(OCOCX$_3$) and PbMe$_2$R(OCOCX$_3$) compounds. When PbMe$_2$R-(OCOCBr$_3$) was prepared in chloroform solution it slowly decomposed to PbBrMe$_2$R and PbClMe$_2$R suggesting (as in the case of tin analogues) decarboxylation followed by carbene elimination and halide exchange: PbMe$_2$R(OCOCBr$_3$) $\rightarrow$ CO$_2$ + PbMe$_2$-RCBr$_3$ $\rightarrow$ CBr$_2$ + PbBrMe$_2$R. 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 PbMe$_4$ and PbMe$_3$R. Carbon dioxide, methane and (Me$_3$Si)$_3$CH 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]

	δ(SiMe)	δ(PbMe)	$\delta(CH_nX_{3-n})$	$^2J(PbH)$
$PbMe_3R$	A 0.17	0.91		53
	B 0.23	0.91		53
$PbClMe_2R$	A 0.28	1.62		54
	B 0.23	1.36		54
$PbCl_2MeR$	A 0.40	2.29		65
	B 0.25	1.74		67
$PbBrMe_2R$	A 0.29	1.72		52
	B 0.23	1.46		53
$PbBr_2MeR$	A 0.41	2.48		61
	B 0.27	1.97		61
$PbIMe_2R$	A 0.30	1.86		50
	B 0.23	1.62		50
$PbMe_2R(OCOCF_3)$	A 0.26	1.73		55
	B 0.11	1.44		55
$PbMe_2R(OCOCCl_3)$	A 0.27	1.76		54
	B 0.15	1.48		55
$PbMe_2R(OCOCBr_3)$	A 0.28	1.76		55
	B 0.17	1.49		56
$PbMe_2R(OCOCHF_2)$	A 0.25	1.71	5.79t[b]	56
	B 0.14	1.48	5.58t[b]	57
$PbMe_2R(OCOCHCl_2)$	A 0.25	1.70	5.87	56
	B 0.17	1.48	5.78	57
$PbMe_2R(OCOCH_2F)$	A 0.24	1.68	4.70d[c]	58
	B 0.17	1.52	4.53d[c]	59
$PbMe_2R(OCOCH_2Cl)$	A 0.24	1.66	4.01	58
	B 0.18	1.49	3.79	59
$PbMe_2R(OCOCH_2Br)$	A 0.24	1.65	3.83	58
	B 0.18	1.50	3.58	59
$PbMe_2R(OCOCH_2I)$	A 0.24	1.64	3.68	58
	B 0.19	1.50	3.40	60
$PbMe_2R(OCOCH_3)$	A 0.23	1.59	1.97	60
	B 0.22	1.53	1.97	62
$PbMe_2R(OCHO)$	A 0.23	1.64	8.18	59
	B 0.19	1.52	8.34	60

[a] d = doublet, t = triplet. [b] $^2J(HF)$ = 55 Hz. [c] $^2J(HF)$ = 48 Hz.

longer g.l.c. retention times than $(Me_3Si)_3CH$. We have attempted to rationalise these observations in terms of:

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

$$2PbMe_2R(OCHO) \rightleftharpoons PbMe_3R + PbMeR(OCHO)_2$$

$$\Big\downarrow HCO_2H$$

$$Pb(OCHO)_2 + CH_4 + (Me_3Si)_3CH + CO_2$$

b) reductive elimination of $(Me_3Si)_3CH$ and CO_2 with subsequent decomposition of $PbMe_2$

$$PbMe_2R(OCHO) \rightarrow (Me_3Si)_3CH + CO_2 + PbMe_2$$

$$\swarrow$$

$$Pb + PbMe_4$$

NMR Spectra

Proton and ^{13}C NMR spectra are listed in Tables III and IV. ^1H chemical shifts were quite strongly solvent dependent between deuterochloroform and deuterobenzene, the differences being greatest for the trihalosubstituted esters. A downfield shift in δ(PbMe) was observed on going from $PbMe_3R$ to its derivatives in both solvents, with $^2J(^{209}Pb-^1H)$ in the range 52–62 Hz, the largest coupling constant being observed for the acetate, $PbMe_2R(OCOCH_3)$. The MeSi proton shifts in C_6D_6 (δ = 0.23–0.28 ppm) were little affected by the substituent, though successive substitution of F, Cl or Br in the series $PbMe_2R(OCOCH_nX_{3-n})$ ($n = 0$–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 δ(PbMe) showed a large downfield shift between $PbMe_3R$ and its derivatives whilst $^1J(PbMe)$ 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.

	δ(SiMe)	δ(PbMe)	$\delta(C_{quat.})$	δ(CHX)	δ(CO)	^1J(PeMe)	^3J(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
$PbMe_2R(OCOCF_3)$	4.6	25.4	33.0	114.9q[b]	161.4q	161	40
$PbMe_2R(OCOCCl_3)$ (50 °C)	4.7	25.5	33.1	92.0	165.3	164	40
$PbMe_2R(OCOCBr_3)$	4.7	25.4	32.7	128.2	165.9	167	39
$PbMe_2R(OCOCHF_2)$	4.6	24.8	31.3	107.3t[c]	167.1t[c]	176	39
$PbMe_2R(OCOCHCl_2)$	4.8	24.9	31.3[e]	65.9	168.5	175	40
$PbMe_2R(OCOCH_2F)$	4.7	24.3	29.6	77.7d[f]	172.6d[f]	198	39
$PbMe_2R(OCOCH_2Cl)$	4.8	24.5	30.0	42.0[g]	169.4	197	39
$PbMe_2R(OCOCH_2Br)$	4.8	24.4	29.9	28.4	169.2	197	39
$PbMe_2R(OCOCH_3)$	4.8	23.5	28.0	22.2	164.4	225	38
$PbMe_2R(OCOCH_3)(C_6D_6)$	5.0	23.3	26.7	21.9	158.6	240	35
$PbMe_2R(OCHO)$	4.9	24.3	29.4[h]		166.8	208	39
$PbMe_2R(OCHO)(C_6D_6)$	4.9	23.9	28.1		166.1	222	37

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

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

Comparison of ^1H and ^{13}C NMR parameters of compounds MMe_3R, $MClMe_2R$ and $MBrMe_2R$ (M = Ge, Sn, Pb) shows large differences in δ(MMe) in both ^1H and ^{13}C spectra (δPbMe) $\gg$ δ(GeMe) > δ(SnMe). There is a roughly linear relationship between $^1J(PbC)$ and $^2J(PbH)$ for the series of $PbMe_2R(OCOCH_nX_{3-n})$ (X = F, Cl; n = 0–3); extrapolation to $^1J(PbC) = 0$ gives a large intercept of 40 Hz for $^2J(PbH)$, similar to observations by Singh [9].

Few of the compounds examined in this work showed parent ions in their mass spectra, but strong $(p\text{-}Me)^+$ ions were present in most cases. Other lead containing ions commonly observed include $PbMe_2R^+$, $PbMeR^+$, $PbCSi_2Me_5^+$, $PbCSi_2Me_4^+$, $PbMe^+$, Pb^+. The spectra of $PbMe_2R(OCOCF_3)$, $PbMeR(OCOCHF_2)$ and $PbMe_2R(OCOMe)$ contained ions due to elimination of CO_2 from the parent and most spectra showed a metastable peak corresponding to the process: $PbMe_2R^+ \rightarrow C_2H_6 + PbR^+$.

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