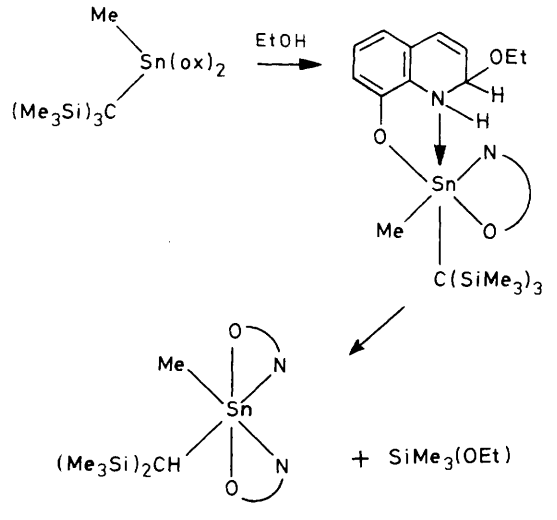
Tris(trimethylsilyl)methyl-lead Oxinates:* Their Solvolysis, Redistribution, and Reductive Elimination Reactions

Frank Glockling and N. M. Nanje Gowda
Chemistry Department, The Queen's University, Belfast BT9 5AG

The complex $PbMe_2[C(SiMe_3)_3](ox)$ (where ox = the anion of 8-hydroxyquinoline) is stable to boiling ethanol over short periods, but on prolonged heating undergoes redistribution and reductive elimination reactions yielding $Pb(ox)_2$, $PbMe_3(ox)$, $PbMe_3[C(SiMe_3)_3]$, and 8-methoxyquinoline. By contrast, when $PbCl_2Me[C(SiMe_3)_3]$ is treated with 8-hydroxyquinoline at pH *ca.* 10 in methanol, ethanol, or aqueous dioxan the bis(trimethylsilyl)methyl complex $PbMe[CH(SiMe_3)_2](ox)_2$ (1) is formed together with $SiMe_3(OR)$ (R = H, Me, or Et) rather than the expected tris(trimethylsilyl)-methyl complex. Refluxing (1) in ethanol or aqueous dioxan results in further nucleophilic displacement of $SiMe_3$ groups yielding, successively, $PbMe(CH_2SiMe_3)(ox)_2$ (2) and $PbMe_2(ox)_2$ (3). These cleavage reactions occur in competition with disproportionation and reductive elimination processes, the final products derived from (3) being $Pb(ox)_2$, $PbMe_4$, $PbMe_3(ox)$, and 8-methoxyquinoline. The corresponding 8-hydroxy-2-methylquinolinate complexes are also examined.

Many tris(trimethylsilyl)methyl metal compounds have been studied; they are usually of high thermal stability and, for steric reasons, the $(Me_3Si)_3C$–M bond is usually resistant to electrophilic or nucleophilic attack.[1–6] However, there are circumstances in which the tris(trimethylsilyl)methyl group undergoes unexpected reactions. For example, $SiIPh_2[C(SiMe_3)_3]$ reacts with NaOMe to give $SiPh_2(OMe)[CH(SiMe_3)_2]$,[7] whilst thermolysis or photolysis of $SiIPh_2[C(SiMe_3)_3]$ yields among other products, $C(SiMe_3)_2(SiMePh_2)(SiMe_2I)$.[8,9] Electrophilic reagents such as $AgNO_3$ also react with compounds of this type to form rearrangement products.[10] Even more striking is the reactivity of the $C(SiMe_3)_3$ group in octahedral complexes of tin such as $SnMe[C(SiMe_3)_3](ox)_2$ and $Sn(OEt)[C(SiMe_3)_3](ox)_2$ (ox = anion of 8-hydroxyquinoline) where one $SiMe_3$ group is cleaved by heating in ethanol, and no further reaction occurs even under forcing conditions (100 °C for 1 week). The mechanism proposed (Scheme 1) involves primary attack by EtO^- at the 2-position of the heterocyclic ring, with protonation at nitrogen, followed by the stereochemically favourable elimination of $SiMe_3(OEt)$,[11] though the reaction might proceed *via* an $Sn{=}C(SiMe_3)_2$ intermediate. This type of reaction prompted us to examine the reactivity of the $C(SiMe_3)_3$ group in corresponding organolead oxinates since differences might be expected because of the sizes and electronegativities of the two metals and because of probable differences in the metal–nitrogen bond strengths. In fact the differences, as described in this paper, were greater than anticipated.



Scheme 1.

Results and Discussion

A number of dimethylbis(substituted oxinato)lead complexes have previously been described;[12] they are evidently stable to water and alcohols and interact with co-ordinating solvents, whereas tin analogues do not. In this work we have converted $PbMe_2[C(SiMe_3)_3]X$ (X = Cl, Br, or O_2CCF_3) and $PbCl_2Me[C(SiMe_3)_3]$ into their complexes with 8-hydroxyquinoline and 8-hydroxyquinaldine (8-hydroxy-2-methylquinolinate, $C_{10}H_8NO$). The former, like the related tin compounds, yield complexes of type $PbMe_2[C(SiMe_3)_3](Y)$ (Y = chelate) as pale yellow solids, soluble in most common organic solvents. On prolonged heating in methanol or ethanol $PbMe_2[C(SiMe_3)_3](ox)$ decomposes by redistribution and reductive elimination processes [equations (v) and (vi) discussed later] since the observed products are $PbMe_3[C(SiMe_3)_3]$, $PbMe_3(ox)$, and $Pb(ox)_2$. Typically some 40% reaction occurs after 7 d at 70 °C. The reaction of 8-hydroxyquinaldine with $PbCl_2Me[C(SiMe_3)_3]$ was not studied in detail: in ethanol solution the lead(II) complex $Pb(C_{10}H_8NO)_2$ was rapidly formed.

8-Hydroxyquinoline and $PbCl_2Me[C(SiMe_3)_3]$ react in aqueous ammoniacal-methanol, -ethanol, or -dioxan to yield a yellow complex soluble in common organic solvents. Elemental analysis and mass and n.m.r. spectroscopy established that this complex is $PbMe[CH(SiMe_3)_2](ox)_2$ rather than the expected product, $PbMe[C(SiMe_3)_3](ox)_2$. Hence loss of one $SiMe_3$ group occurs too rapidly for isolation of the initially formed complex [reaction (i); R = H, Me, or Et]. In contrast

$$PbMe[C(SiMe_3)_3](ox)_2 + ROH \longrightarrow PbMe[CH(SiMe_3)_2](ox)_2 + SiMe_3(OR) \quad (i)$$
(1)

to the tin analogue when, (1) is heated for a limited period in methanol, ethanol, or aqueous dioxan cleavage of a further $SiMe_3$ group occurs [equation (ii)]. This reaction also proceeds

$$(1) + ROH \longrightarrow PbMe(CH_2SiMe_3)(ox)_2 + SiMe_3(OR) \quad (ii)$$
(2)

*Oxinate = 8-hydroxyquinolinate.

slowly at room temperature in MeOH–C_6D_6 (10% over 3 d). When (2) is refluxed for several days in the same solvents nucleophilic cleavage of the remaining $SiMe_3$ group occurs [equation (iii)]. The overall reaction is considerably more

$$(2) + ROH \longrightarrow \underset{(3)}{PbMe_2(ox)_2} + SiMe_3(OR) \quad (iii)$$

complex than is indicated by reactions (i)—(iii) since, at each stage, a yellow insoluble solid is formed which has been identified as $Pb(ox)_2$ contaminated with $PbMe_2(ox)_2$, and it therefore appears that nucleophilic displacement of $SiMe_3$ groups is in competition with redistribution and reductive elimination processes. These reactions are summarised in equations (iv)—(vi), where R′ = $C(SiMe_3)_3$, $CH(SiMe_3)_2$,

$$2\,PbMeR'(ox)_2 \rightleftharpoons PbMe_2R'(ox) + PbR'(ox)_3 \quad (iv)$$

$$2\,PbMe_2R'(ox) \rightleftharpoons PbMe_3R' + PbMeR'(ox)_2 \quad (v)$$

$$PbR'(ox)_3 \longrightarrow Pb(ox)_2 + \text{(8-R′O-quinoline)} \quad (vi)$$

CH_2SiMe_3, or Me. It is possible that in the initial reaction between $PbCl_2Me[C(SiMe_3)_3]$ and 2 mol of 8-hydroxyquinoline nucleophilic cleavage of an $SiMe_3$ group occurs from an intermediate chlorolead oxinate [equation (vii)].

$$PbClMe[C(SiMe_3)_3](ox) \xrightarrow{EtOH} PbClMe[CH(SiMe_3)_2](ox) \xrightarrow{Hox} (1) \quad (vii)$$

Although we have separately established that $PbMe[C(SiMe_3)_3](O_2CMe)_2$ undergoes quantitative reductive elimination of $CMe(SiMe_3)_3$ at room temperature in benzene, the parallel reaction is not observed for the oxinate complexes. Additional complications to the overall reaction scheme are implied by the identification of free 8-hydroxyquinoline (or C_9H_6DNO from reactions examined in CD_3OD). This is due to equilibria between oxinato- and alkoxy-lead complexes.

Most of our evidence for reactions (iv)—(vi) comes from separate experiments on preformed $PbMe_2(ox)_2$ (3). This complex, previously reported as stable in solution,[12] in fact slowly undergoes reactions (iv)—(vi) in C_6D_6 solution since the products unambiguously identified are: $Pb(ox)_2$, $PbMe_3(ox)$, $PbMe_4$, and 8-methoxyquinoline. In C_6D_6–MeOH mixtures these reactions are much slower and since no ethane is formed we suggest that the reaction (vi) is the dominant reductive process.

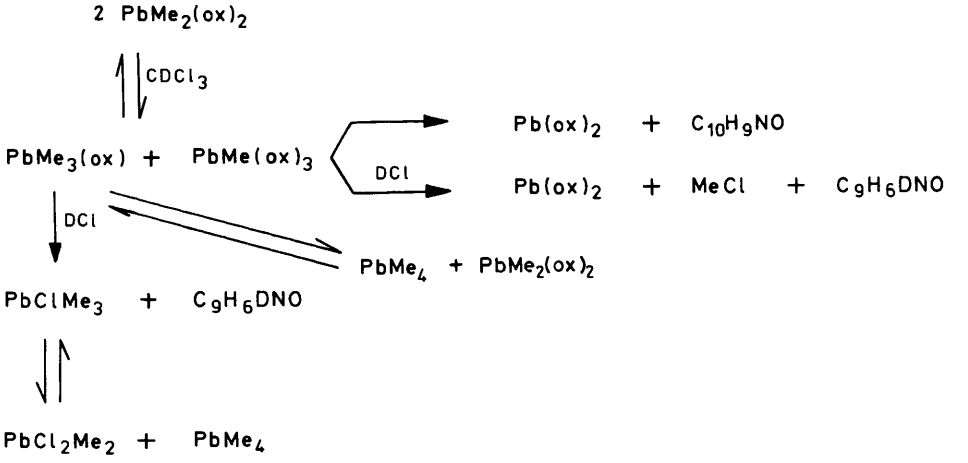
The decomposition of (3) in $CDCl_3$ at 70 °C was also examined: the products are consistent with attack by a limited amount of DCl (from the thermal decomposition of $CDCl_3$) on the primary redistribution complexes as indicated by the oversimplified Scheme 2. Reaction (v) proceeds rapidly since attempts to prepare $PbMe_3(ox)$ by reaction of $PbClMe_3$ with 8-hydroxyquinoline in EtOH–NH_3(aq) gave either pure (3) or a mixture of (3) with $PbMe_3(ox)$.

When reactions (ii) or (iii) were carried out in CD_3OD the volatile products identified were $SiMe_3(OCD_3)$, $SiMe_3(OD)$, and $O(SiMe_3)_2$ and these experiments gave no evidence for $CHMe(SiMe_3)_2$, $SiMe_3Et$, or C_2H_6 suggesting that the reductive elimination reactions [equation (vi)] are slow. Similar experiments in C_6D_6–MeOH led to the identification of the ion $[PbMe_2(CH_2SiMe_3)]^+$ in the mass spectrum of the volatile components, derived from $PbMe_3(CH_2SiMe_3)$. This implies that reactions (iv) and (v) also occur when R′ = CH_2SiMe_3. Evidence for the alkoxyquinoline [equation (vi)] with R′ = CH_2SiMe_3 was not obtained: ^1H and ^{13}C spectra in the $SiMe_4$ region were always complex and even the volatile components contained five ^1H resonances due to trimethylsilyl-containing compounds.

The probable change from five- to six-co-ordination in these oxinato-complexes results in two additional bands in the u.v.–visible spectra, near 260 and 380 nm. This change in co-ordination number also greatly increases the lead–proton $^2J(PbCH_3)$ and lead–carbon $^1J(PbCH_3)$ couplings (Tables 1 and 2). For complex (2) the $SiMe_3$ proton resonance is to high field of values observed in four-co-ordinate lead compounds such as $PbMe_3(CH_2SiMe_3)$.[13]

Experimental

$PbMe_2[C(SiMe_3)_3](ox)$ (4).—8-Hydroxyquinoline (0.4 g) and $PbMe_2[C(SiMe_3)_3](O_2CCF_3)$ (1.0 g) in ethanol (15 cm^3) and ether (15 cm^3) were stirred at room temperature for 18 h when the ether was distilled from the yellow solution. Addition of NaO_2CMe (0.1 g) in aqueous ammonia (5 cm^3) precipitated the *complex* as a pale yellow solid which was washed with ethanol–ammonia (aq) (10:3). Yield 0.8 g (75%), m.p. 138—141 °C (Found: C, 41.9; H, 6.2; N, 2.1. $C_{21}H_{39}NOPbSi_3$ requires C, 41.1; H, 6.4; N, 2.3%). The same procedure, starting from other esters of $PbClMe_2[C(SiMe_3)_3]$, also gave the complex. U.v.–visible bands at [nm (log ε), in EtOH] 203 (4.64),



Scheme 2.

Table 1. Proton n.m.r. data (p.p.m., *J* in Hz) at 35 °C

Complex	Solvent	δ(SiMe$_3$)	δ(PbMe)	δ(PbCH)	δ(2-Me)	^2J(PbMe)	^2J(PbCH)
(1) PbMe[CH(SiMe$_3$)$_2$](ox)$_2$	$CDCl_3$	0.00	1.91	1.40		137	133
	C_6D_6	0.18	1.71	1.55		137	
	CD_3OD	0.00	2.00	1.44		135	135
(2) PbMe(CH$_2$SiMe$_3$)(ox)$_2$	$CDCl_3$	−0.19	1.92	1.82		142	178
	C_6D_6	−0.16	2.06	1.86		165	152
	CD_3OD	−0.37	1.95	1.79		160	174
(3) PbMe$_2$(ox)$_2$	$CDCl_3$		2.03			151	
	C_6D_6 (70 °C)		1.87			157	
	CD_3OD		1.95			160	
(4) PbMe$_2$[C(SiMe$_3$)$_3$](ox)	$CDCl_3$	0.31	1.47			63	
	C_6D_6	0.40	1.40			64	
(5) PbMe$_2$[C(SiMe$_3$)$_3$](C$_{10}$H$_8$NO)	$CDCl_3$	0.31	1.52		2.69	64	
	C_6D_6	0.40	1.50		2.32	65	

Table 2. Carbon-13 n.m.r. data (p.p.m., *J* in Hz) at 35 °C

Complex	Solvent	δ(SiMe$_3$)	δ(PbMe)	δ(PbCN)	δ[*C*(SiMe$_3$)$_3$]	^1J(PbMe)	^1J(PbCH)
(1)	$CDCl_3$	2.50	38.80	46.80		813	290
(1)	C_6D_6	2.70	38.40	47.20		812	305
(1)	C_6D_6–CD_3OD (3 : 1)	2.70	39.40	47.50		796	258
(1)	C_6D_6–CH_3OH (1 : 3)	2.80	39.50	48.20		783	244
(2)	$CDCl_3$	0.80	36.40	40.30		850	577
(2)	C_6D_6	0.85	38.40	40.40			
(2)	C_6D_6–CD_3OD (3 : 1)	0.60	37.20	40.40			
(2)	C_6D_6–CH_3OH (1 : 3)	0.65	37.00	40.90		878	600
(3)	$CDCl_3$		35.60			925	
(4)	$CDCl_3$	5.29	26.43		29.60	283	
(5)	$CDCl_3$	5.29	25.95 (24.54, 2-Me)		29.13	281	

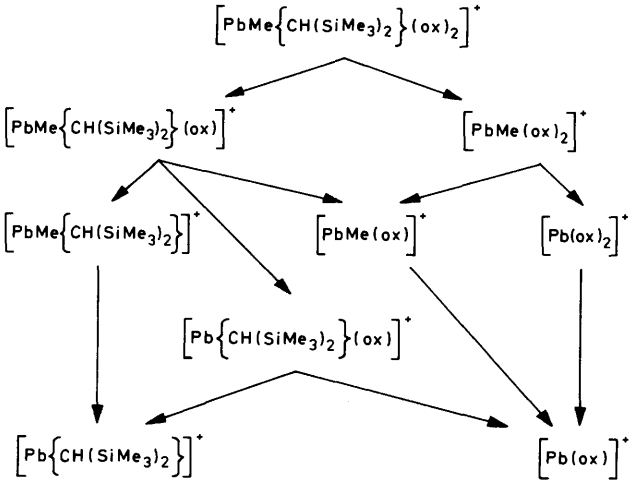
		Aromatic resonances								
		C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
(1)	$CDCl_3$	145.5	120.4	138.5	115.7	130.2	110.6	163.1	140.9	131.4
(2)	$CDCl_3$	145.2	120.7	138.5	115.7	130.4	113.3	163.0	141.0	131.5
(3)	$CDCl_3$	145.6	120.8	138.5	115.4	130.1	111.8	162.4	140.8	131.4
(4)	$CDCl_3$	144.6	120.4	136.2	115.8	128.4	113.6	160.1	142.0	130.0
(5)	$CDCl_3$	153.3	121.3	136.5	116.7	127.1	114.1	159.6	141.5	128.2
8-Methoxyquinoline	$CDCl_3$	149.2	121.6	135.8	119.6	126.7	107.6	155.5	140.3	129.4

241 (4.76), 312 (3.49), 360 (sh) (2.97). I.r. bands in the ν(Pb–C) region at 444vw, 468w, 502m cm^{-1}. Lead-containing ions in its mass spectrum at *m/e* 598m (P − Me)$^+$, 581m, 569m, 533m, 496m, 489m, 469s, 459m, 439s, 431vw metastable, 409vw metastable, 382s, 367w, 352vs, 297vw, 252w, 238w, 223m.

PbMe$_2$[C(SiMe$_3$)$_3$](C$_{10}$H$_8$NO) (5).—The compound PbMe$_2$[C(SiMe$_3$)$_3$](O$_2$CCF$_3$) (1.0 g) and 8-hydroxyquinaldine (0.3 g) gave the yellow *complex*. Yield 0.8 g (80%), m.p. 153—155 °C (Found: C, 41.9; H, 6.7; N, 2.2. C$_{22}$H$_{41}$NOPbSi$_3$ requires C, 42.1; H, 6.6; N, 2.2%). U.v.–visible bands at [nm (log ε), in EtOH] 204 (4.70), 244 (4.78), 300 (3.56), 340 (sh) (3.15). I.r. bands in ν(Pb–C) region at 446m, 472m cm^{-1}. Its mass spectrum showed a strong parent ion at *m/e* 627 and the following lead-containing ions: 612s, 597w, 582s, 553vw metastable, 489m, 469vs, 459w, 439vs, 411w metastable, 396vs, 381m, 366vs, 351w, 338vw metastable, 253s, 238s, 223vs.

PbMe[CH(SiMe$_3$)$_2$](ox)$_2$ (1).—8-Hydroxyquinoline (3.5 g) was added to a freshly prepared sample[3] of PbCl$_2$Me[C(SiMe$_3$)$_3$] (3.3 g) suspended in ethanol (100 cm^3), followed by aqueous ammonia (30 cm^3). After stirring overnight the *complex* was separated as a yellow solid, washed with ethanol–ammonia and crystallised from benzene. Yield, 3.6 g, m.p. 140—143 °C (softening range) (Found: C, 46.4; H, 5.2; N, 4.1. C$_{26}$H$_{34}$N$_2$O$_2$PbSi$_2$ requires C, 46.6; H, 5.1; N, 4.2%). The same complex resulted when the reaction was carried out in aqueous ammonia–dioxane solution. It separated initially as an orange-red oil which solidified on standing. U.v.–visible bands at [nm (log ε), in EtOH] 202 (4.95), 242 (4.73), 260 (4.62), 336 (3.62), 382 (3.71). I.r. bands in ν(Pb–C) region at 472s, 485s, 499vs cm^{-1}. Its mass spectrum contained a weak parent ion at *m/e* 670 together with lead-containing ions at 654w, 598w, 576w, 541m, 526vs, 511s, 496s, 469w, 464w, 454w, 439w, 397vs, 382vs, 367vs, 352vs, 338vw metastable, 325s, 295s, 288m, 274s, 253vs, 238m, 223vs. The ions identified at high resolution are shown in Scheme 3.

Reaction of PbMe$_2$[C(SiMe$_3$)$_3$](ox) *with* MeOH.—The complex in C_6D_6–MeOH showed ^{1}H resonances at 0.35 and 1.39 p.p.m. [^2J(PbH) 64 Hz] due to the complex and at 0.18 and



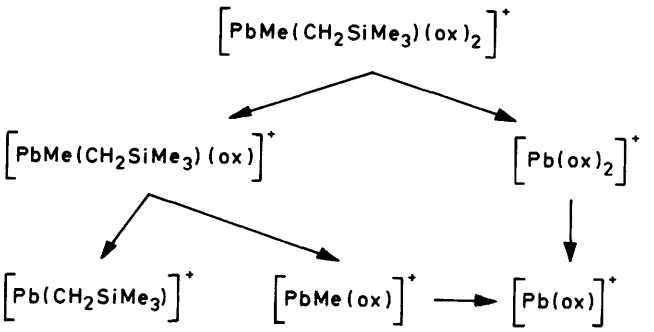
Scheme 3.

1.19 p.p.m. due to $PbMe_2[C(SiMe_3)_3](OMe)$. After 6 d at 70 °C new signals were observed at 0.08 [$SiMe_3(OMe)$], 0.19 and 0.92 p.p.m {$PbMe_3[C(SiMe_3)_3]$} together with unassigned signals at 0.05 and 0.82 p.p.m. [^2J(PbH) 57 Hz]. Volatile components were $SiMe_3(OMe)$ and an unidentified compound with a longer gas–liquid chromatography (g.l.c.) retention time than $CMe(SiMe_3)_3$. The involatile components showed ^{1}H resonances due to $PbMe_3[C(SiMe_3)_3]$, $PbMe_2(ox)_2$, and 8-methoxyquinoline together with unassigned signals at 0.12 and 0.83 p.p.m. The insoluble yellow solid was a mixture of $Pb(ox)_2$ and $PbMe_3(ox)$ (Found: C, 40.5; H, 4.2; N, 5.1%).

Reaction of $PbMe_2[C(SiMe_3)_3](C_{10}H_8NO)$ *with* MeOH.—The complex in C_6D_6–MeOH showed ^{1}H resonances at 0.37, 1.45 (J 66 Hz), and 2.38 p.p.m. due to the complex and at 0.18, 1.16 p.p.m. (53 Hz), due to $PbMe_2[C(SiMe_3)_3](OMe)$. After 4 d at 70 °C new signals appeared due to $SiMe_3(OMe)$ and $PbMe_3[C(SiMe_3)_3]$ together with unassigned signals at 0.04, 0.07, and 0.82 p.p.m. (J 56 Hz). The volatile components contained $SiMe_3(OMe)$ and the same unidentified g.l.c. peak as in the preceding experiment. The insoluble yellow residue corresponded to $Pb(C_{10}H_8NO)_2$ (Found: C, 45.2; H, 3.1; N, 5.0. $C_{20}H_{16}N_2O_2Pb$ requires C, 45.9; H, 3.1; N, 5.4%).

$PbMe(CH_2SiMe_3)(ox)_2$ (2).—An ethanolic solution (50 cm^3) of $PbMe[CH(SiMe_3)_2](ox)_2$ (1) (1.0 g) was refluxed for 4 d. On cooling a small quantity of $Pb(ox)_2$ separated. Concentration of the solution gave the *complex* as a brown solid (0.8 g) which softened at 95 °C (Found: C, 46.1; H, 4.2; N, 4.5. $C_{23}H_{26}N_2O_2PbSi$ requires C, 46.2; H, 4.4; N, 4.7%). However, n.m.r. spectra of the sample showed traces of $PbMe_2(ox)_2$ and 8-methoxyquinoline. The same complex was formed when $PbMe[CH(SiMe_3)_2](ox)_2$ was refluxed in aqueous dioxan, but in pure dioxan no reaction occurred. U.v.–visible bands at [nm (log ε), in EtOH] 202 (4.88), 242 (4.71), 260 (4.69), 320 (3.60), 336 (3.67), 380 (3.80). I.r. bands in the ν(Pb–C) region region at 481m, 498m cm^{-1}. The highest mass ion in its mass spectrum at *m/e* 469m is due to $[PbMe_2(CH_2SiMe_3)(ox)]^+$. Other lead-containing ions at *m/e* 454w, 439w, 397vs, 382w, 367vs, 352s, 325vs, 295vs, 253s, 238m, 223s. The fragment ions in Scheme 4 were identified at high resolution.

This reaction was examined in a ^{13}C n.m.r. tube in C_6D_6–MeOH (5 : 1). After 1 d at 70 °C new resonances were present due to $PbMe(CH_2SiMe_3)(ox)_2$ in addition to those from the starting material (confirmed by an off-resonance spectrum), and a small quantity of yellow solid was present. After prolonged heating (54 d at 70 °C) a considerable amount of yellow solid separated and six new ^{13}C signals appeared at the



Scheme 4.

expense of all others [−1.16, 1.25, 1.83, 3.26 p.p.m. due to $SiMe_3$ groups, at 34.98 p.p.m. due to $PbMe_2(ox)_2$, and at 55.52 p.p.m. due to the methyl resonance of 8-methoxyquinoline]. The latter was confirmed by comparison with the spectrum of an authentic sample. In the aromatic ^{13}C region resonances due to complexed ox were all separated from those due to 8-methoxyquinoline (Table 2).

Separation of the *volatiles* by warming *in vacuo* gave two liquid layers with ^{1}H resonances due to $SiMe_3$ groups at −0.36, 0.04, 0.05, 0.10, 0.15 p.p.m. together with $PbMe_4$ [0.72 p.p.m., ^2J(HPb) 60 Hz], $SiMe_3(OMe)$ (0.10, 3.24 p.p.m.), and a small unidentified PbMe resonance [0.77 p.p.m., ^2J(HPb) 58 Hz]. The mass spectrum of the volatiles contained strong peaks due to ions derived from $O(SiMe_3)_2$ (*m/e* 147) and $SiMe_3(OMe)$ (89) by Me$^\bullet$ loss, together with low intensity lead-containing ions derived from $PbMe_3(ox)$ (253) and $PbMe_2(CH_2SiMe_3)(ox)$ (325, 295).

The *involatiles*, after washing with ethanol, analysed for a mixture of $PbMe_2(ox)_2$ and $Pb(ox)_2$ (Found: C, 45.2; H, 2.8; N, 5.0%). Washing this mixture with $CHCl_3$ left $Pb(ox)_2$ as an insoluble yellow solid (Found: C, 43.8; H, 2.5; N, 5.4. $C_{18}H_{12}N_2O_2Pb$ requires C, 43.6; H, 2.4; N, 5.7%). A $CDCl_3$ extract of the involatile material showed ^{1}H resonances due to $O(SiMe_3)_2$ (0.06), 8-methoxyquinoline (4.08), and $PbMe_2(ox)_2$ [2.07 p.p.m., ^2J(HPb) 149 Hz]. Lead-containing ions in the mass spectrum of this mixture gave good evidence for $PbMe_2(ox)_2$ (*m/e* 510, 496), $PbMe_3(ox)$ (397, 253), and $PbMe_2(CH_2SiMe_3)(ox)$ (469, 439, 325, 295). 8-Methoxyquinoline gave a strong parent ion at 159.

$PbMe_2(ox)_2$ (3).—This complex was prepared from $PbCl_2Me_2$ and 8-hydroxyquinoline.[12] U.v.–visible bands were at [nm (log ε), in EtOH] 202 (4.80), 242 (4.71), 258 (4.64), 320 (3.53), 336 (3.62), 378 (3.75); i.r. bands in the ν(Pb–C) region at 481m and 498m cm^{-1}. Lead-containing ions in the mass spectrum were present at *m/e* 524vw, 510vw, 496m (P − 2Me)$^+$, 396w, 382s, 366m, 352vs, 253vs, 238m, 223vs.

Decomposition of $PbMe_2(ox)_2$.—(*a*) *In* C_6D_6. The solution at 70 °C showed a ^{1}H resonance at 1.87 p.p.m. [^2J(HPb) 157 Hz]. After heating for 11 d at 70 °C three new Pb–Me signals were observed with satellites together with a signal at 3.61 p.p.m. due to the methyl resonance of 8-methoxyquinoline (confirmed by comparison with an authentic specimen). The PbMe signals were assigned as follows [δ p.p.m., ^2J(HPb) in Hz]: $PbMe_4$ (0.72, 61); $PbMe_3(ox)$ (1.08, 66); $PbMe(ox)_3$ (2.12, 252); the last two assignments are somewhat tentative. Further heating (34 d, 70 °C) increased the intensity of the signals at 0.72 and 3.61 p.p.m.

(*b*) *In* C_6D_6–MeOH (4 : 1). The ^{1}H n.m.r. spectrum was unchanged over 10 d at 70 °C, but after 35 d $PbMe_4$ was detected (0.72 p.p.m.) and its intensity increased over 66 d. Other sig-

nals were obscured by the MeOH resonance. A small amount of pale yellow solid, impure $Pb(ox)_2$, was separated.

(*c*) *In* $CDCl_3$. The complex [δ(Me) 2.27 p.p.m., ^2J(HPb) 156 Hz] was heated at 70 °C for 3 d when four new signals were present, two of which showed Pb satellites. After 7 d at 70 °C all of the starting material had reacted. Assignments, based on comparison with authentic materials, are as follows [δ p.p.m., ^2J(HPb) in Hz]: $PbMe_4$ (0.73, 61); $PbClMe_3$ (1.59, 68); MeCl (3.01 p.p.m.); 8-methoxyquinoline (Me, 4.11 p.p.m.). An intense ion at *m/e* 146 in the mass spectrum was due to C_9H_6DNO. After 38 d at 70 °C the signal due to $PbClMe_3$ had disappeared and a reddish brown sticky solid was present. A separate experiment showed that when $PbClMe_3$ is heated in $CDCl_3$ at 70 °C for 24 d $PbMe_4$ is formed together with a white solid, $PbCl_2Me_2$. After 55 d at 70 °C methyl chloride was also present in the mixture.

Reaction between $PbClMe_3$ *and 8-Hydroxyquinoline.*—(*a*) Stirring $PbClMe_3$ (1.5 g) and 8-hydroxyquinoline (2.0 g) in $MeOH–NH_3$(aq) (1 : 1, 40 cm^3) gave some yellow crystals. Addition of aqueous ammonia to the filtrate produced a further crop of yellow crystals analysing as a mixture of $PbMe_2(ox)_2$ and $PbMe_3(ox)$ (Found: C, 44.0; H, 3.7; N, 4.8. $PbMe_3(ox)$ requires C, 36.4; H, 3.8; N, 3.5%). Its mass spectrum contained ions derived from $PbMe_2(ox)_2$ [*m/e* 510w, 496s] and from $PbMe_3(ox)$ (397w) together with lower mass ions at 382s, 367m, 352vs, 253vs, 238s, and 223s. Its ^1H n.m.r. spectrum in $CDCl_3$ corresponded to $PbMe_2(ox)_2$ (Table 1). (*b*) Addition of aqueous ammonia (15 cm^3) to a yellow ethanolic solution of $PbClMe_3$ (1.4 g) and 8-hydroxyquinoline (0.8 g) followed by stirring gave pure $PbMe_2(ox)_2$ as yellow crystals (Found: C, 45.2; H, 3.6; N, 4.8. $C_{20}H_{18}N_2O_2Pb$ requires C, 45.7; H, 3.5; N, 5.3%).

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