Synthesis and Crystal Structures of the Compounds [Sn{C(SiMe$_2$Ph)$_3$}Cl]$_2$, [Pb{C(SiMe$_3$)$_3$}Cl]$_3$, and [M{C(SiMe$_3$)$_2$(SiMe$_2$OMe)}Cl]$_2$ (M = Sn or Pb)

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The title compounds have been made by treatment of SnCl$_2$ or PbCl$_2$ in tetrahydrofuran with the appropriate reagent LiR, where R = (PhMe$_2$Si)$_3$C, (Me$_3$Si)$_3$C, or (MeOMe$_2$Si)(Me$_3$Si)$_2$C, and their crystal structures determined. In all four compounds, as in the previously reported [Pb{C(SiMe$_2$Ph)$_3$}Cl]$_2$, the metal atoms are linked by bridging Cl atoms, unsymmetrically except in the case of the trimeric [Pb{C(SiMe$_3$)$_3$}Cl]$_3$ (in which the six-membered ring has a distorted boat form). In [M{C(SiMe$_3$)$_2$(SiMe$_2$OMe)}Cl]$_2$, M = Sn or Pb, which are isomorphous, there are (relatively weak) intramolecular MeO···M interactions in addition. The compounds [Pb{C(SiMe$_2$Ph)$_3$}Cl]$_2$ and [Pb{C(SiMe$_3$)$_3$}Cl]$_3$ are the only known σ-bonded mono(organo)lead(II) compounds to have been structurally characterized, and [Sn{C(SiMe$_2$Ph)$_3$}Cl]$_2$ is only the second solvent-free mono(alkyl)tin(II) compound. All of the compounds are yellow and air-sensitive in the solid and in solution, and the lead compounds are readily decomposed in solution by exposure to daylight.

Introduction

We previously reported the first preparation of a σ-bonded heteroleptic organolead(II) compound of the type PbRX, namely PbR*Cl, where R* denotes the bulky group (PhMe$_2$Si)$_3$C.[1] In the crystal, the compound is present as the dimer **1**, which has a form fairly similar to that shown for the corresponding tin compound in Figure 2, with one longer and one shorter metal−Cl bond in each of the Cl bridges.

$(\mathrm{PbR^*Cl})_2$ **1** $(\mathrm{SnR^*Cl})_2$ **2** $(\mathrm{PbR^\dagger Cl})_3$ **3** $(\mathrm{PbR'Cl})_2$ **4** $(\mathrm{SnR'Cl})_2$ **5**

$\mathrm{R^* = (PhMe_2Si)_3C}$ $\mathrm{R^\dagger = (Me_3Si)_3C}$ $\mathrm{R' = (MeOMe_2Si)(Me_3Si)_2C}$

We now describe the preparation and structural characterization of (a) an orthorhombic form of **1**; (b) the analogous tin compound **2**; (c) the related lead compound PbR†Cl, where R† = (Me$_3$Si)$_3$C, which crystallizes as a trimer, **3**; and (d) the compounds MR′Cl, where R′ = (MeOMe$_2$Si)(Me$_3$Si)$_2$C and M = Pb or Sn, which crystallize from light petroleum as dimers **4** and **5**, respectively, in which there is intramolecular coordination of the MeO group to the metal.

Since this work was completed, Power and colleagues have reported the preparation and characterization of the aryltin(II) compound (SnArCl)$_2$, where Ar = 2,6-{2,4,6-Me$_3$C$_6$H$_2$}$_2$C$_6$H$_3$); they also made the (structurally very different) germanium compound (GeArCl)$_2$ but were unable to obtain the corresponding lead(II) compound PbArCl.[2] (In their review of relevant literature, the authors appear to have overlooked our report of (PbR*Cl)$_2$.[1])

An analog of **5**, *viz.* Sn{C(SiMe$_3$)$_2$(NC$_5$H$_4$-2)}Cl, is known; in this analog there is intramolecular coordination of the pyridyl N to tin, but the compound is monomeric, and the tin is, thus, only three-coordinate.[3]

Results and Discussion

Compound 1. The structure of compound **1** that we described previously was that of a monoclinic crystal obtained by crystallization from methylcyclohexane after preparation in tetrahydrofuran (THF).[1] We later obtained an orthorhombic form of the same compound from the reaction between R*Li and PbCl$_2$ in THF and subsequent crystallization from heptane. The X-ray data from the orthorhombic form were of poorer quality than those from the monoclinic form, but the molecular structure was unambiguous and revealed that the centrosymmetrical dimeric molecules differ from those in the monoclinic form only in the conformations of the C(SiMe$_2$Ph)$_3$ groups. (The dimer of the orthorhombic form is, in fact, isomorphous with the tin compound **2**, and so its structure is essentially the same as that shown in Figure 1.)

We previously[4] showed that C(SiMe$_2$Ph)$_3$ groups can adopt one of several configurations depending on how each PhMe$_2$Si group is oriented with respect to the substituents at the adjacent central carbon, which in the present case are one Pb and two Si atoms. The

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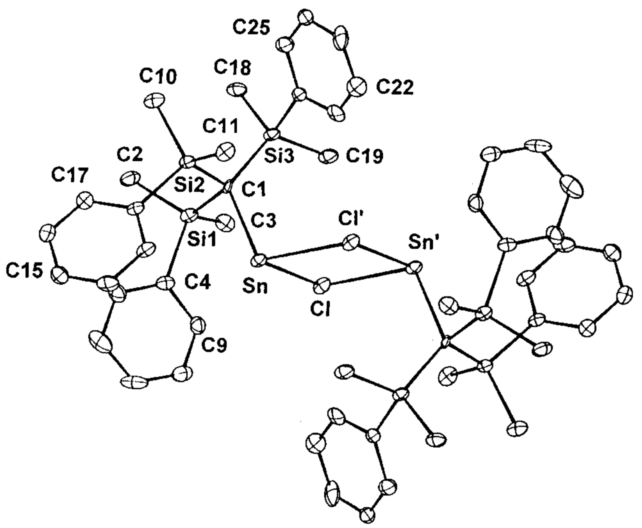

Figure 1. Molecular structure of $[Sn\{C(SiMe_2Ph)_3\}Cl]_2$, **2**. (The orthorhombic form of compound **1** has a similar form.)

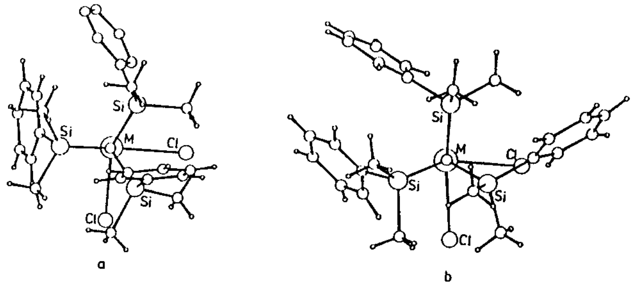

Figure 2. Projections along C−M bonds in $(MR^*Cl)_2$: (a) The monoclinic form of **1** (M = Pb). (b) The orthorhombic form of **1** (M = Pb) or **2** (M = Sn).

monoclinic form of **1** has two $PhMe_2Si$ fragments with methyl groups *anti* to Pb and the third $PhMe_2Si$ with the phenyl group *anti* to Pb, whereas in the more symmetrical orthorhombic form all three $PhMe_2Si$ fragments are oriented so that methyl groups are *anti* to Pb; the difference can be seen from Figure 2.

Compound 2. This compound was made by treatment of $SnCl_2$ with 1 mol equiv of LiR* in THF, and after removal of the solvent, it was extracted into light petroleum and isolated as yellow air-sensitive crystals.

The structure of **2** is shown in Figure 1, and selected geometrical data are listed in Table 1 alongside those for the monoclinic form of **1**. As will be evident from the discussion of the two forms of **1** above, the structure of **2** and that of the monoclinic form of **1** differ mainly in the configurations of one of the $SiMe_2Ph$ groups, but in addition the geometries of the four-membered bridging rings in the two compounds differ in that the M−Cl−M′ angles and Cl−M−Cl′ angles in the monoclinic form of **1** are, respectively, 7−9° narrower and 7−9° wider than those in the orthorhombic form and than those in **2**. The lower symmetry of the R* group in the monoclinic form also affects the mismatch between the Pb−Cl and Pb−Cl′ bonds, which is *ca.* 0.11 Å in the orthorhombic and 0.223 Å in the monoclinic form (*cf.* 0.183 Å in **2**). The mean lengths of the C(1)−Si bonds are identical within experimental uncertainty. Because of the differing configurations of the $C(SiMe_2Ph)_3$ groups, the Si−C(1)−Si angles range more widely in **1**, from 108.8(5) to 116.7(5)° to 118.7(5)°, than in **2**, from 110.1(5) to 111.2(5)° to 113.9(5)°, although the means of these angles, 114.7° and 111.7°, are not very different. That the Si−C bond lengths and Si−C−Si angles in the two compounds are similar is as expected in view of the similar electronegativities of the two metals.[5]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[\{(PhMe_2Si)_3CMCl\}_2]$

	M = Pb (**1**)[a]	M = Sn (**2**)
M−C(1)	2.435(10)	2.296(10)
M−Cl	2.729(3)	2.596(3)
M−Cl′	2.962(3)	2.779(3)
C(1)−Si (mean)	1.89(1)	1.90(1)
M−Cl−M′	92.92(8)	101.63(9)
Cl−M−Cl′	87.08(8)	78.37(9)
Cl−M−C(1)	98.5(2)	99.1(3)
Cl′−M−C(1)	112.0(2)	111.1(2)
Si1−C(1)−Si2	116.7(5)	113.9(5)
Si1−C(1)−Si3	118.7(5)	111.2(5)
Si2−C(1)−Si3	108.8(5)[b]	110.1(5)
C(1)−Si−Me (mean)	115.4(5)[c]	113.7(5)
C(1)−Si−Ph (mean)	109.9(5)	112.7(4)
M−C(1)−Si1	97.2(4)	99.2(4)
M−C(1)−Si2	101.5(4)	100.6(4)
M−C(1)−Si3	111.9(4)	121.3(4)
M−C(1)−Si (mean)	103.5[d]	(107.0)[e]
Me−Si−Me,Ph (mean)	105(1)	105(1)

[a] Monoclinic form. The numbers of the atoms Si2 and Si3, as shown in ref 1, have here been interchanged to match those for **2**. [b] Incorrectly reported previously as 118.7(5)°.[1] [c] Values ranged from 108.0(4)° to 117.8(5)°. [d] Values ranged from 97.2° to 111.9°. [e] Values ranged from 99.2° to 121.3°.

The Sn−C bond in **2**, 2.296(10) Å, is significantly longer than that in the aryltin chloride $(SnArCl)_2$ with Ar = 2,6-$\{2,4,6\text{-}Me_3C_6H_2\}_2C_6H_3$), 2.222(5) Å.[2] The lengths of the (stronger) Sn−Cl bonds are effectively the same in the two compounds, but those of the (weaker) Sn−Cl′ bond are significantly different, that in the aryl derivative being only 0.085 Å longer than the Sn−Cl bond, so that the bridge is much more symmetrical than in **2**. The Sn−Cl−Sn′ and Cl−Sn−Cl′ angles do not differ much between the compounds, but the C(1)−Sn−Cl′ angle in the aryl derivative, 92.35(14)°, is markedly smaller than that in **2**, 111.1(2)°, which means that the Sn−C(1) bond lies closer to the plane of the four-membered ring in the latter.

Our attempts to make the compound $SnR^{\dagger}Cl$ have so far been unsuccessful (There are strong indications that the reactions of LiR , R = R* or R†, with $SnCl_2$ both initially give a salt $Li[SnRCl_2]$, which then breaks down to RSnCl, but the latter has been isolated only for R = R*.)

Compound 3. This compound was made by treatment of $PbCl_2$ with 1 mol equiv of LiR† in THF, and after removal of the solvent, it was extracted into toluene from which it separated in 85% yield as yellow-orange crystals. (The same compound was formed when 2 mol equiv of LiR* was used.) Like **1**, it is very air sensitive and readily decomposed by light in solution (but more slowly in the solid).

An X-ray diffraction study revealed the trimeric structure shown in Figure 3, and selected bond lengths and angles are shown in Table 2. The trimer has its six-membered ring in a distorted boat form, as shown in Figure 4, in which the prow of the boat, represented by the Pb1−Cl3−Pb3 triangle, lies almost at right angles to the base, Pb1−Cl1−Cl2−Pb3. The R† groups

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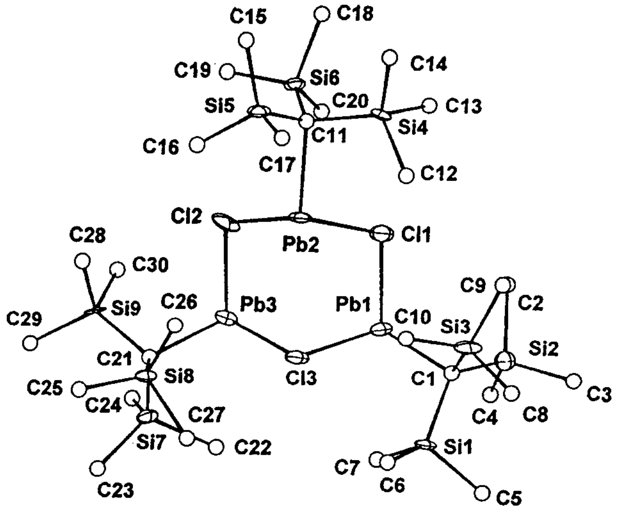

Figure 3. Molecular structure of $[Pb\{C(SiMe_3)_3\}Cl)_3]$, **3**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[\{(Me_3Si)_3CPbCl\}_3]$, 3

Pb1−C(1)	2.37(4)	Pb2−C(11)	2.41(6)
Pb3−C(21)	2.27(6)	Pb1−Cl1	2.71(1)
Pb1−Cl3	2.73(1)	Pb2−Cl1	2.74(2)
Pb2−Cl2	2.71(2)	Pb3−Cl2	2.71(2)
Pb3−Cl3	2.74(1)	Si−C(1,11,21) (mean)	1.88(6)
		Si−Me (mean)	1.87(6)
C(1)−Pb1−Cl1	102.7(10)	Cl2−Pb3−Cl3	91.2(4)
C(1)−Pb1−Cl3	100.7(10)	Pb1−Cl1−Pb2	115.7(5)
C(11)−Pb2−Cl1	99.6(13)	Pb1−Cl3−Pb3	90.9(4)
C(11)−Pb2−Cl2	99.5(14)	Pb2−Cl2−Pb3	112.0(6)
C(21)−Pb3−Cl2	103(2)	Pb−C−Si (mean)	106(3)[a]
C(21)−Pb3−Cl3	101(2)	Si−C(1,11,21)−Si (mean)	113(3)
Cl1−Pb1−Cl3	87.7(4)	Me−Si−Me (mean)	106(2)
Cl1−Pb2−Cl2	92.6(5)		

[a] Values ranged from 99(2)° to 116(3)°.

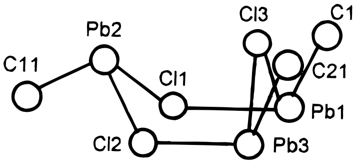

Figure 4. Structure of $[Pb\{C(SiMe_3)_3\}Cl)_3]$, **3**, showing the form of the six-membered ring.

linked to Pb1 and Pb3 point up and away from the base of the boat, with Cl2−Pb3−C21 and Cl1−Pb1−C(1) angles of ca. 103°, whereas the $R^{\dagger}$ group linked to Pb2 points downward with Cl1−Pb2−C(11) and Cl2−Pb−C(11) angles of ca. 99.5°. These orientations allow the bulky groups $R^{\dagger}$ to point outward from the ring; they have been found previously, e.g., in the boat form of $(Me_2AlNHMe)_3$.[6]

The six Pb−Cl bonds in **3** have lengths which differ insignificantly from the mean, 2.72 Å, which is similar to that of the shorter Pb−Cl bonds in **1**. If the atoms within the $R^{\dagger}$ groups are ignored, the molecule is roughly symmetrical about the plane through C11, Pb2, and Cl3; the C−Pb−Cl angles range between 99° and 103° and the Cl−Pb−Cl angles between 88° and 93°. The Pb−C bond lengths in **3** (mean 2.35(6) Å) and **1** (mean 2.435(10) Å) are not significantly different, and neither are the $C-SiMe_3$ bond lengths in **3** (mean 1.88(4)) Å) and the $C-SiMe_2Ph$ bond lengths (mean 1.889(10) Å) in **1**.

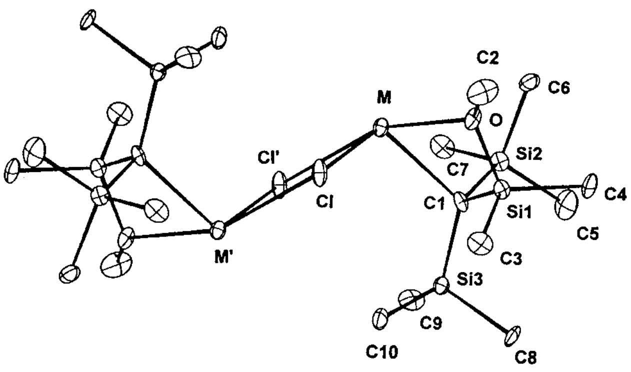

Figure 5. Molecular structure of $\overline{M\{C(SiMe_3)_2(SiMe_2O}Me)\}$-$Cl]_2$, M = Pb (**4**) or Sn (**5**).

It is of interest to consider why PbR^*Cl forms a dimer in the solid and $PbR^{\dagger}Cl$ a trimer. The electronic effects of the R^* (i.e., $(PhMe_2Si)_3C$) and $R^{\dagger}$ (i.e., $Me_3Si)_3C$) groups must be very similar, and so the differences between the two compounds are presumably to be attributed to the difference in the sizes of R^* and $R^{\dagger}$. When the smaller $R^{\dagger}$ is present, a six-membered ring, which would be disfavored on entropy grounds, is evidently more stable and so this must be the form with the lowest free energy when the ring strain (determined largely by the intra-ring bond angles and lengths) and the steric interactions between the R groups and between these and the neighboring Cl atoms are taken into account. In the four-membered ring species, not only will the steric interaction with the neighboring Cl atoms be lower (compare the R^*−Pb−Cl angles of 98.5° and 112.0° in **1** and $R^{\dagger}$−Pb−Cl angles between 99.5° and 103° in **3**) but also, probably more importantly, that between the R^* groups, which are far apart in their *trans* disposition in the dimer. The shortest C···C distances between the $R^{\dagger}$ groups in **3** are 4.08 Å between C7 and C22 and 4.19 Å between C10 and C12, values only slightly larger than twice the van der Waals radius (2.0 Å[7]) of the Me group. It, thus, seems likely that replacement of some Me by Ph groups would lead to significant steric repulsion between the R^* ligands if PbR^*Cl were to form trimers rather than dimers. A comparable relation was observed previously for the compounds $CdR^{\dagger}Cl$ and CdR^*Cl; the former crystallizing as a tetramer[8] and the latter as a dimer.[4]

Compound 4. Reaction of LiR′ with $PbCl_2$ in a 1:1 mol ratio gave the product RPb′Cl, which crystallized as the Cl-bridged dimer **4**, having the structure shown in Figure 5 and selected bond lengths and angles as given in Table 3. In the dimer, each MeO group is intramolecularly coordinated to its adjacent Pb atom, so that the Pb(II) atoms are four-coordinate, but in terms of the dispositions of the Cl, Cl′, Pb, and C(1) atoms, the skeleton of **4** is rather similar to that in the dimer **1** in which the Pb atoms are three-coordinate. All of the atoms bound to lead lie on one side. The coordination may be described as distorted trigonal bipyramidal with the electronegative ligands Cl and O in the axial positions and the stereochemically active

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Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[M\{C(SiMe_3)_2(SiMe_2OMe)\}Cl]_2$

	M = Pb (**4**)[a]	M = Sn (**5**)[a]
M−C(1)	2.37(2)	2.294(5)
M−Cl	2.680(5)	2.538(2)
M−Cl′	2.868(5)	2.952(3)
M−O	2.598(12)	2.416(4)
C(1)−Si (mean)	1.87(2)	1.872(5)
Si(1)−O	1.684(14)	1.686(4)
O−C2	1.45(3)	1.445(7)
M−Cl−M′	97.67(14)	99.57(7)
Cl−M−Cl′	82.33(14)	80.43(7)
C(1)−M−Cl	103.4(4)	103.12(13)
C(1)−M−Cl′	100.9(4)	99.45(13)
O−M−Cl	83.2(3)	84.85(11)
O−M−Cl′	157.4(3)	158.79(10)
M−C(1)−Si1	96.7(8)	94.6(2)
M−C(1)−Si2	97.7(8)	98.1(2)
M−C(1)−Si3	120.8(8)	123.2(2)
M−O−Si1	93.2(5)	94.9(2)
Si−C(1)−Si (mean)	113.4(9)	113.0(2)
C(1)−Si1−C3	116.4(9)	117.0(3)
C(1)−Si1−C4	117.8(9)	119.4(3)
C(1)−Si(2,3)−Me (mean)	112.6(9)	112.5(3)

[a] The dimer lies on a crystallographic inversion center. Symmetry operation: $-x, -y, -z$.

lone pair equatorial. The small C−Pb−O angle, 65.9(5)°, is noteworthy.

The Pb−O bond length, 2.598(12) Å, is significantly larger than the sum, 2.20 Å, of the covalent radii of Pb and O, than the Pb−O bond lengths of 2.221(2), 2.249(2), and 2.481(1) Å in the orthorhombic form of PbO or 2.30 Å in the tetragonal form,[9] and than those of 2.37(2) and 2.44(2) Å in the Pb(IV) compound Ph_3PbOH.[10] However, Pb(II) often achieves coordination numbers higher than 2 or 3 by forming secondary bonds of 2.4−2.8 Å in length,[11] and so in this context the Pb−O interaction in **4** is not unusual, but not particularly strong. The Si−O bond, 1.684(14) Å, is markedly longer than the great majority of Si−OR bonds, which commonly fall within the range 1.63−1.66 Å,[12] and is essentially the same as that in $[YbR'I{\cdot}OEt_2]_2$,[13] but perhaps a little shorter than that in MgR'_2, *viz.* 1.705(6) Å.[14] (In $Bu^t_3SiOH_2^+$, in which a lone pair of the O atom is fully engaged in interaction with the proton, the Si−O bond is lengthened to 1.779(9) Å.[15]) The geometry at the O atom in **4** is not quite planar, the sum of the angles being 351.3°.

The coordination to lead of the oxygen atom on Si(1) results in a small Pb−C−Si1 angle of 96.7(8)°. The Pb−C−Si2 angle is similar (97.7(8)°), but Pb−C−Si3 is 120.8(8)°. However, the CSi_3 system as a whole is not distorted, the three Si−C(1)−Si angles all remaining at ca. 113°, as in the case of **2** and **3**.

Compound 5. Reaction of LiR′ with $SnCl_2$ readily gave the product **5**, which proved to be closely isomorphous with the lead analog **4**, so that a single diagram, Figure 5, serves for both compounds. Selected bond lengths and angles are given in Table 3 alongside those for **4**.

As in **4**, the metal−O bond, 2.416(4) Å, is rather long (compare the sum, 2.06 Å, of the covalent radii, the lengths of the Sn−O bonds in SnO, 2.224(8) Å,[16] and $SnCl_2{\cdot}2H_2O$, 2.325(5)°,[17] and that of 1.999(6) Å in the monomeric Sn(IV) hydroxide $(2,4,6\text{-}Me_3C_6H_2)_3SnOH$.[18] The Si−O bond length is the same as that in **4**. The sum of the angles at O is 353.8°. The presence of the stereochemically active lone pair between the O−M and M−Cl′ bonds leads to an O−Sn−Cl′ angle of 158.8(1)°. The shape of the four-membered O−Sn−C−Si ring is closely similar to that of the corresponding ring in **4**, but the O−Sn−C angle, 69.1(2)°, not quite as narrow as the O−Pb−C angle, 65.9(5)°, in **4**. As in **4**, there is a large asymmetry in the locations of the Si2 and Si3 atoms (larger than in **2**), the Sn−C(1)−Si2 and Sn−C(1)−Si3 angles being 98.1(2)° and 123.2(2)°, respectively, but again the CSi_3 system is undistorted, all three Si−C(1)−Si angles remaining at ca. 113°.

Comparison of **1** with **4** and of **2** with **5** reveals that the introduction of the chelate ring has surprisingly little effect on the rest of the molecule. The internal coordination increases the difference between the lengths of the Sn−Cl and Sn−Cl′ bonds from 0.183 Å in **2** to 0.414 Å in **5** and the difference between the lengths of the Pb−Cl and Pb−Cl′ bonds from 0.11 Å in the orthorhombic form of **1** to 0.188 Å in **4**. The observations are consistent with the generalization that the effect of the lone pair is much more evident in the chemistry of Sn(II) than in that of Pb(II).[19] Put in another way, tin is more reluctant than lead to increase its coordination number beyond three. The difference in length between the third and fourth longest bond to the metal is 0.28 Å in $SnCl_2$[20] but only 0.13 Å in $PbCl_2$.[21] The M−Cl bonds in **4** and **5** show a similar pattern.

NMR Data. The NMR data were mainly recorded for solutions, and we cannot be sure that they refer to the dimers or trimers present in the solids, although we observed no indication that dissociation occurred. Attempts to resolve the uncertainty for the tin compounds by determination of solid state ^{119}Sn and ^{207}Pb spectra failed because no signal could be obtained for either nucleus, probably because of severe chemical shift anisotropy. With one exception for the compounds examined, there was no significant difference between the positions of the solution and solid state ^{29}Si resonances. The exception was provided by the chelated tin compound **5**, for which chemical shifts of δ 33 and 39.5, respectively, were observed for the Si of the $SiMe_2OMe$ group in the solid and in a C_6D_6 solution but a shift only δ 18 for a solution in C_4D_8O. Since this last value is in the region found, for example, for the parent molecule R′H, *viz.*, 15.9,[22] the related iodide R′I (15.2) (in $CDCl_3$),[14]

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Table 4. Summary of Crystallographic Data for 2, 3, and 4

	2[a]	**3**	**4**[a]	**5**[a]
empirical formula	$C_{50}H_{66}Cl_2Si_6Sn_2$	$C_{30}H_{81}Cl_3Pb_3Si_9$	$C_{20}H_{54}Cl_2O_2Pb_2Si_6$	$C_{20}H_{54}Cl_2O_2Si_6Sn_2$
fw	1143.9	1422.7	980.5	803.5
cryst size (mm)	0.30 × 0.15 × 0.05	0.3 × 0.3 × 0.3	0.4 × 0.4 × 0.1	0.4 × 0.4 × 0.2
cryst syst	orthorhombic	monoclinic	triclinic	triclinic
space group	*Pbca* (No. 61)	*P*2/*c* (No. 13)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	16.146(13)	13.772((9)	9.070(4)	9.049(6)
b (Å)	13.793(5)	8.835(4)	9.212(3)	9.214(6)
c (Å)	24.027(9)	44.35(2)	12.781(7)	12.805(5)
α (deg)	90	90	84.51(3)	82.99(4)
β (deg)	90	90.62(4)	77.76(4)	76.81(4)
γ (deg)	90	90	60.90(3)	60.88(5)
V (Å^3)	5351(5)	5397(5)	911.8(7)	908.0(9)
Z	4	4	1	1
d_c (Mg m^{-3})	1.42	1.75	1.79	1.47
F(000)	2336	2736	472	408
μ (mm^{-1})	1.20	9.70	9.58	1.74
θ range (deg)	2−22	2−18	2−25	2−25
index range	$0 < h < 17$	$0 < h < 11$	$0 < h < 10$	$0 < h < 10$
	$0 < k < 14$	$0 < k < 7$	$-9 < k < 10$	$-9 < k < 10$
	$0 < l < 25$	$-38 < l < 38$	$-14 < l < 15$	$-14 < l < 15$
no. of rflns collected	3262	3917	3195	3182
no. of unique reflns	3262	3708 ($R_{int} = 0.2768$)	3195	3182
no. of rflns with $I > 2(\sigma)I$	2173	2338	2873	3004
R1; wR2 ($I > 2\sigma(I)$	0.061; 0.137	0.098; 0.246	0.073; 0.224	0.038; 0.129
R1; wR2 (all data)	0.105; 0.165	0.155; 0.318	0.081; 0.242	0.040; 0.138
no. of data/restraints/parameters	3261/0/271	3688/0/256	3191/0/145	3178/0/145
GOF on F^2	1.029	1.034	1.128	1.132
max shift/error	0.001	0.005	0.002	0.001
largest diff peak/hole (e Å^{-3})	1.09, −1.8 (near Sn)	2.16, −2.19	4.1, −6.4 (near Pb)	1.68, −1.51 (near Sn)
abs corr T_{max}; T_{min}	1.00; 0.70	0.99; 0.64	1.00; 0.22	1.00; 0.84

[a] The molecule lies on a crystallographic inversion center.

$(MeOMe_2Si)_3CSiMe_2H$ (14.0),[23] ZnR′$_2$ (17.1),[24] and even Me_3SiOMe (17.2),[25] it seems reasonable to conclude that in THF, coordination of the solvent to tin replaces the internal coordination of OMe. Comparison of the shifts of ca. 33 and 39.5 observed for **5** in the solid and in benzene solution, respectively, with those of 19.6 (in C_6D_6) and 18.8 (in toluene-d_8) observed for solutions of LiR′·2THF[14] and [YbR′I·OEt$_2$]$_2$[13] suggests that in both of these latter cases the MeO···M coordination observed in the solid is absent for solutions even in hydrocarbons, probably because of the presence of ether molecules in the compounds. (We previously[14] reported a shift of 0.7 for LiR′·2THF in C_6D_6, but reinvestigation in light of the results discussed in the present paper showed this to be in error.) The shift of δ 17.7 observed for **4** in solution in C_6D_6 likewise suggests that there is no MeO coordination even in this solvent, but the value for the solid in this case is puzzlingly close, at 21, even though the X-ray diffraction study reveals an unambiguous (though weak) O···Pb interaction. We do not, of course, know whether or not **4** and **5** remain dimeric in solution; in **5**, in particular, the length of the Sn−Cl′ bond in the solid suggests that dissociation in solution might be a real possibility.

We failed in many attempts to detect ^{207}Pb signals from **1** and **3** either in the solid or in solution and also observed no coupling between Pb and the attached (quaternary) carbon nucleus in the ^{13}C NMR spectra of solutions. However, for **4**, a ^{207}Pb NMR signal was observed, at δ 4249, from a solution in C_6D_6, a value which may be compared with that of δ 3870 for PbAr$_2$ with Ar = 2,6-{2,4,6-$Me_3C_6H_2$}$_2C_6H_3$).[2] A ^{119}Sn shift of 777 was observed for **2** in C_6D_6 and one of δ 469 for **5** in C_6D_6 and 267 in C_4D_8O; the substantial change in the position of the signal from **5** is consistent with a change in the nature of the compound on going from benzene to the donor solvent. Shifts of δ 635 and 562, respectively, were reported for the aryltin compounds SnAr$_2$ and (SnArCl)$_2$, Ar = 2,6-{2,4,6-$Me_3C_6H_2$}C_6H_3), in C_6D_6.[2]

The other NMR solution data are unexceptional, but the small variation in the chemical shift for the ^{13}C atom of the OMe group over a range of compounds is noteworthy, the values (for solutions in C_6D_6 or toluene-d_8) all lying between δ 49.5 and 51.5 for **4**, **5**, R′H,[22] R′I,[14] LiR′·2THF,[14] MgR′$_2$,[14] and YbR′$_2$.[13] (A shift of δ 55 was observed for **4** in the solid.)

In the solid state NMR spectra of **4**, in the Me_3Si region, there are two ^{29}Si signals at δ −2.7 and −8.4 and four ^{13}C signals at 5.6, 7.6, 11.5, and 14.0. Likewise, for **5** there are two ^{29}Si signals at δ −1.0 and −3.0; the ^{13}C spectrum was not recorded. These effects can be attributed to inhibition of rotation about the M−C or Si−C bonds; it is such restriction of rotation about Si−C bonds that gives rise to the polymorphism of compound **1**.

Failure To Make Dialkylmetal Compounds. In the reactions of PbCl$_2$ with LiR* or LiR†, use of 2 mol equiv of the lithium reagent did not change the outcome, only the monoalkyl compounds **1** and **3** being obtained. Our failure to obtain the dialkyllead compounds, even though the diaryl compounds MAr$_2$ with M = Sn or Pb and Ar = 2,6-{2,4,6−$Me_3C_6H_2$}$_2C_6H_3$) were readily made by Power and colleagues,[2] is probably to be attributed to a greater effective bulk of the alkyl than of the aryl ligands. We attempted to convert **1** into R*PbPh by treatment with LiPh in Et$_2$O, but a complex mixture

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was formed, from which the only species isolated was the dilead compound $Ph_3PbPbPh_3$, which was identified by a single-crystal X-ray diffraction study.

Experimental Section

All operations were carried out under argon in Schlenk tubes. For reactions involving lead compounds, the Schlenk tubes were made of amber-colored glass.

The organolithium reagents LiR†·2THF,[26] LiR*·THF,[27] and LiR′·2THF[14] were prepared as solids as previously described, except that LiR′·2THF was recrystallized from light petroleum (bp 40−60 °C) rather than heptane−THF.

NMR Spectra. Unless otherwise stated, the NMR spectra were determined for solutions in C_6D_6. The frequencies (MHz) used for the various nuclei were ^{1}H, 300.1; ^{13}C, 125.8 ; ^{29}Si, 99.4; ^{119}Sn, 186.6; ^{207}Pb, 104.3. Chemical shifts are relative to $SiMe_4$ for H, C, and Si, $SnMe_4$ for Sn, and $PbMe_4$ for Pb. Mass spectra were obtained by EI at 70 eV; *m*/*z* values refer to ^{35}Cl, ^{120}Sn, and ^{208}Pb. Additional spectra recorded for previously reported compounds were as follows: (a) $(Me_3Si)_2(MeOMe_2Si)CH$ ^{13}C NMR δ 1.4 ($SiMe_2$), 3.2 ($SiMe_3$), 6.4 (CH), 49.5 (OMe); ^{29}Si NMR δ −1.3 ($SiMe_3$), 15.9 (SiOMe). (b) $(Me_3Si)_2(MeOMe_2Si)CLi$·2THF ^{1}H NMR δ 0.43 ($SiMe_3$), 0.45 ($SiMe_2$), 3.11 (OMe), 1.28 (THF), and 3.40 (THF); ^{13}C NMR δ 3.35 ($SiMe_2$), 7.9 ($SiMe_3$), 7.1 (CLi), 49.7 (OMe), 25.3 (THF), and 68.1 (THF).

Orthorhombic Form of (PbR*C1)$_2$, 1. This was prepared in the manner described for the monoclinic form,[1] but the recrystallization was from heptane as yellow-orange plates.

Preparation of (PbR†Cl)$_3$, 3. A solution of LiR†·2THF (3.50 g, 9.15 mmol) in THF (35 cm^3) was added dropwise to a stirred suspension of $PbCl_2$ (2.54 g, 9.15 mmol) in THF (25 cm^3), and the mixture was stirred overnight at room temperature. The solvent was removed under vacuum, the residue extracted with toluene (20 cm^3), and the extract filtered through Celite, concentrated to 10 cm^3, and then kept at −6 °C to deposit yellow-orange crystals of (R†PbCl)$_3$, **3** (3.7 g, 85%), mp 148 °C (with onset of decomposition). ^{1}H NMR: δ 0.36. ^{13}C NMR: δ 6.7 ($SiMe_3$), 97.5 (CSi_3). ^{29}Si NMR: δ −8.4. MS: *m*/*z* 439 (18, R†Pb), 231 (35, R†), 201 (100, $Me_2SiC(SiMe_2OMe){=}SiMe_2$). Because of the instability of the compound, a satisfactory elemental analysis could not be obtained.

Preparation of (SnR*Cl)$_2$, 2. A solution of LiR*·THF (1.00 g, 2.0 mmol) in THF (20 cm^3) was added to a stirred solution of $SnCl_2$ (0.38 g, 2.0 mmol) in THF (15 cm^3), and the mixture was stirred at room temperature overnight. The solvent was removed under vacuum, and the residue was extracted with light petroleum (bp 40−60 °C; 30 cm^3). The extract was filtered and concentrated to 10 cm^3, then kept at 10 °C to deposit a fine yellow powder. Two recrystallizations from light petroleum gave good quality yellow crystals. Yield: 0.80 g (70%). (The crystals became orange at 80 °C and melted at 145−148 °C to give an orange liquid, which turned black with decomposition at ca. 154 °C.) Anal. Calcd for $C_{50}H_{66}Cl_2Si_6Sn_2$: C, 52.5; H, 5.8. Found: C, 52.3; H, 5.8. ^{1} H NMR: δ 0.60 (s, 18H, Me_2Si), 7.1−7.5 (m, 15H, Ph). ^{13}C NMR: δ 5.4 (Me), 37.1 (^1J(SiC) = 34 Hz, ^1J(^{119}SnC) = 420 Hz, CSi_3), 129.9−138.5 (Ph). ^{29}Si NMR: δ −9.5. ^{119}Sn NMR: δ 777. MS: *m*/*z* 572 (10, SnR*Cl), 495 (50, SnR*Cl − Ph), 417 (5, R*), 402 (60, R* − Me), 135 (100, $PhMe_2Si$), 73 (45, Me_3Si).

Preparation of (PbR′Cl)$_2$, 4. A solution of LiR′·2THF (1.0 g, 2.50 mmol) in THF (20 cm^3) was added to a stirred suspension of $PbCl_2$ (0.70 g, 2.50 mmol) in THF (15 cm^3) at −10 °C. The stirred mixture was allowed to warm to room temperature, the solvent removed under vacuum, and the residue extracted with light petroleum (bp 40−60 °C; 25 cm^3). The bright yellow extract was concentrated to 5 cm^3, then kept at 5 °C to deposit yellow crystals of (PbR′Cl)$_2$, **4** (0.74 g, 60%), mp 160 °C (with onset of decomposition at ca. 165 °C). Anal. Calcd for $C_{20}H_{54}Cl_2O_2Pb_2Si_6$: C, 24.5; H, 5.6. Found: C, 24.2; H, 5.7. ^{1}H NMR: δ 0.41 (s, 6H, $SiMe_2$), 0.42 (s, 18H, $SiMe_3$), 3.12 (s, 3H, OMe). ^{13}C NMR: δ 6.77($SiMe_3$), 6.42 ($SiMe_2$), 50.35 (OMe), 83.0 (CSi_3); and for the solid (at 100.6 MHz) 5.55, 7.61, 11.5, 14.00 (all four from Me_3Si and Me_2Si), 54.9 (OMe). ^{29}Si NMR: δ −8.1 ($SiMe_3$), 17.7 (SiOMe); for the solid (at 79.5 MHz) −2.7 and −8.4 (both Me_3Si), 20.8 (SiOMe). ^{207}Pb NMR: δ 4249. MS: *m*/*z* 490 (5, R′PbCl), 475 (40, R′PbCl − Me), 455 (25, R′Pb), 247 (15, R), 233 (60, RH − Me), 217 (100), 187 (35), 129 (35, $Me_2SiCH{=}SiMe_2$), 73 (70, Me_3Si).

Preparation of (SnR′Cl)$_2$, 5. A solution of LiR′·2THF (0.73 g, 1.83 mmol) in THF (20 cm^3) was added dropwise under argon to a stirred solution of $SnCl_2$ (0.35 g, 1.83 mmol) in THF (15 cm^3) at −10 °C. The stirred mixture was allowed to warm to room temperature during 14 h, and the solvent was then removed under vacuum. The residue was extracted with light petroleum (bp 40−60 °C; 30 cm^3), the pale yellow extract filtered, and the filtrate concentrated to 10 cm^3 then cooled to 5 °C to give yellow crystals of **5** (0.68 g, 93%). Anal. Calcd for $C_{20}H_{54}Cl_2O_2Si_6Sn_2$: C, 29.9; H, 6.8. Found: C, 28.5; H, 6.4. ^{1}H NMR: δ 0.25 (s, 6H, $SiMe_2$), 0.28 (s, 18H, $SiMe_3$), 2.84 (s, 3H, OMe).^{13}C NMR: δ 5.4 ($SiMe_3$), 5.5 ($SiMe_2$), 51.8 (OMe), 32.7 (^1J(C−Si) = 36.3 and 46.1 Hz; ^1J(CSn) = 348 Hz, CSi_3). ^{29}Si NMR: δ −4.8 ($SiMe_3$), 39.5 (SiOMe); and in the solid δ −1.0 and −3.0 (both $SiMe_3$), 33.0. ^{119}Sn NMR: δ 469. MS *m*/*z* 402 (5, R′SnCl), 387 (25, R′SnCl − Me), 367 (5, R′Sn), 233 (10, R′H − Me), 217 (100), 187 (25), 129 (20), 73 (35).

Crystal Structure Determinations. Data were collected on an Enraf-Nonius CAD4 diffractometer and corrected for Lorentz and polarization effects and for absorption; details are given in Table 4. The structures were determined by direct methods, with SHELXS-86 and SHELXL-93 programs used for structure solution and refinement on F^2 using all reflections. The H atoms were refined in riding mode with U_{iso}(H) = 1.5U_{eq}(C). Non-hydrogen atoms were normally anisotropic, but in the case of **3**, only Pb, Cl, and Si atoms were. For **3**, the diffraction was weak and was complicated by overlap arising from the extremely long *c* axis of the unit cell. For **2**, **4**, and **5**, the dimers lie on crystallographic inversion centers.

Crystal data for the orthorhombic form of (PbR*Cl)$_2$: $C_{50}H_{66}Cl_2Pb_2Si_6$, M = 1320.8, a = 16.067(8) Å, b = 13.861(6) Å, c = 24.012(13) Å, V = 5348 Å^3, space group *Pbca* (No. 61), Mo Kα radiation, λ = 0.710 73 Å, Z = 4, F(000) 2592, T = 173(2) K, 2° < θ < 15°. Direct methods. R1 = 0.054 ($I > 2\sigma(I)$), wR2 = 0.141 (all data) for 1073 independent reflections from a crystal 0.20 × 0.10 × 0.05 mm. Because of the small size of the crystal and the limited data, the only aspects of the structure referred to in the discussion are the conformation and the Pb−Cl and Pb−Cl′ distances within the ring of 2.834(9) and 2.724(9) Å.

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Supporting Information Available: Tables of atom coordinates, bond lengths and angles, and anistropic displacement parameters for **2**−**5** and the orthorhombic form of **1** (17 pages). Ordering information is given on any current masthead page.

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