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A Novel Organolead(II) Species, the Plumbacycloalkane Derivative [$CH_2SiMe_2C(SiMe_3)_2PbC(SiMe_3)_2SiMe_2CH_2$]

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Summary: The title lead(II) derivative was obtained as dark blue crystals by treatment of $PbCl_2$ with [Li(TMEDA)$_2$][$CH_2SiMe_2C(SiMe_3)_2LiC(SiMe_3)_2SiMe_2CH_2$] (TMEDA = N,N,N′,N′-tetramethylethylenediamine) in tetrahydrofuran and its structure determined by X-ray diffraction. The compound is in effect the first dialkylead(II) species to be structurally characterized. The C−Pb−C angle is 117.1(2)°. Analogous treatment of $SnCl_2$ yielded a yellow solid, which was judged from spectroscopic data to be the TMEDA complex of the analogous stannacycloalkane.

Two diaryllead(II) compounds, $PbAr_2$, have recently been structurally characterized, those with Ar = 2,4,6-$(CF_3)_3C_6H_2$, (**1**)[1] and Ar = 2,6-{2,4,6-$Me_3C_6H_2$}$_2C_6H_3$[2] (**2**), but only one corresponding dialkyl species has been isolated, namely Pb{$CH(SiMe_3)_2$}$_2$ (**3**), which was obtained in only 3% yield and was not characterized by an X-ray structure analysis.[3] We recently obtained the alkyllead chlorides PbRCl with R = $C(SiMe_3)_3$ or $C(SiMe_2Ph)_3$ but were unable to make the corresponding PbR_2 compounds.[4] We have now, however, obtained a very closely related species, **4**, containing the bulky dicarbanionic ligand {$(Me_3Si)_2CSiMe_2CH_2$}$_2$, the "siamyl" ligand, so called because it can be looked on as a Siamese twin pair of $(Me_3Si)_3C$ ("trisyl") ligands.[5] Compound **4** can be regarded as in effect a dialkyl derivative, but with the added novelty that the lead(II) center is part of a seven-membered ring. (More pedantically it can be described as the first diorganolead(II) compound with the metal attached to two sp^3-hybridized carbon centers.) Compound **4** was made by treatment of $PbCl_2$ with [Li(TMEDA)$_2$][$CH_2SiMe_2C(SiMe_3)_2LiC(SiMe_3)_2SiMe_2CH_2$][5] in tetrahydrofuran (THF) and isolated from heptane in 85% yield as dark blue crystals, which melted at 128−130 °C without apparent decomposition.[6] An X-ray diffraction study revealed the molecular structure shown in Figure 1.[7] The overall form of the molecule, including the conformation of the seven-membered ring, is quite similar to that of the mercury derivative [$CH_2SiMe_2C(SiMe_3)_2HgC(SiMe_3)_2SiMe_2CH_2$],[5] except that the C−Pb−C angle (117.1(2)°) is much narrower than the C−Hg−C angle (165.8(2)°) and the endocyclic Pb−C−Si angles (mean 118.9(3)°) consequently much wider than the Hg−C−Si angles (97.6(2)°). (The exocyclic Pb−C−Si angles, which range from 96.2(2) to 104.7(2)°, are thus correspondingly smaller than the related Hg−C−Si angles, 106.8(2) and 109.4(2)°). The C−Pb−C angle in **4** is slightly larger than that in **2** (114.5(6)°)[2] and substantially larger than that in **1** (94.5(1)°),[1] in which the angle may possibly be influenced by the observed intramolecular F···Pb interactions. (In **4** there are fairly short distances of 3.41, 3.38, 3.39, and 3.38 Å, respectively, between the Pb atom and the C6, C7, C14, and C17 atoms, which could possibly represent very weak agostic interactions; the sum of the covalent radii of C and Pb is 3.70 Å.)

$$Pb\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2$$
1

$$Pb[C_6H_3\{C_6H_2Me_3\text{-}2,4,6\}_2\text{-}2,6]_2$$
2

$$Pb\{CH(SiMe_3)_2\}_2$$
3

$$[CH_2SiMe_2C(SiMe_3)_2PbC(SiMe_3)_2SiMe_2CH_2]$$
4

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(6) A solution of Li(TMEDA)$_2$][$CH_2SiMe_2C(SiMe_3)_2LiC(SiMe_3)_2SiMe_2CH_2$][5] (0.50 g, 0.70 mmol) in THF (15 cm^3) was added at room temperature to a stirred slurry of anhydrous $PbCl_2$ (0.20 g, 0.70 mmol) in THF (10 cm^3) under argon with protection from light. The mixture was stirred overnight, the solvent then removed under vacuum, and the residue extracted with heptane (25 cm^3). The extract was filtered and the dark green filtrate was concentrated to 5 cm^3 and kept at −20 °C to deposit dark blue crystals of **4**: yield 0.40 g, 85%; mp 128−130 °C. Because of the sensitivity of the compound a satisfactory analysis could not be obtained (Anal. Calcd for $C_{20}H_{52}PbSi_6$: C, 35.9; H, 7.8. Found: C, 33.9; H, 7.6). UV/vis (hexane): λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}) 610 (ca. 700), 385 (ca. 1300). ^{1}H NMR (C_6D_6): δ 0.19 (s, 36H, Me_3Si), 0.38 (s, 12H, Me_2Si), 1.13 (s, 4H, CH_2). ^{13}C NMR: δ 4.8 (Me_3Si), 11.2 (Me_2Si), 16.6 (CH_2Si), 114.7 (^1J(CSi) = 34.2 Hz, CSi_3). ^{29}Si NMR: δ −15.4 (Me_3Si), −4.1 (Me_2Si). ^{207}Pb NMR: δ +10 050. MS (EI, 70 eV): *m/z* 668 (10, M$^+$), 424 (40, [$PbC(SiMe_3)_2SiMe_2$]$^+$), 217 (100, [$(Me_3Si)_2CHSiMe_2$]$^+$). HRMS: *m/z* calcd for M$^+$ 668.245 113, found 668.244 931.

(7) Crystal data for **4**: $C_{20}H_{52}PbSi_6$, M_r = 668.4, triclinic, *a* = 8.911(2) Å, *b* = 8.939(4) Å, *c* = 21.701(8) Å, α = 84.33(3)°, *β* = 89.48(3)°, *γ* = 63.45(3)°, *V* = 1537.6(10) Å^3, space group $P\bar{1}$ (No. 2), Mo Kα radiation, *λ* = 0.710 73 Å, *Z* = 2, D_c = 1.44 Mg m^{-3}, *F*(000) = 676, crystal dimensions 0.3 × 0.2 × 0.1 mm, *μ* = 5.73 mm^{-1}, CAD4 diffractometer, $\theta-2\theta$ mode, *T* = 253(2) K, 2 < *θ* < 25°, 5403 unique reflections measured and 4955 with $I > 2\sigma(I)$ used, absorption correction from ψ scans (T_{max} = 1.00, T_{min} = 0.41), structure analysis by direct methods (SHELXS-86), full-matrix least-squares refinement on F^2 (SHELXL-93) with non-H atoms anisotropic, H atoms in riding mode with $U_{iso} = 1.2U_{eq}$ or $1.5U_{eq}$ for Me groups, $R1(I > 2\sigma(I)) = 0.036$, wR2 = 0.092, R1(all data) 0.041, wR2 = 0.095, *S* = 1.049.

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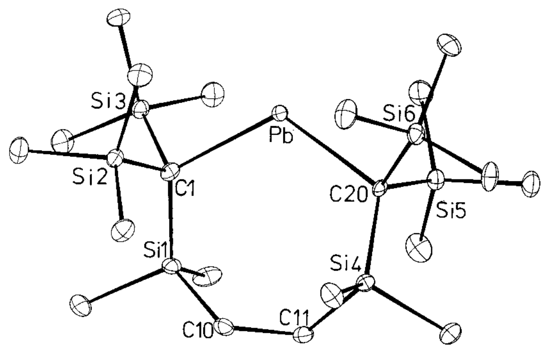

Figure 1. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Pb−C1 = 2.397(6), Pb−C20 = 2.411(5), C1−Si1 = 1.868(6), C1−Si2 = 1.886(6), C1−Si3 = 1.901(5), C20−Si4 = 1.886(6), C20−Si5 = 1.885(6), C20−Si6 = 1.884(5), Si1−C10 = 1.882(6), Si4−C11 = 1.890(6), C10−C11 = 1.539(8); C1−Pb−C20 = 117.1(2), Pb−C1−Si1 = 118.6(3), Pb−C20−Si4 = 119.2(3), Pb−C1−Si2 = 104.7(2), Pb−C1−Si3 = 96.8(2), Pb−C20−Si5 = 104.6(2), Pb−C20−Si6 = 96.2(2), C1−Si1−C10 = 115.2(3), C20−Si4−C11 = 116.1(2), Si1−C10−C11 = 118.8(4), Si4−C11−C10 = 117.5(4).

The Pb−C distance in **4** (mean 2.404(6) Å) is not significantly different from those in **1** (2.366(5) Å)[1] and **2** (2.334(12) Å).[2] The molecule as a whole has an approximate C_2 axis bisecting the C20−Pb−C1 angle, so that Si2 and Si5 are almost equidistant from the Pb atom, as are Si3 and Si6. The shortest Pb···Pb distance is 8.91 Å; therefore, there is no tendency for the molecules to dimerize, in contrast to those of **3**.

The ^{207}Pb NMR chemical shift for **4**, δ 10 050 (in C_6D_6), is, as far as we can ascertain, the largest downfield shift ever observed for ^{207}Pb, but it is not very far removed from those of δ 9112 for **3** (in toluene-d_8, but δ 2956 in Et_2O, in which it is presumably present as an ether complex),[8] δ 8888 for Pb(Tbt)(Tip) (Tbt = 2,4,6-$\{(Me_3Si)_2CH\}_3C_6H_2$; Tip = 2,4,6-$(Me_2CH)_3C_6H_2$), and δ 8873 for Pb(Tbt)(Ttm) (Ttm = 2,4,6-$(Me_3SiCH_2)_3C_6H_2$) (the last two in toluene-d_8).[9] However, for reasons that are not apparent, much smaller shifts were recorded for **1** (δ 4878 in C_6D_6) and **2** (δ 3870 in C_6D_6). Whereas **4** is deep blue and **2**, **3**, Pb(Tbt)(Tip), and Pb(Tbt)(Ttm) are purple, **1** is yellow. The color of **3** was attributed to charge transfer between the lone pair and vacant silicon 3d levels.[3]

The ease of formation and stability of **4** suggest that there should be no thermodynamic barrier to formation of the closely related Pb$\{C(SiMe_3)_3\}_2$ and thus that our failure[4] to obtain the latter can be attributed to unfavorable kinetic effects.

Reaction of $\{Li(TMEDA)_2\}[CH_2SiMe_2C(SiMe_3)_2LiC(SiMe_3)_2SiMe_2CH_2]$ with $SnCl_2$ in THF gave a red solution in which the tin analogue of **4** may have been present. However, the compound which crystallized was pale yellow and contained TMEDA.[10] Crystals suitable for an X-ray diffraction study have not yet been obtained, but the spectroscopic properties of this product leave no doubt that the stannacycloalkane analogous to that in **4** has been formed and apparently isolated as the TMEDA complex $CH_2SiMe_2C(SiMe_3)_2SnC(SiMe_3)_2SiMe_2CH_2]\cdot$TMEDA. The ^{119}Sn NMR spectrum (in C_6D_6) shows signals at δ 410, consistent with four-coordination at tin. In contrast, the (dark red) chelated two-coordinate tin compound $CH_2(Me_3Si)_2CSnC(SiMe_3)_2CH_2$ shows a shift of δ 2323 (in C_6D_6),[11] the monomeric form of Sn$\{CH(SiMe)_2\}_2$ a shift of δ 2328, and the dimer [Sn$\{CH(SiMe)_2\}_2]_2$, containing three-coordinate tin, shifts of δ 725 and 740 (two conformations).[12]

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Supporting Information Available: Tables of atom coordinates, bond lengths and angles, and anistropic displacement parameters for **4** (3 pages). Ordering information is given on any current masthead page.

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[10] A solution of $[Li(TMEDA)_2][CH_2SiMe_2C(SiMe_3)_2LiC(SiMe_3)_2SiMe_2CH_2]^5$ (0.50 g, 0.70 mmol) in THF (25 cm^3) was added at room temperature to a stirred slurry of anhydrous $SnCl_2$ (0.20 g, 1.00 mmol) in THF (10 cm^3) under argon with protection from light. The mixture was stirred overnight, the solvent then removed under vacuum, and the residue extracted with light petroleum (bp 40−60 °C, 25 cm^3). The extract was filtered, and the dark red filtrate was concentrated to 5 cm^3 and kept at 5 °C to deposit small yellow crystals judged to be of $[CH_2SiMe_2C(SiMe_3)_2SnC(SiMe_3)_2SiMe_2CH_2]\cdot$TMEDA: yield 0.36 g, 51%. Because of the sensitivity of the compound a satisfactory analysis could not be obtained. ^{1}H NMR (C_6D_6): δ 0.28 (s, 12H, Me_2Si), 0 65 (s, 36H, Me_3Si), 0.74 (s, 4H, CH_2Si), 1.70 (s, 4H, TMEDA), 1.90 (s, 12H, TMEDA). ^{13}C NMR: δ 6.2 (Me_3Si), 2.1 (Me_2Si), 13.9 (CH_2Si), 45.4 and 56.1 (TMEDA); no signal detected from CSi_3. ^{29}Si NMR: δ −4.0 (Me_3Si), −0.05 (Me_2Si). ^{119}Sn NMR: δ +410. MS (EI, 70 eV): *m/z* 580 (50, $[M - TMEDA]^+$), 336 (10, $[SnC(SiMe_3)_2SiMe_2]^+$, 217 (100).

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