Synthesis of molecular lead–pnictogen compounds including [$Pb_4(SbSi\textit{i}Pr_3)_6$], the first structurally characterised compound with a lead–antimony bond†

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Received (in Cambridge, UK) 14th October 2009, Accepted 22nd December 2009
First published as an Advance Article on the web 22nd January 2010
DOI: 10.1039/b921473a

The first structurally characterised lead(II) antimony compound with a chemical bond between lead and antimony, [$Pb_4(SbSi\textit{i}Pr_3)_6$] (3), was obtained by the reaction of $\textit{i}Pr_3SiSb(SiMe_3)_2$ with $PbCl_2$ in Et_2O at 0 °C. The Pb_4Sb_6 cage structure can be described as a Pb_4Sb_4 heterocube where two $SbSi\textit{i}Pr_3$ edges are replaced by $(SbSi\textit{i}Pr_3)_2$. The average Pb–Sb bond length is 297.7 pm. The heterocubane compounds [$PbESi\text{-}\textit{t}Bu_2Ph$]$_4$ (E = P, As) were obtained from the reactions of $Pb\{N(SiMe_3)_2\}_2$ with $\textit{t}Bu_2PhSiEH_2$.

Molecular compounds of group 14/15 elements have been investigated well by different research groups.[1] However, the systems Pb/E (E = P, As) are pretty scarce.[2] Examples are the cyclic compound [$Pb\{P(SiMe_3)_2\}_2$]$_2$ obtained from the reaction of $Pb\{N(SiMe_3)_2\}_2$ with $HP(SiMe_3)_2$ or the hexagonal prism [$PbAsSi\textit{i}Pr_3$]$_6$ which was synthesised by the reaction of $\textit{i}Pr_3SiAs(SiMe_3)_2$ with $PbCl_2$. Schumann described the lead(IV) pnictogen compounds $E(PbR_3)_3$ (E = P, As, Sb; R = Me, Ph) and Ph_3PbEPh_2 (E = As, Sb), but to the best of our knowledge, no structure information of these compounds has been made available so far. Moreover, the quaternary phase $K_8PbNbAs_5$ containing Pb–As bonds is known.[3]

Besides fundamental aspects of the formation and stability of chemical bonds between heavy main group elements, binary, ternary, and quaternary phases of these elements are of considerable interest due to their potential use as thermoelectrics. Cluster compounds of the element combination Pb/As and Pb/Sb are potential precursors of such materials.[4]

The reaction of $Pb\{N(SiMe_3)_2\}_2$ and $\textit{t}Bu_2PhSiPH_2$ at a molar ratio of 1 : 1 leads to the formation of [$PbPSi\textit{t}Bu_2Ph$]$_4$ (**1**) which can be isolated as orange crystals by cooling the reaction mixture to 4 °C.‡ **1** crystallises in the triclinic space group $P\bar{1}$ and consists of a distorted Pb_4P_4 cube, the average Pb–P–Pb angle is 98.02° and the average P–Pb–P angle is 81.59° (Fig. 1).§ The deviation of these angles from 90° probably is a result of the large difference of the covalent radii of Pb and P atoms. The P–Pb bond lengths are between 271.1(4) and 274.6(4) pm long. For comparison, the endocyclic Pb–P bond lengths in the cyclic compound [$Pb\{P(SiMe_3)_2\}_2$]$_2$ are in the same range (274.7 and 279.6 pm).

The $^{31}P\{^1H\}$ NMR spectrum shows a singlet signal with a significant high field shift at −512.7 ppm. Similarly strong high field shifts were observed for tin–phosphorus cage compounds such as [$SnPSi\textit{i}Pr_3$]$_6$.[5]

[$PbAsSi\textit{t}Bu_2Ph$]$_4\cdot$2THF (**2**) was obtained from the reaction of $Pb\{N(SiMe_3)_2\}_2$ with the primary silylarsine $\textit{t}Bu_2PhSiAsH_2$.‡ It crystallises in the triclinic space group $P\bar{1}$ with four THF molecules in the elementary cell.§ The molecular structure (Fig. 2) is almost identical to the phosphorus compound **1**, but with $AsSi\textit{t}Bu_2Ph$ groups as building blocks instead of the $PSi\textit{t}Bu_2Ph$ fragments. The average Pb–As–Pb angle is 98.92° and the average As–Pb–As angle is 80.45°. The As–Pb bond length are between 279.84 and 283.63 pm and comparable with the bond lengths in the hexagonal prism [$PbAsSi\textit{i}Pr_3$]$_6$ (279.41–283.72 pm).[2g]

We succeeded in synthesising and structurally characterising a lead–antimony compound produced by the reaction of $\textit{i}Pr_3SiSb(SiMe_3)_2$ with $PbCl_2$ in Et_2O at 0 °C. Black crystals form during a period of three weeks at −35 °C. Crystal structure analysis shows the formation of the cage compound [$Pb_4(SbSi\textit{i}Pr_3)_6$] (**3**).‡ Compound **3** crystallises in the monoclinic space group $P2_1/c$.§ The Pb_4Sb_6 cage structure can be described as a Pb_4Sb_4 heterocube where two $SbSi\textit{i}Pr_3$ corners are replaced by $(SbSi\textit{i}Pr_3)_2$ (Fig. 3). The two remaining $SbSi\textit{i}Pr_3$ corners (Sb(5) and Sb(6)) coordinate μ_3 to three Pb

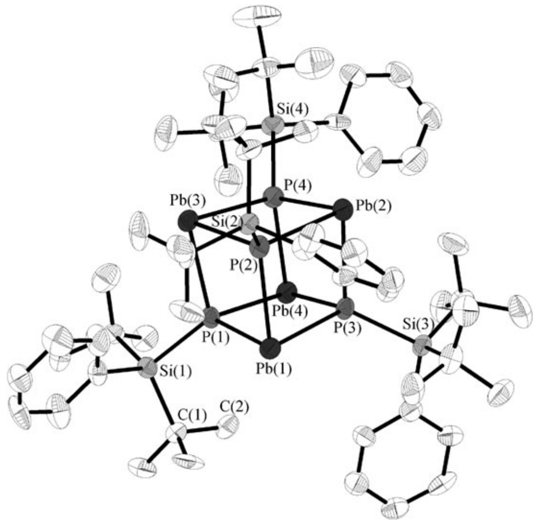

Fig. 1 Molecular structure of **1**; thermal ellipsoids represent a 40% probability level, hydrogen atoms are not shown, selected bond lengths (pm) and angles (°): P–Pb 271.1(4)–274.6(4), P–Si 223.1(5)–225.3(5); Pb–P–Pb 97.34(1)–99.02(1), P–Pb–P 80.39(1)–82.61(1).

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† CCDC 751816–751818. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b921473a

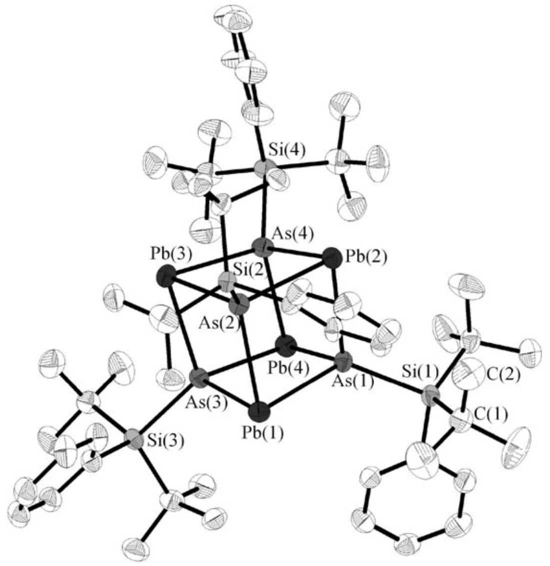

Fig. 2 Molecular structure of **2**; thermal ellipsoids represent a 40% probability level, hydrogen atoms are not shown, selected bond lengths (pm) and angles (°); As–Pb 279.84(1)–283.63(1), As–Si 235.1(2)–235.8(2); Pb–As–Pb 97.68(4)–100.16(4), As–Pb–As 79.40(3)–81.49(4).

atoms. In contrast to this, the $(SbSi\textit{i}Pr_3)_2$ units coordinate η^2 to three Pb atoms, such that one of the Sb atoms binds to two lead atoms (Sb(1) and Sb(4), whereas the other Sb atom binds to only one Pb atom (Sb(2) and Sb(3)). As a whole, the cage consists of two four-membered Pb_2Sb_2 rings and four five-membered Pb_2Sb_3 rings. The formation of the antimony barbells probably results from a redox process with the formation of elemental lead as a by-product. The Pb–Sb bonds are between 294.56(1) and 301.43(1) pm long and are in the range expected for the Pb–Sb bond length (the sum of the covalent radii is about 295 pm). The average Sb–Sb bond length is 282.09 pm and, hence, exactly corresponds to the sum of the covalent radii (Sb 141 pm). It is in the same range as in other antimony compounds with Sb–Sb bonds such as $[Sb_4(AsSi\textit{i}Pr_3)_4]$ (Sb–Sb 288–289 pm).[6]

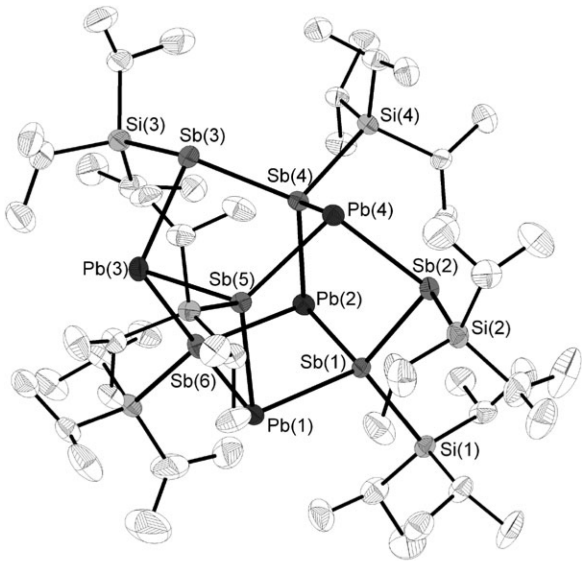

Fig. 3 Molecular structure of **3**; thermal ellipsoids represent a 40% probability level, hydrogen atoms are not shown, selected bond lengths (pm) and angles (°): Sb(1)–Sb(2) 281.62(1), Sb(3)–Sb(4) 282.55(1), Sb(1)–Pb(1) 300.06(1), Sb(1)–Pb(2) 300.77(1), Sb(6)–Pb(1) 301.43(1), Sb(6)–Pb(2) 294.66(1), Sb(6)–Pb(3) 297.28(1), Sb(3)–Pb(3) 295.74(1), Sb(4)–Pb(4) 297.74(1), Sb(4)–Pb(2) 298.94(9), Sb(5)–Pb(1) 294.56(1), Sb(5)–Pb(3) 297.00(1), Sb(5)–Pb(4) 296.05(1), Sb(2)–Pb(4) 294.82(9), Sb–Si 256.3(3)–260.7(3); Sb(1)–Pb(1)–Sb(2) 82.06(3), Pb(1)–Sb(6)–Pb(2) 97.89(3), Pb(1)–Sb(1)–Sb(6) 119.78(3), Sb(1)–Sb(2)–Pb(4) 96.61(3), Sb(2)–Pb(4)–Sb(4) 88.37(3), Sb(4)–Sb(3)–Pb(3) 95.45(3), Sb(6)–Pb(3)–Sb(3) 100.64(3), Pb(2)–Sb(4)–Sb(3) 118.31(3).

To sum up, pnictogen compounds with large silyl groups are possible precursors to achieve pnictogen bridged lead compounds. It is proposed to carry out further studies to achieve chemical bonds between bismuth and tin as well as bismuth and lead. Such compounds are of fundamental interest concerning the formation and stability of bonds between these elements. Moreover, such compounds are promising precursors for thermoelectric devices.

Notes and references

‡ *Experimental*: All manipulations were performed under rigorous exclusion of oxygen and moisture using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before use. The starting materials were prepared according to literature: $Pb\{N(SiMe_3)_2\}_2$,[7] $\textit{t}Bu_2PhSiCl$,[8] $[LiEH_2(dme)]$ (E = P, As),[9] $\textit{i}Pr_3SiSb(SiMe_3)_2$.[10] The NMR spectra were recorded with a Bruker Ultrashield 300 spectrometer. MALDI-MS spectra were recorded on a "Applied Biosystems Voyager-DE Pro" with 1,8,9-anthracenetriol as matrix.

$\textit{t}Bu_2PhSiPH_2$: A solution of 7.33 g $\textit{t}Bu_2PhSiCl$ (0.0287 mol) in 50 mL THF was added to a suspension of 3.72 g $[LiPH_2(dme)]$ (0.0287 mol) in 75 mL THF at 0 °C. After stirring for 16 h at room temperature, the THF was replaced by 100 mL of pentane. The precipitated LiCl was subsequently removed by filtration. After removal of the solvent, a vacuum distillation yielded a colourless oil of 5.34 g (74%) $\textit{t}Bu_2PhSiPH_2$ (bp 83–84 °C at 10^{-3} mbar). ^1H NMR (C_6D_6): δ 1.06 [s, 18H, CH_3]; 1.44 [d, $^1J_{P,H}$ = 186 Hz, 2H, PH_2]; 7.16 [m, 3H, Ph]; 7.69 [m, 2H, Ph]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 21.9 [d, $^2J_{C,P}$ = 5.2 Hz, $C(CH_3)_3$]; 30.2 [d, $^3J_{C,P}$ = 1.9 Hz, CH_3]; 128.7 [s, Ph]; 130.1 [s, Ph]; 136.2 [d, $J_{C,P}$ = 7.1 Hz]; 136.7 [d, $J_{C,P}$ = 5.4 Hz, Ph]. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 17.9 [d; $^1J_{Si,P}$ = 30 Hz]. ^{31}P NMR (C_6D_6): δ −265.4 [t with Si satellites, $^1J_{P,H}$ = 186 Hz, $^1J_{Si,P}$ = 30 Hz]. MS (EI, 70 eV) *m*/*z* (%): 252.1 [M^+] (8). IR (KBr): 402 (w), 455 (s), 477 (s), 511 (s), 579 (s), 602 (s), 700 (s), 738 (s), 818 (s), 936 (m), 1012 (m), 1101 (s), 1195 (m) 1261 (w), 1364 (s), 1388 (s), 1426 (s), 1471 (s), 2303 (s), 2711 (w), 2858 (s), 2931 (vs), 3050 (m), 3071 (s).

$\textit{t}Bu_2PhSiAsH_2$: A solution of 9.43 g $\textit{t}Bu_2PhSiCl$ (0.0370 mol) in 25 mL DME was added to a suspension of 4.99 g $[LiAsH_2(dme)]$ (0.0287 mol) in 150 mL DME at 0 °C. After stirring for 16 h at room temperature, the DME was replaced by 100 mL of pentane. The precipitated LiCl was subsequently removed by filtration. After removal of the solvent, a vacuum distillation yielded a colourless oil of 5.72 g (52%) $\textit{t}Bu_2PhSiAsH_2$ (bp 109–115 °C at 10^{-3} mbar). ^1H NMR (C_6D_6): δ 0.94 [s, 2H, AsH_2]; 1.08 [s, 18H, CH_3]; 7.16 [m, 3H, Ph]; 7.70 [m, 2H, Ph]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 21.7 [s, $\textit{C}(CH_3)$]; 29.85 [s, CH_3]; 128.1 [s, Ph]; 129.5 [s, Ph]; 136.4 [s, Ph]; 137.0 [s, Ph]. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 24.6 [s]. MS (EI, 70 eV) *m*/*z* (%): 296.1 [M^+] (5) IR (KBr): 402 (w), 453 (m), 477 (s), 493 (s), 571 (s), 621 (m), 642 (m), 700 (s), 737 (s), 819 (s), 935 (m), 955 (m), 1011 (s), 1099 (s), 1194 (m), 1260 (m), 1363 (s), 1388 (s), 1470 (s), 2098 (s), 2710 (w), 2858 (vs), 2931 (vs), 3071 (m).

$[\textit{t}Bu_2PhSiPPb]_4$ (**1**): At 0 °C, 0.45 mL $Pb\{N(SiMe_3)_2\}$ (1 mmol) were added to a solution of 0.25 mL $\textit{t}Bu_2PhSiPH_2$ (1 mmol) in 10 mL of THF. The yellow solution was allowed to warm up to room temperature and was stirred for 16 h. After 1 d, orange crystals of **1** were obtained at 4 °C, the yield being 0.128 g (28%). ^1H NMR (THF-D_8): δ 1.28 [s, 18H, CH_3]; 7.29–7.41 [m, 3H, Ph]; 7.75 [m, 2H, Ph]. $^{13}C\{^1H\}$ NMR (THF-D_8): δ 30.5 [s, CH_3]; 31.5 [s, $\textit{C}(CH_3)_3$]; 129.0 [s, Ph]; 129.9 [s, Ph]; 136.3 [s, Ph]; 141.6 [s, Ph]. $^{29}Si\{^1H\}$ NMR (THF-D_8): δ −10.2 [s];

^{31}P NMR (THF-D$_8$): δ −512.7 [s, Pb satellites, $^1J_{P,Pb}$ = 762 Hz]. MALDI-MS: *m*/*z*: 1815.82 (M$^+$ − Me); IR (KBr): 506 (vs), 575 (s), 700 (m), 814 (m), 1009 (w), 1095 (s), 1261 (w), 1382 (w), 1424 (m), 1467 (s), 2849 (s), 2922 (s), 3062 (w). $Pb_4P_4Si_4C_{56}H_{92}$: Calc.: C 36.75, H 5.07. Found: C 36.89, H 5.28%.

[(tBu$_2$PhSiAsPb)$_4$]·2THF (**2**): At 0 °C, 0.45 mL Pb{N(SiMe$_3$)$_2$} (1 mmol) were added to a solution of 0.297 mL tBu$_2$PhSiAsH$_2$ (1 mmol) in 10 mL of THF. The yellow solution was allowed to warm up to room temperature and was stirred for 16 h. After 1 d, orange crystals of **2** were obtained at room temperature, the yield being 0.107 g (22%). ^{1}H NMR (THF-D$_8$): δ 1.33 [s, 18H, CH$_3$]; 7.45–7.49 [m, 3H, Ph]; 7.75 [dd, 2H, Ph]. ^{13}C{^{1}H} NMR (THF-D$_8$): δ 30.2 [s, CH$_3$]; 31.9 [s, *C*(CH$_3$)$_3$]; 128.9 [s, Ph]; 129.8 [s, Ph]; 136.7 [s, Ph]; 141.2 [s, Ph]. ^{29}Si{^{1}H} NMR (THF-D$_8$): δ −7.2 [s]. MALDI-MS: *m*/*z*: 1991.69 (M$^+$ − Me); IR (KBr): 458 (m), 485 (vs), 572 (m), 613,3 (m), 700 (m), 736 (m), 813 (m), 1009 (m), 1094 (m), 1177 (w), 1260 (w), 1356 (w), 1382 (w), 1424 (m), 1467 (m), 2849 (s), 2922 (s), 3065 (w). $Pb_4As_4Si_4C_{56}H_{92}$: Calc.: C 33.53, H 4.62. Found: C 33.66, H 4.36%.

[iPr$_3$SiSb)$_6$Pb$_4$] (**3**): At 0 °C, 0.424 mL iPr$_3$SiSb(SiMe$_3$)$_2$ (1 mmol) were added to a suspension of 0.278 g PbCl$_2$ (1 mmol) in 10 mL of Et$_2$O. The solution was allowed to warm up slowly to room temperature and was stirred for 16 h. The dark precipitate was removed by filtration and the solution was concentrated to approximately 5 mL. After 3 weeks, a few black crystals of **3** were obtained reproducibly. IR (KBr): 493 (m), 553 (w), 633 (m), 656 (m), 683 (m), 750 (m), 880 (vs), 1016 (s), 1097 (s), 1260 (s), 1461 (m), 2865 (vs), 2944 (vs).

§ *Crystal data* for **1**: $Pb_4P_4Si_4C_{56}H_{92}$ (180 K), triclinic, $P\bar{1}$, a = 1418.7(3), b = 1549.1(3), c = 1599.8(3) pm, α = 73.32(3), β = 84.69(3), γ = 80.68(3)°, V = 3319.6(11) Å^3, Z = 2, D_c = 1.831 g cm^{-3}, μ = 10.313 mm^{-1}, $F(000)$ = 1744, GOF = 1.063. A total of 15043 reflections were collected, 8256 of which were unique (R_{int} = 0.1194). $R1$ ($wR2$) = 0.0789 (0.2033) for 613 parameters and 7323 reflections ($I > 2\sigma(I)$).

Crystal data for **2**: $Pb_4As_4Si_4C_{64}H_{108}O_2$ (180 K), triclinic, $P\bar{1}$, a = 1432.4(3), b = 1640.4(3), c = 1863.0(4) pm, α = 66.81(3), β = 71.53(3), γ = 81.69(3)°, V = 3815.5(13) Å^3, Z = 2, D_c = 1.872 g cm^{-3}, μ = 10.619 mm^{-1}, $F(000)$ = 2048, GOF = 0.869. A total of 22737 reflections were collected, 13420 of which were unique (R_{int} = 0.0557). $R1$ ($wR2$) = 0.0430 (0.1208) for 653 parameters and 11090 reflections ($I > 2\sigma(I)$).

Crystal data for **3**: $Pb_4Sb_6Si_6C_{54}H_{122}$ (180 K), monoclinic, $P2_1/c$, a = 2378.6(5), b = 1326.6(3), c = 2639.1(5) pm, β = 105.03(3)°, V = 8043(3) Å^3, Z = 4, D_c = 2.064 g cm^{-3}, μ = 10.438 mm^{-1}, $F(000)$ = 4656, GOF = 1.028. A total of 33876 reflections were collected, 14477 of which were unique (R_{int} = 0.0530). $R1$ ($wR2$) = 0.0458 (0.1181) for 630 parameters and 12169 reflections ($I > 2\sigma(I)$).

The intensity data were collected on a STOE-IPDS2 (Mo-Kα radiation, λ = 0.71073 A). The structure was resolved by direct methods and refined against F^2 by the full-matrix least-squares technique (Pb, P, As, Sb, Si, O, C refined anisotropically, all H atoms calculated at ideal positions).

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