π-Indenyl tin(II) and lead(II) compounds

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The syntheses and structures of the first indenyl-substituted tin(II) complexes, [Sn{1,3-$(SiMe_3)_2C_9H_5$}$_2$] and [Sn(C_5Me_5)-{1,3-$(SiMe_3)_2C_9H_5$}], are described; the lead(II) analogue of the latter compound has also been prepared and structurally characterized.

Given that stannocene, [Sn(η^5-C_5H_5)$_2$], is the longest known tin(II) organyl,[1] it is curious that a bis(indenyl) analogue has not been reported. Interest in π-indenyl complexes has been rekindled recently because of a new interpretation[2] of the so-called "indenyl effect," *i.e.* the significantly more facile η^5-to-η^3 rearrangement of the indenyl *vis-à-vis* the cyclopentadienyl ligand. However, in contrast to the abundant structural data that are available for d-block π-indenyl complexes,[3] there is only a paltry amount of such information for main group compounds. In fact, structurally authenticated π-indenyl complexes of the post-transition elements are confined to [Pb{1,3-$(SiMe_3)_2C_9H_5$}$_2$][4] and [Ge(C_5Me_5){1,3-$(SiMe_3)_2C_9H_5$}].[5] Herein, we describe the syntheses and structures of [Sn{1,3-$(SiMe_3)_2C_9H_5$}$_2$] (**1**), [Sn(C_5Me_5){1,3-$(SiMe_3)_2C_9H_5$}] (**2**) and [Pb(C_5Me_5){1,3-$(SiMe_3)_2C_9H_5$}] (**3**).

Compound **1** was prepared in 62% yield by treatment of $SnCl_2$ with 2.0 equivalents of [Li{1,3-$(SiMe_3)_2C_9H_5$}] (**4**)[6] in THF solution at 0 °C. Initially formed as a thick red oil, **1** crystallizes slowly upon storage at −20 °C. Red, crystalline **1** decomposes at room temperature over the course of a few weeks. The elemental composition of **1** was established by HRMS.† The presence of four and six resonances in the ^{1}H and ^{13}C NMR spectra, respectively, indicated the equivalence of the indenyl rings in solution† but did not establish the conformation. An X-ray crystal structure determination‡ revealed that **1** is isostructural with the lead analogue, [Pb{1,3-$(SiMe_3)_2C_9H_5$}$_2$],[4] and crystallizes with two enantiomeric molecules per asymmetric unit, one of which is illustrated in Fig. 1(a). The indenyl ligands are arranged in a *gauche* fashion such that interactions between the Me_3Si groups are minimized (Fig. 1(b)). The Sn atom is bonded to the five-membered ring of both indenyl ligands. However, for enantiomer 1, the average C–Sn distance to the upper ring junction carbon atoms C4 and C9 (2.762(4) Å) is longer than that to the remaining carbon atoms C1, C2 and C3 (av. 2.692(4) Å). For the lower ring, the corresponding average distances are 2.810(3) and 2.630(3) Å. The difference between these two values, which is often referred to as the "slip parameter" $\Delta_{M\text{–}C}$, is an indicator of hapticity.[7] For perfect η^5 coordination, $\Delta_{M\text{–}C}$ = 0, while for η^3-bonded complexes, $\Delta_{M\text{–}C}$ ranges from 0.69–0.79 Å. In the case of **1**, the average $\Delta_{Sn\text{–}C}$ is of an intermediate value (0.125 Å) and thus a possible example of what has been called η^2–η^3 coordination.[8] The average C_5 ring centroid–Sn distance of 2.421 Å is slightly longer than that in [Sn(η^5-C_5Me_5)$_2$] (2.396 Å).[9] The ring centroid–Sn–ring centroid angle is close to linear (175.9°) hence, like the sterically encumbered stannocenes [Sn(C_5Ph_5)$_2$]$_2$[10] and [Sn($C_5{}^iPr_5$)$_2$],[11] the tin lone pair presumably resides in a 5s orbital.

Compounds **2** and **3** were prepared in 45 and 36% yields, respectively, *via* the reactions of [M(C_5Me_5)Cl] (M = Sn,[12] Pb[13]) with one equivalent of **4** in THF solution at 0 °C. Crystals of **2**

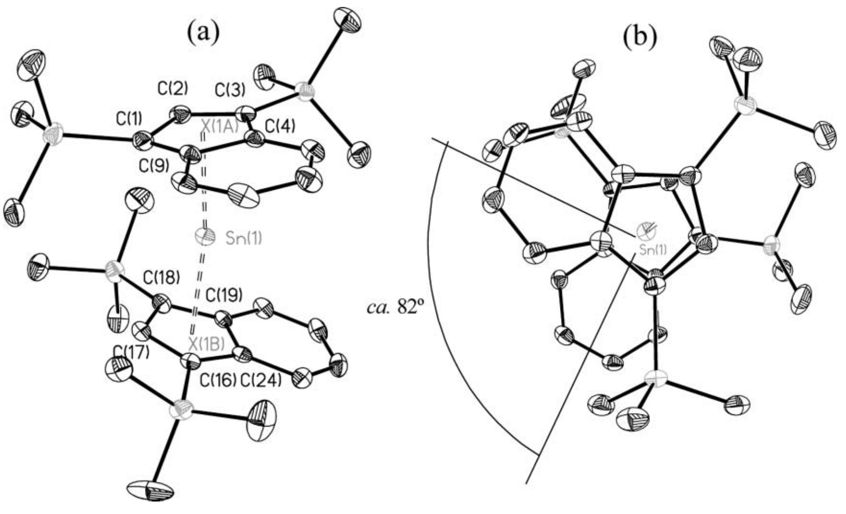

Fig. 1 (a) Side view of enantiomer 1 of [Sn{1,3-$(SiMe_3)_2C_9H_5$}$_2$] (**1**) showing the atom numbering scheme. The hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Sn(1)–C(1) 2.639(4), Sn(1)–C(2) 2.670(4), Sn(1)–C(3) 2.767(4), Sn(1)–C(4) 2.789(4), Sn(1)–C(9) 2.735(4), Sn(1)–C(16) 2.711(3), Sn(1)–C(17) 2.580(3), Sn(1)–C(18) 2.600(3), Sn(1)–C(19) 2.773(3), Sn(1)–C(24) 2.843(3). (b) View down the Cp ring centroid–Sn(1)–Cp ring centroid vector showing the *gauche* conformation.

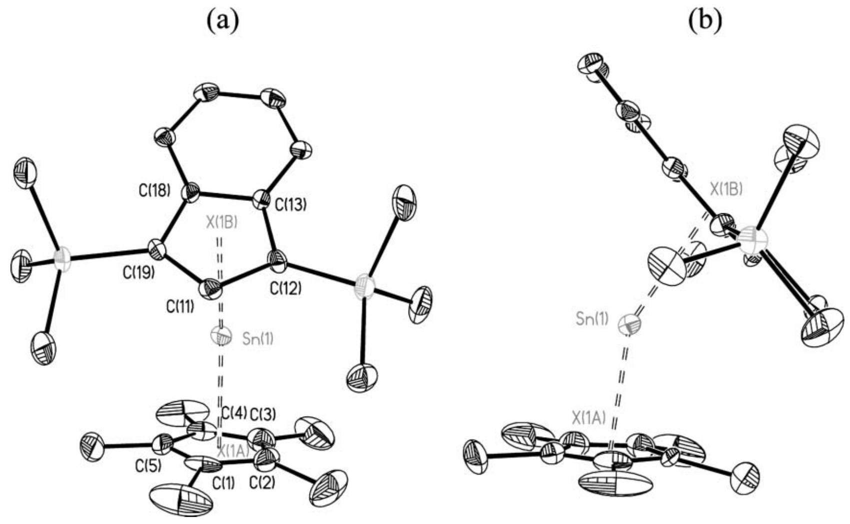

Fig. 2 Two views of [Sn(C$_5$Me$_5$){1,3-(SiMe$_3$)$_2$C$_9$H$_5$}] (**2**) showing the atom numbering scheme. The hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Sn(1)–C(1) 2.474(7), Sn(1)–C(2) 2.565(7), Sn(1)–C(3) 2.701(7), Sn(1)–C(4) 2.708(7), Sn(1)–C(5) 2.570(8), Sn(1)–C(11) 2.695(7), Sn(1)–C(12) 2.791(7), Sn(1)–C(13) 2.966(7), Sn(1)–C(18) 2.976(7), Sn(1)–C(19) 2.800(7).

(yellow) and **3** (red) were obtained by storage of the initially formed oils at −20 °C. Both compounds, which decompose within a few days at room temperature, were characterized by HRMS and multinuclear NMR spectroscopy.† The X-ray crystal structures of **2** and **3** are very similar and that of **2** is shown in Fig. 2. Perhaps the most conspicuous feature of both structures is the fact that the C$_5$Me$_5$ ring centroid–metal distances (2.313 Å for **2** and 2.409 Å for **3**) are shorter than the corresponding distances to the indenyl five-membered ring centroids (2.561 for **2** and 2.633 for **3**) thus implying that the η^5-C$_5$Me$_5$ ring is bound more strongly to Sn or Pb than to the η^5-indenyl ring. Such a conclusion is in agreement with the views of Calhorda *et al.*[2,8] The average ring centroid–M–ring centroid angles for **2** (151.6°) and **3** (147.3°) are similar to those in [Sn(η^5-C$_5$Me$_5$)$_2$] (144.1°)[9] and Pb(η^5-C$_5$Me$_5$)$_2$ (145.8°)[14]; however, the average metal–carbon (Cp*) distances are slightly shorter in **2** (2.604(8) Å) and **3** (2.69(7) Å) than in the corresponding decamethylmetallocenes. The slip parameters for **2** (0.155 Å) and **3** (0.171 Å) are comparable to that for **1** (0.105 Å) and thus are suggestive of η^2–η^3 bonding.

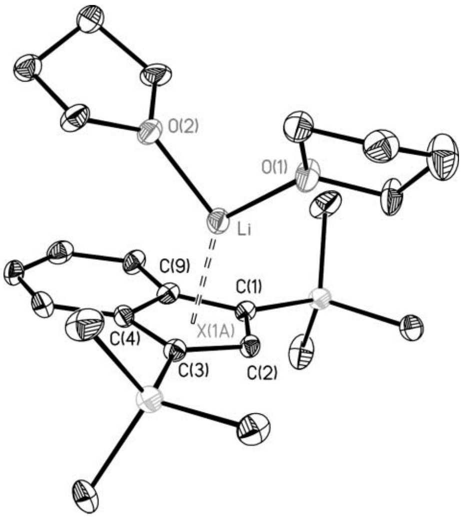

Fig. 3 View of [Li(THF)$_2${1,3-(Me$_3$Si)$_2$C$_9$H$_5$}] (**4**·2THF) showing the atom numbering scheme. The hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Li–C(1) 2.320(9), Li–C(2) 2.243(9), Li–C(3) 2.327(10), Li–C(4) 2.414(9), Li–C(9) 2.410(9), Li–O(1) 1.913(8), Li–O(2) 1.915(8).

Finally, in the course of the foregoing synthetic work, it was possible to isolate [Li(THF)$_2${1,3-(SiMe$_3$)$_2$C$_9$H$_5$}] (**4**·2THF). The crystalline state of **4**·2THF comprises monomeric units in which a Li(THF)$_2$ moiety is bonded to the five-membered ring of the indenyl ligand (Fig. 3).‡ The slip parameter $\Delta_{\text{Li–C}}$ is 0.115 Å.

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Notes and references

† **1**: HRMS (CI, CH$_4$) calc. for C$_{30}$H$_{46}$Si$_4$Sn *m*/*z* 639.1777; found 639.1788. ^{1}H NMR (300 MHz, 295 K, C$_6$D$_6$) δ 0.35 [s, 36H, SiMe$_3$], 6.36 [s, H(2)], 6.99–7.02 and 7.49–7.52 [AA′BB′ system, H(5)–H(8)]. ^{13}C{^{1}H} NMR (125.69 MHz, 295 K, C$_6$D$_6$) δ 1.09 [s, Me$_3$Si], 110.41 [s, C(1) and C(3)], 122.76–122.92 [s, C(4), C(9) and C(2)], 124.00 [s, C(6) and C(7)], 141.01 [s, C(5) and C(8)]. ^{119}Sn NMR (500 MHz, 295 K, C$_6$D$_6$) δ −2168. **2**: HRMS (CI, CH$_4$) calc. for C$_{24}$H$_{35}$Si$_2$Sn *m*/*z* 499.1299; found, 499.1319. ^{1}H NMR (300 MHz, 295 K, C$_6$D$_6$) δ 0.50 [s, Me$_3$Si], 1.72 [s, (CH$_3$)$_5$C$_5$], 6.41 [s, H(2)], 7.08–7.11 and 7.80–7.83 [AA′BB′ system, H(5)–H(8)]. ^{13}C{^{1}H} NMR (125.69 MHz, 295 K, C$_6$D$_6$) δ 0.97 [s, Me$_3$Si], 9.42 [s, (CH$_3$)$_5$C$_5$], 111.54 [s, C(1) and C(3)], 118.37 [s, (CH$_3$)$_5$C$_5$], 122.22–122.34 [s, C(4), C(9) and C(2)], 124.06 [s, C(6) and C(7)], 141.03 [s, C(5) and C(8)]. ^{119}Sn NMR (500 MHz, 295 K, C$_6$D$_6$) δ −2121. **3**: HRMS (CI, CH$_4$) calc. for C$_{25}$H$_{38}$PbSi$_2$ *m*/*z* 603.2356; found 603.2372. ^{1}H NMR (300 MHz, 295 K, C$_6$D$_6$) δ 0.49 [s, Me$_3$Si], 1.99 [s, (CH$_3$)$_5$C$_5$], 6.46 [s, H(2)], 7.12–7.14 and 7.82–7.85 [AA′BB′ system, H(5)–H(8)]. ^{13}C{^{1}H} NMR (125.69 MHz, 295 K, C$_6$D$_6$) δ 1.20 [s, Me$_3$Si], 9.06 [s, (CH$_3$)$_5$C$_5$], 111.77 [s, C(1) and C(3)], 119.99 [s, (CH$_3$)$_5$C$_5$], 121.85–121.88 [s, C(4), C(9) and C(2)], 123.66 [s, C(6) and C(7)], 126.94 [s, C(5) and C(8)]. ^{207}Pb NMR (500 MHz, 295 K, CDCl$_3$) δ −4402.

‡ *Crystal data*: for **1**: C$_{30}$H$_{46}$Si$_4$Sn, triclinic, space group $P\bar{1}$, a = 11.440(5), b = 17.300(5), c = 18.587(5) Å, α = 103.452(5), β = 105.369(5),

$\gamma = 91.091(5)^\circ$, $V = 3437(2)$ Å^3, $Z = 2$, $D_c = 1.201$ g cm^{-3}, μ(Mo–Kα) = 0.898 mm^{-1}, $R_1 = 0.0433$, $wR_2 = 0.0798$, GOF = 1.052. For **2**: $C_{25}H_{38}Si_2Sn$, orthorhombic, space group $P2_12_12$, $a = 21.232(5)$, $b = 24.238(5)$, $c = 10.398(5)$ Å, $\alpha = \beta = \gamma = 90.0^\circ$, $V = 5351(3)$ Å^3, $Z = 4$, $D_c = 1.275$ g cm^{-3}, μ(Mo–Kα) = 1.053 mm^{-1}, $R_1 = 0.0590$, $wR_2 = 0.0850$, GOF = 1.049. For **3**: $C_{25}H_{38}PbSi_2$ orthorhombic, space group $Pna2_1$, $a = 35.144(5)$, $b = 10.548(5)$, $c = 31.090(5)$ Å, $\alpha = \beta = \gamma = 90.0^\circ$, $V = 11{,}525(6)$ Å^3, $Z = 4$, $D_c = 1.388$ g cm^{-3}, μ(Mo–Kα) = 5.946 mm^{-1}, $R_1 = 0.0806$, $wR_2 = 0.1657$, GOF = 1.019. For **4**·2THF: $C_{23}H_{39}LiSi_2O$, orthorhombic, space group $Pna2_1$, $a = 15.226(5)$, $b = 10.240(5)$, $c = 16.141(5)$ Å, $\alpha = \beta = \gamma = 90.0^\circ$, $V = 2517(2)$ Å^3, $Z = 4$, $D_c = 1.087$ g cm^{-3}, μ(Mo–Kα) = 0.155 mm^{-1}, $R_1 = 0.0769$, $wR_2 = 0.1084$, GOF = 1.056. All four data sets were collected at 153 K on a Nonius-Kappa CCD diffractometer. CCDC 244711–244714. See http://www.rsc.org/suppdata/cc/b4/b410549d/ for crystallographic data in .cif or other electronic format

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