Novel Binary Compounds of Group 15 Elements: Synthesis and Characterisation of $[Sb_4(PSiMe_2Thex)_4]$, $[Sb_4(AsSi\textit{i}Pr_3)_4]$ and $[Sb_2(PSiPh_2\textit{t}Bu)_4]$

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The low-temperature reactions of $Me_2ThexSiPLi_2$ (Thex = CMe_2*i*Pr) and $\textit{i}Pr_3SiAsLi_2$ with $SbCl_3$ in a 3:2 molar ratio yields the cage compounds $[Sb_4(PSiMe_2Thex)_4]$ (**1**) and $[Sb_4(AsSi\textit{i}Pr_3)_4]$ (**2**), respectively. The metal salt $SbBr_3$ reacts with $\textit{t}BuPh_2SiPLi_2$ at –70 °C to give the bicyclic compound $[Sb_2(PSiPh_2\textit{t}Bu)_4]$ (**3**). Compounds **1–3** were characterised by NMR and IR spectroscopy, mass spectrometry, elemental analysis and single-crystal X-ray diffraction. The structures of **1** and **2** reveal that the both compounds adopt a structure similar to those of realgar (As_4S_4). The central structural motif is an Sb_4Y_4 cage (Y = P, As), consisting of four five-membered rings with common edges. The bicyclic compound **3** is composed of five-membered and three-membered rings sharing a common Sb_2 bridgehead.

Introduction

The formation of homonuclear cyclic, polycyclic and cage-like compounds of group 15 elements has been the focus of intensive research efforts for a long time.[1–3] These studies have revealed a very diverse range of structure types, which extend from simple small rings like $P_3\textit{t}Bu_3$ [2] through five- and six-membered rings, to polycycles and cages containing up to fourteen atoms.[3] Few analogous binary compounds containing a combination of heavier group 15 elements have been structurally characterised. Although not as widely studied as the organophosphorus homocycles, cyclic As/P and Sb/P compounds are known. The first P_2As heterocycle was synthesized by cyclocondensation of $\textit{t}Bu_2P_2K_2$ with $\textit{t}BuAsCl_2$.[4] Other reported species are the bicyclic compounds $[As_2(PAr)_2]$ and $[Sb_2(PAr)_2]$, which are obtained by the reaction of $ArP(SiMe_3)Li$ [Ar = 2,4,6-$(\textit{t}Bu)_3C_6H_2$] with $Cp^*E'Cl_2$ (E′ = As, Sb) as well as $[(\textit{t}BuP)_3As]_2$ and $[(\textit{t}BuP)_3Sb]_2$.[5] The most recent extension of group 15 element chemistry is the formation of heterocyclic compounds containing Sb–As bonds. To the best of our knowledge, the only structurally characterised Sb/As heterocycle is the coordination complex $[Sb_2Cl_6\{\textit{o}\text{-}C_6H_4(AsMe_2)_2\}]$.[6]

Herein we report on the synthesis and crystal structures of the cage and bicyclic compounds $[Sb_4(PSiMe_2Thex)_4]$ (**1**), $[Sb_4(AsSi\textit{i}Pr_3)_4]$ (**2**) and $[Sb_2(PSiPh_2\textit{t}Bu)_4]$ (**3**), obtained from the reactions of lithium phosphanides and arsanides with the antimony salts $SbCl_3$ and $SbBr_3$, respectively.[7]

Results and Discussion

The reaction of $Me_2ThexSiPLi_2$ (Thex = CMe_2*i*Pr) with $SbCl_3$ in a 3:2 molar ratio leads to the formation of **1**, which can be isolated as orange crystals by cooling the reaction mixture to −35 °C. Compound **1** crystallises in the orthorhombic space group $P4_2/n$. The central structural motif is an Sb_4P_4 cage (Figure 1). It consists of four Sb_3P_2 five-membered rings with common Sb–P–Sb edges. The structure can be thought of as being derived from an Sb_4 tetrahedron by placing bridging $PSiMe_2Thex$ fragments above four of the six edges. All of the phosphorus atoms are coordinated to two antimony atoms and one $ThexMe_2Si$ group, forming a trigonal-pyramidal environment; the Sb atoms possess no exocyclic ligands and also have a coordination number of three. The availability of the Sb–Sb bonds (Sb1–Sb1′′ and Sb1′–Sb1′′′) in the molecule is indicative of a reduction process that must have taken place parallel to the lithium chloride elimination reaction. The Sb–Sb bond length in **1** is 287.9 pm, which is in the usual range for single Sb–Sb bonds. Similar Sb–Sb bond lengths of 286.7 pm, for example, can be observed in $Sb_2(SiMe_3)_4$,[8] whereas in the polycycles Sb_8R_6 and Sb_8R_4 [R = $CH(SiMe_3)_2$] these bonds are slightly shorter (278.4–287.3 pm).[9] The Sb–P bond lengths in **1** are in the range 249.4–252.4 pm and therefore are similar to the spread of values observed in $[(tmeda)(Me_2NH)Na(CyP)_4Sb]_2$ (248.9–254.1 pm).[10] In the bicycle $[Sb_2(PAr)_2]$ (Ar = 2,4,6-$\textit{t}Bu_3C_6H_2$) mentioned above these bonds are significantly longer (average value

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257.3 pm).[5b] It is assumed that the longer Sb−P bonds in the latter compound are due to the large steric requirements of the 2,4,6-tBu$_3$C$_6$H$_2$ substituents. The Sb$_4$P$_4$ motif in **1** can be regarded as being related to the P$_8$ segment in the structure of Hittorf's violet phosphorus; an analogous P$_8$R$_4$ compound, however, could not be isolated in a pure form,[11] whereas a variety of transition metal complexes with P$_8$ ligands have been described in the literature.[12] The closest structural relative of **1** is the antimony cage Sb$_8$R$_4$ [R = CH(SiMe$_3$)$_2$], isolated from the reduction of RSbCl$_2$with Mg.[9]

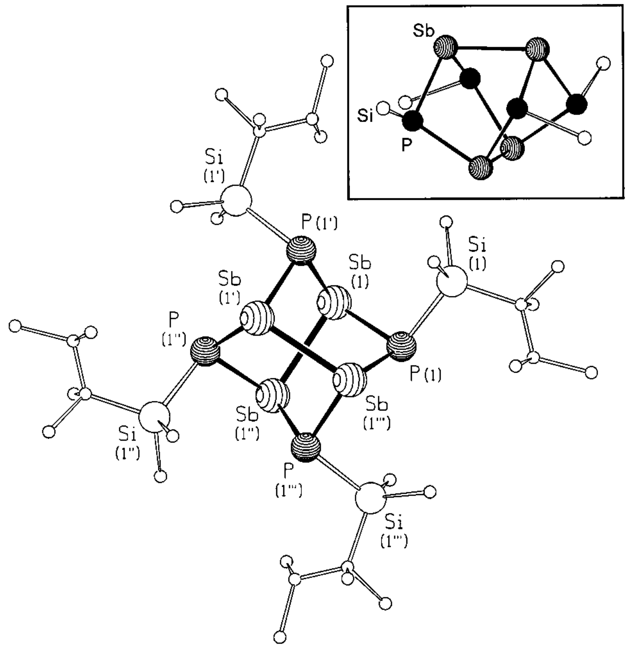

Figure 1. Molecular structure of **1** (inset: side view of the heavy atom frame); selected bond lengths [pm] and angles [°]: Sb(1)−P(1) 249.4(2), Sb(1′′)−P(1) 252.4(2), Sb−Sb 287.9(1), P(1)−Si(1) 228.5(2); Sb(1′′)−Sb(1)−P(1) 90.42, Sb(1′′)−Sb(1)−P(1′) 104.71, P(1)−Sb(1)−P(1′) 92.97, Sb(1)−P(1)−Sb(1′′′) 102.23, Si(1)−P(1)−Sb(1) 105.10, Si(1)−P(1)−Sb(1′′′) 106.22

The ^{31}P{^{1}H} NMR spectrum of **1** displays, as expected, one singlet at $\delta = -104.5$ ppm. An additional singlet appears at $\delta = -65.1$ ppm in the ^{31}P{^{1}H} NMR spectrum of the reaction mixture, which presumably can be attributed to significant amounts of (PSiMe$_2$Thex)$_n$ (n = 4 or 6), which is obtained as a by-product from the reduction process. Unfortunately, this by-product could not be isolated.

[Sb$_4$(AsSiiPr$_3$)$_4$] (**2**) is obtained from the reaction of iPr$_3$SiAsLi$_2$ and SbCl$_3$. It crystallises in the monoclinic space group $C2/c$ with two independent inversion-symmetric molecules in the elementary cell. The molecular structure of **2** (Figure 2) is almost identical to the phosphorus compound **1**, but with AsSiiPr$_3$ groups as building blocks instead of the PSiMe$_2$Thex fragments. The Sb−Sb bonds in **2** are slightly longer (288.1−289.0 pm) than those in **1**. The Sb−As bonds are in the range 260.1−261.6 pm, whereas in the coordination compound [Sb$_2$Cl$_6${o-C$_6$H$_4$(AsMe$_2$)$_2$}] these bonds are significantly longer (266.4 pm).

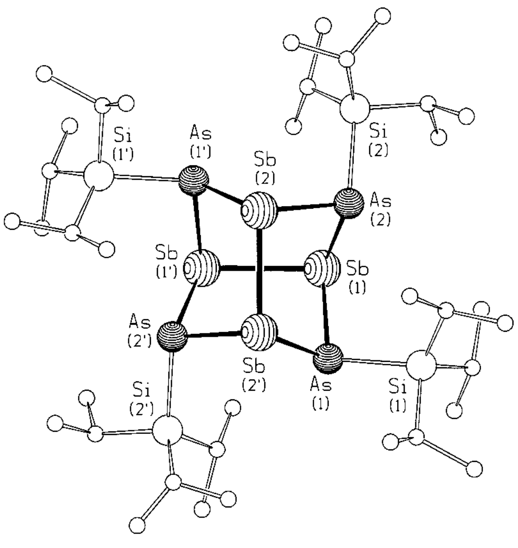

Figure 2. Molecular structure of **2**; selected bond lengths [pm] and angles [°]: Sb(1)−Sb(1′) 289.0(2), Sb(2)−Sb(2′) 288.4(2), Sb−As 260.1(2)−261.6(2), Si−As 239.3−240.2; Sb(1)−As(1)−Sb(2) 101.24(5), Sb(1′)−As(2)−Sb(2) 100.69(5), As(1)−Sb(1)−As(2) 93.72(5), As(1)−Sb(2)−As(2) 92.09(5), As(1)−Sb(1)−Sb(1′) 94.94(5), As(2′)−Sb(1)−Sb(1′) 103.96(5), As(1)−Sb(2)−Sb(2′) 103.99(5), As(2)−Sb(2)−Sb(2′) 95.46(5)

In the mass spectra of **1** and **2** the molecular ion peaks at m/z = 1184 and 1416, respectively, as well as the characteristic fragments [Sb$_4$P$_4$(SiMe$_2$Thex)$_3$]$^+$, [Sb$_3$P$_4$Me$_2$-(SiMe$_2$Thex)$_3$]$^+$ and [Sb$_4$As$_4$(SiiPr$_3$)$_3$]$^+$, [Sb$_4$(AsSiiPr$_3$)$_3$]$^+$, [Sb$_4$As$_3$(SiiPr$_3$)$_2$]$^+$, [Sb$_2$(AsSiiPr$_3$)$_2$]$^+$ can be observed.

The novel bicyclic compound **3** was isolated as yellow crystals from the LiBr elimination reaction of tBuPh$_2$SiPLi$_2$ and SbBr$_3$ in a 3:2 molar ratio. The compound crystallizes in the triclinic space group $P\bar{1}$. It is composed of five-membered P$_3$Sb$_2$ and three-membered PSb$_2$ rings sharing a common Sb$_2$ bridgehead (Figure 3). Both the P and the Sb atoms are three-coordinate, with the antimony atoms possessing no exocyclic ligands. The central Sb$_2$P$_4$ unit shows a non-planar configuration; the plane through Sb(1), Sb(2), P(4) is virtually perpendicular to the Sb$_2$P$_3$ ring. Examination of the bond lengths and angles found in the bicyclic Sb$_2$P$_4$ core of **3** indicates that there is a considerable amount of strain in this arrangement. The fold angles P(1)−Sb(1)−P(4) and P(3)−Sb(2)−P(4) are 86.11° and 104.3° respectively. The comparatively large difference between these angles results from the manner of orientation of the sterically demanding silyl groups coordinated to P(1) and P(3). The tBuPh$_2$Si substituent of P(1) is in a *trans* position to the Sb(1)−P(4) bond, whereas the silyl group bonded to P(3) is in a *cis* position to the Sb(2)−P(4) bond. The torsion angles Si(3)−P(3)−Sb(2)−P(4) and Si(1)−P(1)−Sb(1)−P(4) are 46.1° and 135.7° respectively. A similar molecular structure occurs in the homonuclear bicyclic compound tBu$_4$P$_6$ reported by Baudler and co-workers.[13] However the arrangement of the *t*Bu groups in this structure is all-*trans*. Of particular interest in comparison of **3** with the other title compounds is the appearance of P−P bonds in the structure, resulting from oxidation of the P atoms and corresponding reduction of the Sb atoms to Sb−Sb bonds. The Sb−Sb bond in **3** is 276.8 pm, and is therefore shorter than the corresponding bonds in **1** and **2**. This bond shortening is possibly a consequence of the fact that the Sb_2 unit is bridged by the P(4) atom. The average P−P bond length is 219.6 pm, and the Sb−P bonds are 255.2 pm on average. These values lie in the usual range for single bonds between these elements.

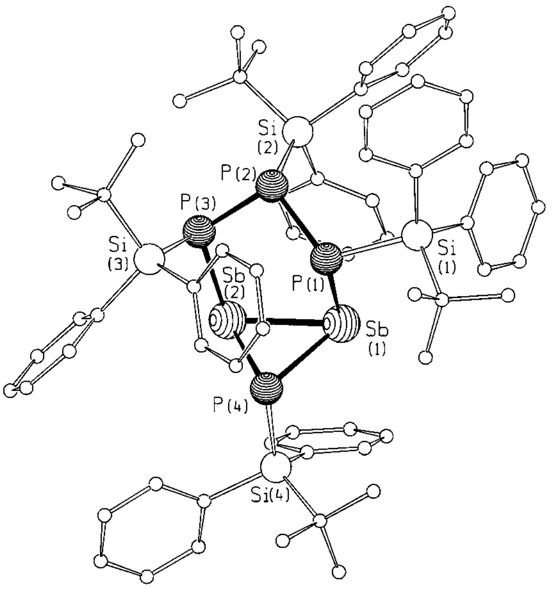

Figure 3. Molecular structure of **3**; selected bond lengths [pm] and angles [°]: Sb(1)−Sb(2) 276.8(2), Sb(1)−P(1) 255.3(2), Sb(1)−P(4) 255.3(2), Sb(2)−P(3) 255.9(2), Sb(2)−P(4) 254.4(2), P(1)−P(2) 219.9(2), P(2)−P(3) 219.9(2), P(1)−Si(1) 228.7(2), P(2)−Si(2) 229.4(2), P(3)−Si(3) 226.9(2), P(4)−Si(4) 227.8(2); Sb(1)−Sb(2)−P(4) 57.28(5), Sb(2)−Sb(1)−P(1) 92.63(4), Sb(2)−Sb(1)−P(4) 56.94(5), Sb(1)−P(4)−Sb(2) 65.77(6), Sb(1)−P(1)−P(2) 110.71(7), Sb(2)−P(3)−P(2) 112.99(6), P(1)−P(2)−P(3) 99.86(8), P(1)−Sb(1)−P(4) 86.11(6), P(3)−Sb(2)−P(4) 104.30(6)

The structure of **3** can be deduced from $^{31}P\{^1H\}$ NMR spectrum (Figure 4), which shows at room temperature two triplet signals at $\delta = -245$ and -31 ppm for the P(4) and P(2) centres, respectively. An additional broad signal appears at $\delta = -120$ ppm. At +70 °C the signal at $\delta = -120$ ppm appears as a doublet of doublets, which is consistent with chemically identical P(1) and P(3) atoms (AM_2X spin system, $^1J_{P,P} = 400$, $^2J_{P,P} = 96$ Hz). At −50 °C the $^{31}P\{^1H\}$ NMR spectrum of **3** shows four multiplets corresponding to the four different P atoms observed in the crystal structure (AEMX spin system). The mass spectrum of **3** does not show the molecular peak, although the characteristic fragment $[(PSi\mathit{t}BuPh_2)_3]^+$ is observed at $m/z = 810$.

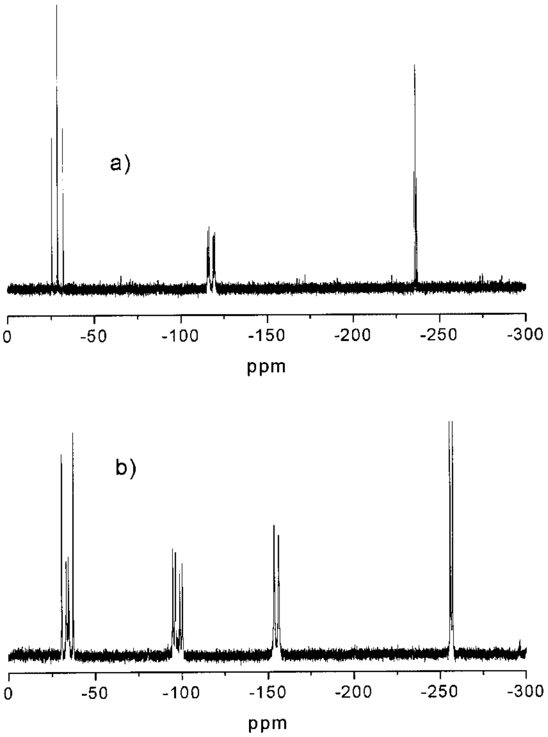

Figure 4. $^{31}P\{^1H\}$ NMR spectra of **3** in [D$_8$]toluene: a) at +70 °C, b) at−50 °C

Experimental Section

General: All manipulations were carried out with rigorous exclusion of oxygen and moisture, using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before use. The starting materials $\mathit{i}Pr_3SiAsH_2$ and $ThexMe_2SiPH_2$ were prepared according to relevant procedures found in the literature.[14] $SbCl_3$ and $SbBr_3$ were obtained from Aldrich and sublimed before use. The ^1H and ^{31}P NMR spectra were recorded on a Bruker AC 250 spectrometer. All isolated compounds gave elemental analyses consistent with their formulas.

$\mathit{t}BuPh_2SiPH_2$: A solution of $\mathit{t}BuPh_2SiCl$ (41.2 g, 0.15 mol) in 50 mL of THF was added dropwise to a solution of $[(dme)LiPH_2]$ (19.5 g, 0.15 mol) in 150 mL of THF at 0 °C. After stirring the mixture overnight at room temperature, the THF was replaced by 100 mL of pentane. The precipitated lithium chloride was subsequently removed by filtration. After removal of the solvent, a vacuum distillation yielded 20 g (50%) of $\mathit{t}BuPh_2SiPH_2$, B.p.: 100−103 °C (10^{-3} mbar). ^1H NMR (C_6D_6): $\delta = 1.20$ [s, 9 H, $C(CH_3)_3$], 1.73 (d, $^1J_{P,H} = 187$ Hz, 2 H, PH_2), 7.26 (m, 5 H, Ph), 7.78 (m, 5 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 19.8$ [d, $^2J_{P,C} = 21.5$ Hz, $C(CH_3)_3$], 28.1 [d, $^3J_{P,C} = 6.8$ Hz, $C(CH_3)_3$], 129.9 (s, Ph), 135.7 (d, $J_{P,C} = 8.9$ Hz, Ph), 136.3 (d, $J_{P,C} = 8.9$ Hz, Ph). ^{31}P NMR (C_6D_6): $\delta = -252.2$ (t, $^1J_{P,H} = 187$ Hz) ppm.

1: *n*-Butyllithium [1.2 mL (1.92 mmol) of a 1.6 M solution] was added to a solution of $ThexMe_2SiPH_2$ (0.17 g, 0.96 mmol) in 5 mL of Et_2O at 0 °C. After stirring for 10 min, this solution was added to a solution of $SbCl_3$ (0.15 g, 0.64 mmol) in 15 mL of toluene at

Table 1. Crystallographic data for **1**−**3**[7]

	1	**2**	**3**
Empirical formula	$C_{32}H_{76}P_4Sb_4Si_4$	$C_{36}H_{84}As_4Sb_4Si_4$	$C_{64}H_{76}P_4Sb_2Si_4$
Space group	$P4_2/n$	$C2/c$	$P\bar{1}$
Formula units	2	8	2
Temperature	220 K	200 K	200 K
Lattice constants	a = 1881.7(3) pm	a = 2691.7(5) pm	a = 1391.8(3) pm
	b = 1881.7(3) pm	b = 1620.5(3) pm	b = 1414.0(3) pm
	c = 698.8(1) pm	c = 2655.6(5) pm	c = 2133.2(4) pm
	α = 90°	α = 90°	α = 106.25(3)°
	β = 90°	β = 110.27(3)°	β = 92.17(3)°
	γ = 90°	γ = 90°	γ = 118.74(3)°
Volume	2474.3(7) Å^3	10866(4) Å^3	3459.0(12) Å^3
Density	1.589 g/cm^3	1.723 g/cm^3	1.272 g/cm^3
2Θ range	3−46°	3−48°	3.5−52°
Reflections measured	3571	15734	12686
Independent reflections	1697 (R_{int} = 0.0304)	7299 (R_{int} = 0.0476)	9753 (R_{int} = 0.0525)
Independent reflections with $F_o > 4\sigma(F_o)$	1246	5693	7520
Parameters	100	422	667
μ(Mo-K_α)	2.407 mm^{-1}	4.496 mm^{-1}	0.977 mm^{-1}
$R1$	0.0351	0.0598	0.0536
$wR2$ (all data)	0.0962	0.1796	0.1565
Residual electron density	0.664 e/Å^3	2.539 e/Å^3	1.266 e/Å^3

−70 °C. The reaction mixture was allowed to warm to −35 °C and then kept at the same temperature for an additional 12 h. The resulting orange solution was filtered to remove the precipitated LiCl and cooled to −35 °C. Orange crystals of **1** were obtained over a period of 5 d. Yield: 0.05 g (26%). $C_{32}H_{76}P_4Sb_4Si_4$ (1184.2): calcd. C 32.46, H 6.47; found C 32.89, H 6.46. ^{1}H NMR (C_6D_6): $\delta = 0.39$ (s, 24 H, $SiCH_3$), 1.08 (m, 48 H, overlap of $SiCCH_3$ and $SiCCCH_3$), 2.14 [sept, $^3J_{H,H} = 6.9$ Hz, 4 H, $SiCH(CH_3)_2$] ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -104.5$ (s) ppm. MS (EI, 70 eV, 200 °C): m/z (%) = 1184 (13) [M$^+$], 1041 (100) [M$^+$ − SiThexMe$_2$], 949 (9.4) [$Sb_3P_4Me_2(SiThexMe_2)_3$]$^+$. IR (KBr): $\tilde{\nu}$ = 2957 (s), 2867 (m), 1459 (m), 1389 (w), 1376 (m), 1363 (w), 1261 (m), 1241 (s), 1088 (m), 1033 (m), 915 (w), 870 (m), 835 (s), 798 (vs), 773 (w), 760 (w), 685 (w), 666 (m), 601 (m), 501 (w), 441 (s) cm^{-1}.

2: *n*-Butyllithium [1.13 mL (1.81 mmol) of a 1.6 M solution] was added to a solution of iPr$_3$SiAsH$_2$ (0.21 g, 0.9 mmol) in 10 mL of Et$_2$O at 0 °C. After warming to room temperature, the solution of iPr$_3$SiAsLi$_2$ was added to a solution of SbCl$_3$ (0.14 g, 0.60 mmol) in 15 mL of Et$_2$O at −70 °C. The red mixture was subsequently warmed to −35 °C while stirring and kept at the same temperature overnight. After filtration and cooling of the solution to −35 °C red crystals of **2** crystallised over a period of 5 d. Yield: 0.06 g (29%) $C_{36}H_{84}As_4Sb_4Si_4$ (1416.1): calcd. C 30.53, H 5.98; found C 31.24, H 6.09. MS (EI, 70 eV, 200 °C): m/z (%) = 1416 (11) [M$^+$], 1259 (36) [M$^+$ − SiiPr$_3$], 1184 (19) [Sb$_4$(AsSiiPr$_3$)$_3$]$^+$, 1027 (23) [Sb$_4$As$_3$(SiiPr$_3$)$_2$]$^+$, 708 (19) [M/2]$^+$. IR (KBr): $\tilde{\nu}$ = 2937 (vs), 2861 (vs), 1457 (s), 1382 (m), 1362 (m), 1288 (w), 1261 (m), 1226 (m), 1068 (m), 1018 (s), 989 (m), 966 (w), 915 (m), 875 (s), 803 (m), 660 (s), 630 (vs), 588 (m), 555 (s) 499 (vs), 466 (m), 419 (w) cm^{-1}.

3: *n*-Butyllithium [1.15 mL (1.84 mmol) of a 1.6 M solution] was added to a solution of tBuPh$_2$SiPH$_2$ (0.25 g, 0.92 mmol) in 5 mL of Et$_2$O at 0 °C. The resulting yellow solution was added dropwise at −70 °C to a stirred solution of SbBr$_3$ (0.22 g, 0.61 mmol) in 15 mL of toluene. The purple-red mixture was allowed to warm to room temperature and stirred for an additional 16 h. The solvent was removed in vacuo and the residue was dissolved in 5 mL of heptane. After filtration and cooling of the solution to 0 °C yellow crystals of **3** were obtained over a period of 3 d. Yield: 0.20 g (66%). $C_{64}H_{76}P_4Sb_2Si_4$ (1325.0): calcd. C 58.01, H 5.78; found C 57.14, H 6.28. ^{1}H NMR ([D$_8$]toluene): $\delta = 1.16$ (s, 9 H, SitBu), 1.21 (s, 9 H, SitBu), 1.33 (s, 18 H, SitBu), 6.78 (m), 7.19 (m), 7.28 (m), 7.43 (m), 7.68 (m), 7.93 (m) (all Si−Ph, 40 H) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]toluene, 70 °C): $\delta = -235.6$ (t, $^2J_{P,P} = 96$ Hz), −117.3 (dd, $^1J_{P,P} = 400$, $^2J_{P,P} = 96$ Hz), −28.8 (t, $^1J_{P,P} = 400$ Hz) ppm. MS (EI, 70 eV, 210 °C): m/z (%) = 810 (100) [(PSitBuPh$_2$)$_3$]$^+$, 753 (29) [P$_3$(SitBuPh$_2$)$_2$SiPh$_2$]$^+$, 239 (33) [SitBuPh$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 2940 (vs), 2862 (vs), 2097 (w), 1703 (vs, br), 1461 (s), 1379 (m), 1362 (m), 1293 (w), 1227 (m), 1157 (vw), 1068 (m), 1049 (m), 1014 (m), 992 (s), 881 (vs), 700 (vs), 633 (vs), 570 (s), 502 (s), 465 (s), 380 (m) cm^{-1}.

X-ray Crystallography: A summary of the crystallographic data for all three compounds can be found in Table 1 and ref.[7]

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[1] Review articles: [1a] L. Balázs, H. J. Breunig, *Coord. Chem. Rev.* **2004**, *248*, 603−621. [1b] H. J. Breunig, R. Rösler, *Coord. Chem. Rev.* **1997**, *163*, 33−53. [1c] M. Baudler, *Angew. Chem.* **1987**, *99*, 429−451; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 419−441. [1d] M. Baudler, *Angew. Chem.* **1982**, *94*, 520−539; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 492−512.

[2] [2a] J. Hahn, M. Baudler, *Z. Naturforsch., Teil B* **1982**, *37*, 797−805. [2b] O. Mundt, G. Becker, H.-J. Wessely, *Z. Anorg. Allg. Chem.* **1982**, *486*, 70−89. [2c] M. Baudler, P. Bachmann, *Angew. Chem.* **1981**, *93*, 112−113; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 123−124.

[3] [3a] M. Westerhausen, S. Weinrich, P. Mayer, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1153−1156. [3b] G. Linti, W. Köstler, *Z. Anorg. Allg. Chem.* **2002**, *628*, 63−66. [3c] C. von Hänisch, D. Fenske, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1040−1042. [3d] M.

Baudler, H. Jachow, B. Lieser, K.-F. Tebbe, M. Fehér, *Angew. Chem.* **1989**, *101*, 1245–1247; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1231–1232. [3e] C. Mujica, D. Weber, H.-G. Schnering, *Z. Naturforsch., Teil B* **1986**, *41*, 991–999. [3f] M. Baudler, S. Wietfeldt-Haltenhoff, *Angew. Chem.* **1985**, *97*, 986–987; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 991–992. [3g] M. Baudler, S. Wietfeldt-Haltenhoff, *Angew. Chem.* **1984**, *96*, 361–362; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 379–380. [3h] M. Baudler, P. Bachmann, *Z. Anorg. Allg. Chem.* **1982**, *485*, 129–132. [3i] M. Baudler, J. Hellmann, P. Bachmann, K.-F. Tebbe, R. Fröhlich, M. Feher, *Angew. Chem.* **1981**, *91*, 415–417; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 406–407. [3j] H.-G. von Schnering, D. Fenske, W. Hönle, M. Binnewies, K. Peters, *Angew. Chem.* **1979**, *91*, 755–756; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 679. [3k] A. Tzschach, V. Kiesel, *J. Prakt. Chem.* **1971**, *313*, 259–264.

[4] [4a] M. Baudler, S. Klautke, *Z. Naturforsch., Teil B* **1981**, *36*, 527–531. [4b] M. Baudler, D. Habermann, *Angew. Chem.* **1979**, *91*, 939–940; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 877–878.

[5] [5a] A. Bashall, F. Garcia, G. T. Lawson, M. McPartlin, A. Rothenberger, A. D. Woods, D. S. Wright, *Can. J. Chem.* **2002**, *80*, 1421–1427. [5b] P. Jutzi, U. Meyer, S. Opiela, M. Olmstead, P. P. Power, *Organometallics* **1990**, *9*, 1459–1463. [5c] M. Baudler, Y. Aktalay, T. Heinlein, K.-F. Tebbe, *Z. Naturforsch., Teil B* **1982**, *37*, 299–305.

[6] A. R. J. Genge, N. J. Hill, W. Levason, G. Reid, *J. Chem. Soc., Dalton Trans.* **2001**, 1007–1012.

[7] STOE-IPDS2 (Mo-K_α radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares techniques against F^2 (Sb, As, P, Si, C refined anisotropically, H atoms were calculated at ideal positions). CCDC-242997 (**1**), -242995 (**2**) and -242996 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

[8] G. Becker, H. Freudenblum, C. Witthauer, *Z. Anorg. Allg. Chem.* **1982**, *492*, 37–51.

[9] [9a] G. Balázs, H. J. Breunig, E. Lork, S. Mason, *Organometallics* **2003**, *22*, 576–585. [9b] H. J. Breunig, R. Rösler, E. Lork, *Angew. Chem.* **1997**, *109*, 2333–2334; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2237–2238.

[10] M. A. Beswick, N. Choi, A. D. Hopkins, M. McPartlin, M. E. G. Mosquera, P. R. Raithby, A. Rothenberger, D. Stalke, A. J. Wheatley, D. S. Wright, *Chem. Commun.* **1998**, 2485–2486.

[11] [11a] M. Baudler, B. Koll, C. Adamek, R. Gleiter, *Angew. Chem.* **1987**, *99*, 371–373; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 347–348. [11b] M. Baudler, V. Arndt, *Z. Naturforsch., Teil B* **1984**, *39*, 275–283.

[12] [12a] M. Scheer, U. Becker, E. Matern, *Chem. Ber.* **1996**, *129*, 721–724. [12b] M. E. Barr, B. R. Adams, R. R. Weller, L. F. Dahl, *J. Am. Chem. Soc.* **1991**, *113*, 3052–3060.

[13] M. Baudler, Y. Aktalay, K.-F. Tebbe, T. Heinlein, *Angew. Chem.* **1981**, *93*, 1020–1022; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 967–969.

[14] [14a] M. Westerhausen, M. Wieneke, W. Schwarz, *J. Organomet. Chem.* **1999**, *572*, 249–257. [14b] H. R. G. Bender, M. Nieger, E. Niecke, *Z. Naturforsch., Teil B* **1993**, *48*, 1742–1752.

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