

The First Monoorganolead(II) Derivative, $[\{\text{PbR}(\mu\text{-Cl})\}_2]$ where $\text{R} = \text{C}(\text{SiMe}_2\text{Ph})_3$

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The title compound, thought to be the first monoorganolead(II) compound, has been prepared and structurally characterized; the organic ligands are in a *trans*-disposition and the lone-pair on lead is stereochemically active.

The diorganolead(II) species PbR_2 with $\text{R} = \text{CH}(\text{SiMe}_3)_2^1$ or $\text{C}_6\text{H}_2(\text{CF}_3)_3^2$ are known, the latter having been structurally characterised; they appear to be the only sigma-bonded organolead(II) compounds, though some interesting pi-bonded cyclopentadienyllead(II) species are known.³ Here we report what we believe to be first monoorganolead(II) compound of the type PbRX , namely PbR^*Cl , where R^* denotes the very bulky ligand $\text{C}(\text{SiMe}_2\text{Ph})_3$. In the crystal the compound is present as the dimer $[\{\text{PbR}^*(\mu\text{-Cl})\}_2]$ **1**.

The yellow–orange compound **1** was obtained by treatment of PbCl_2 in THF with 1 or 2 equiv. of the organolithium reagent $\text{LiR}^*\cdot 2\text{THF}$;† it is highly air sensitive, and is rapidly decomposed by exposure to light with separation of metallic lead. It was recrystallised from methylcyclohexane, and shown by an X-ray diffraction study‡ to have the dimeric structure depicted in Fig. 1, with the R^* groups in a *trans*-disposition. The dimer lies on a crystallographic inversion centre. Selected bond lengths and angles are shown in the legend to Fig. 1, and it will be seen that the chlorine bridges are not symmetrical, the $\text{Pb}–\text{Cl}'$ being 0.23 Å longer than the $\text{Pb}–\text{Cl}$ bond. The geometry around the metal can be regarded as distorted tetrahedral with a stereochemically active lone pair occupying one of the coordination sites.

It is of interest that no sigma-bonded organotin(II) compounds of the type SnRX seem to have been made. However, the amidotin(II) halides $[\{\text{Sn}(\mu\text{-X})\text{NR}_2\}_2]$, with $\text{X} = \text{Cl}$ or F ,

$\text{NR}_2 = \text{NCMe}_2(\text{CH}_2)_3\text{CMe}_2$ or $\text{N}(\text{SiMe}_3)_2$, are known, that with $\text{X} = \text{Cl}$ and $\text{NR}_2 = \text{N}(\text{SiMe}_3)_2$ in both *cis*- and *trans*-forms.^{4,5} The geometry around the metal in *trans*- $[\{\text{Sn}(\mu\text{-Cl})\text{NR}_2\}_2]$ $\text{R} = \text{SiMe}_3$ shows an overall similarity to that in **1**, with a $\text{Cl}–\text{Sn}–\text{Cl}$ angle of $81.33(4)^\circ$ and $\text{Cl}–\text{Sn}–\text{N}$ angles of $94.20(9)$ and $101.08(8)^\circ$, and the $\text{Cl}–\text{Sn}$ bonds differing in length by 0.15 Å, but the angle between the $\text{Sn}–\text{N}$ bond and the plane defined by metal and Cl atoms, *viz.* 79° , is significantly larger than the corresponding angle, 67° , in **1**.

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Footnotes

† All operations were carried out under argon. A solution of LiR^* (6.16 mmol) in THF (25 cm³) was added dropwise to a solution of PbCl_2 (6.16 mmol) in THF (25 cm³) and the mixture was stirred overnight (*ca.* 16 h) at room temp. The THF was then removed under vacuum and the residue extracted with methylcyclohexane (35 cm³). The extract was concentrated and then kept at *ca.* 5 °C. Yellow–orange crystals formed. *Selected data:* δ_{H} (C_6D_6) 0.25 (s, Me) and 7.13–7.43 (m, Ph); δ_{C} ($\text{C}_6\text{D}_6–\text{C}_6\text{H}_6$) 7.22 (Me), 27.19 (quat. C; no Pb satellites visible) and 129.5–135.5 (Ph); δ_{Si} (C_6D_6) –10.79. The ²⁰⁷Pb signal has not yet been located. When heated a sample does not melt but starts to turn brown at *ca.* 80 °C and by *ca.* 135 °C is completely black. Extensive decomposition prevented recording of a satisfactory EI or CI mass spectrum.

‡ *Crystal Data* for **1**: $\text{C}_{50}\text{H}_{66}\text{Cl}_2\text{Pb}_2\text{Si}_6$, $M = 1320.9$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.755(6)$, $b = 29.044(9)$, $c = 9.238(6)$ Å, $\beta = 110.95(5)^\circ$, $U = 2695(3)$ Å³, $Z = 2$, $D_c = 1.63$ g cm⁻³, $F(000) = 1296$. Monochromated Mo-K α radiation, $\lambda = 0.71073$ Å, $\mu = 6.5$ mm⁻¹. Data were collected at 173(2) K on an Enraf-Nonius CAD4 diffractometer in the ω - 2θ mode for the range $2 < \theta < 25^\circ$. The structure was solved by heavy atom methods with absorption correction by ψ -scans. The phenyl group on Si(3) was disordered equally between two slightly different orientations, and these were refined as rigid bodies of idealised geometry with isotropic thermal parameters. All other non-hydrogen atoms were anisotropic, and hydrogen atoms were included in riding mode with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or, for Me groups, $1.5 U_{\text{eq}}(\text{C})$. Final residuals were: for all 4728 independent reflections, $R_1 = 0.070$, $wR_2 = 0.208$; for the 3749 reflections with $I > 2\sigma(I)$, $R_1 = 0.048$, $wR_2 = 0.118$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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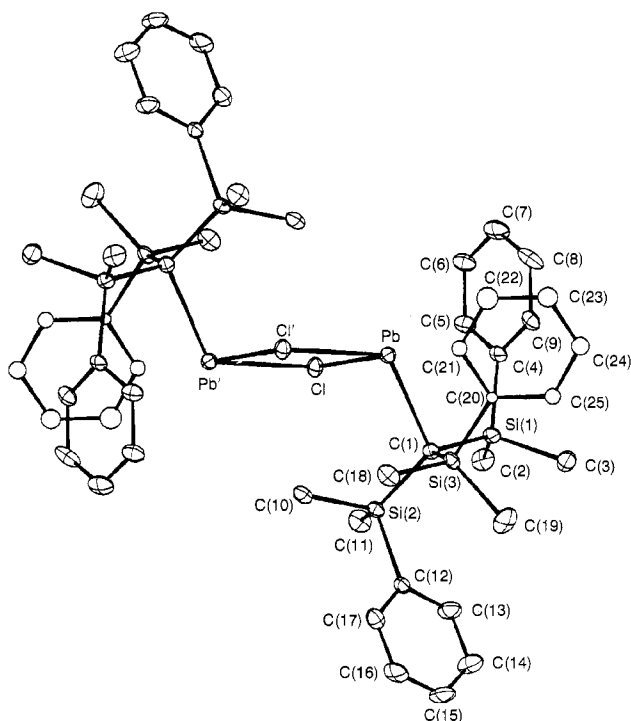


Fig. 1 Molecular structure of **1**. [Only one of the two orientations of the Ph group on Si(3) is shown.] Selected bond lengths (Å) and angles (°): $\text{Pb}–\text{C}(1)$ 2.435(1), $\text{Pb}–\text{Cl}$ 2.729(3), $\text{Pb}–\text{Cl}'$ 2.962(3), $\text{Si}(1)–\text{C}(1)$ 1.875(10), $\text{Si}(2)–\text{C}(1)$ 1.897(10), $\text{Si}(3)–\text{C}(1)$ 1.896(9); $\text{C}(1)–\text{Pb}–\text{Cl}$ 98.5(2), $\text{C}(1)–\text{Pb}–\text{Cl}'$ 112.0(2), $\text{Cl}–\text{Pb}–\text{Cl}'$ 87.08(8), $\text{Pb}–\text{Cl}–\text{Pb}'$ 92.92(8), $\text{Si}(1)–\text{C}(1)–\text{Si}(2)$ 118.7(5), $\text{Si}(1)–\text{C}(1)–\text{Si}(3)$ 116.7(5), $\text{Si}(2)–\text{C}(1)–\text{Si}(3)$ 118.7(5) (Symmetry element: $-x, -y, -z$).