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Homoleptic silyl complexes of arsenic and antimony

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Abstract

Several homoleptic silyl complexes of arsenic(III) and antimony(III), namely $As(SiR_2R')_3$ ($R = Me$, $R' =$ cyclohexyl (Cy); $R = Me$, $R' = Ph$; $R = R' = Ph$) and $Sb(SiPh_3)_3$, have been prepared via salt elimination reactions of $R_2R'SiCl$ and Na_3E ($E = As$ or Sb). The structures of two complexes, $As(SiMe_2Cy)_3$ and $Sb(SiPh_3)_3$, have been determined by X-ray crystallography. Both structures possess a three-coordinate Group 15 element centre with a pyramidal geometry of the ESi_3 core. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There has been a significant amount of interest in the chemistry of silyl complexes of arsenic(III) and antimony(III) over the last few decades. These compounds, in combination with Group 13 species (e.g. halides and alkyls), are excellent starting materials for preparing molecules containing Group 13 element-arsenic or -antimony bonds [1]. Such compounds have attracted a great deal of attention due to their potential applications as single-source precursors for the deposition of thin films of the corresponding semiconductor material by organometallic chemical vapour deposition (OMCVD) [1,2]. Silylarsines have also been used for the preparation of inter-Group 15 element phases [3].

Tris(silyl)arsenic and antimony complexes were first synthesised about 30 years ago [4–10], with further developments occurring some years later [11–15]. Although there have been studies into the synthesis and reactivity of silyl Group 15 complexes [4], structural characterisation of these compounds have emerged only very slowly. Until recently, single crystal X-ray diffraction studies of silyl complexes of As and Sb were limited to $E_2(SiMe_3)_4$ ($E = As$ or Sb) [16,17] and the lithium–arsenide and antimonide salts, $[Li(L)_n][E(SiMe_3)_2]$ (where $n = 1$, $E = As$ or Sb, $L = DME$; $n = 2$, $E = As$, $L =$ thf) and $[Li(thf)_2][As(SiPr^i_3)(SiFAr_2)]$ ($Ar =$ 2,4,6-triisopropylphenyl) [18–20]. The only examples of structures of tris(silyl)arsenic and antimony complexes include $As(SiMe_2Bu^t)_3$ (**1**) [21], $As(SiMe_3)_2(SiPh_3)$ (**2**) [21], and $Sb(SiMe_2Ph)_3$ (**3**) [22].

In this contribution, we present the synthesis and characterisation of a series of tris(silyl) complexes of arsenic(III) and antimony(III). Our motivation was to explore further the structural characteristics of these complexes and to isolate a range of stable silyl complexes.

2. Results and discussion

The reaction between Na_3As (generated in situ from arsenic powder and sodium metal in thf) and chlorodimethylcyclohexylsilane in thf at reflux temperature afforded, after work-up, colourless crystals of the complex $As(SiMe_2Cy)_3$ (**4**) ($Cy =$ cyclohexyl), according to Eq. (1):

$$Na_3E + 3R_2R'SiCl \rightarrow E(SiR_2R')_3 + 3NaCl \qquad (1)$$

4; $E = As$, $R = Me$, $R' = Cy$
5; $E = As$, $R = Me$, $R' = Ph$

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6; E = As, R = Ph, R′ = Ph
7; E = Sb, R = Ph, R′ = Ph

Similar methods for the preparation of other tris(silyl)arsenic complexes have been described previously [14,15]. Spectroscopic and analytical data were consistent with the anticipated formula of **4** and the structure was confirmed by X-ray crystallography, the results of which are shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The solid state structure of **4** consists of individual molecules with no unusually short intermolecular contacts between the monomeric units. Although not required crystallographically, individual molecules of **4** possess approximate C_3 symmetry. The geometry about the arsenic centre is pyramidal [av. Si–As–Si 101.6(3)°] with the average As–Si bond length of 2.361(7) Å being similar to those observed in **1** and **2** [21]. The relative orientation of the three dimethylcyclohexylsilyl groups at the arsenic centre is all-staggered with each cyclohexyl group placed between two methyl groups of a neighbouring silyl group. As such, the structure is similar to that observed for **1** [21] and the related antimony complex $Sb(SiMe_2Ph)_3$ (**3**) [22].

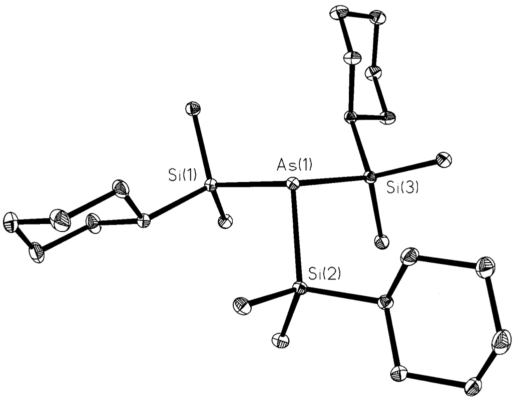

Fig. 1. Molecular structure of compound **4** showing the atom numbering scheme. Atoms are drawn as 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for **4** and **7**

$As(SiMe_2Cy)_3$ (**4**)		$Sb(SiPh_3)_3$ (**7**)	
Bond lengths			
As(1)–Si(1)	2.3567(8)	Sb(1)–Si(1)	2.5977(12)
As(1)–Si(2)	2.3609(7)	Sb(1)–Si(2)	2.5992(12)
As(2)–Si(3)	2.3664(7)	Sb(1)–Si(3)	2.6037(12)
Bond angles			
Si(1)–As(1)–Si(2)	102.22(3)	Si(1)–Sb(1)–Si(2)	103.33(4)
Si(1)–As(1)–Si(3)	100.94(3)	Si(1)–Sb(1)–Si(3)	110.09(4)
Si(2)–As(1)–S(3)	101.74(3)	Si(2)–Sb(1)–S(3)	106.48(4)

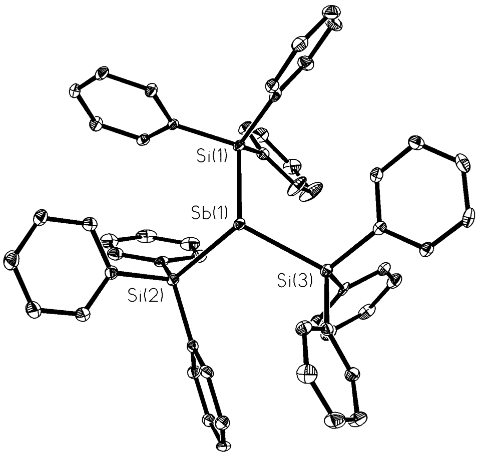

Fig. 2. Molecular structure of compound **7** showing the atom numbering scheme. Atoms are drawn as 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

A similar reaction between Na_3As and chlorodimethylphenylsilane in thf at reflux temperature afforded, after work-up, colourless crystals of the complex $As(SiMe_2Ph)_3$ (**5**) (Eq. (1)). Spectroscopic and analytical data for **5** were consistent with the expected formula. Unfortunately, an attempted crystal structure determination was only partially successful due to disorder problems. However, the structure of **5** is apparently similar to that of compound **1** [21], **4** and the related antimony derivative **3** [22].

The analogous reaction between Na_3As and chlorotriphenylsilane in thf at reflux temperature (Eq. (1)) resulted in a cream crystalline solid, spectroscopic and analytical data for which were consistent with the formula $As(SiPh_3)_3$ **6**. Unfortunately X-ray quality crystals of **6** could not be isolated. Interestingly, previous attempts to prepare **6** and the antimony analogue, $Sb(SiPh_3)_3$ (**7**), via the reaction between 3 equivalents of triphenylsilyllithium and the appropriate element(III) chloride were reported to be unsuccessful [23]. However, compound **7** has reportedly been prepared from the reaction of $SbEt_3$ and 3 equivalents of triphenylsilane, although **7** was poorly characterised [9]. A related reaction between $Sb(SiEt_3)_3$ and 3 equivalents of triphenylsilane was also reported to result in the formation of **7**; no characterisation of this material was published [7]. However, compound **7** can be prepared in a similar manner to the arsine complexes **4**–**6** as described in Section 3. Spectroscopic and analytical data for **7** were consistent with the expected formula and the structure was confirmed by X-ray crystallography, the results of which are shown in Fig. 2. Selected bond distances and angles are given in Table 1. The solid state structure of **7** consists of individual molecules with no unusually short intermolecular contacts between the monomeric units. Although not required crystallographically, individual molecules of **7** possess approximate C_3 symmetry. The geometry about the antimony centre is pyramidal [av. Si–Sb–Si 106.60(4)°] with the average Sb–Si bond length of 2.600(12) Å being slightly longer than that observed in **3** [av. Sb–Si 2.559 Å] [22]. The greater deviation from ideal tetrahedral coordination geometry and the longer Sb–Si bond lengths observed in **7** are probably a result of the increased steric requirements of the Ph_3Si ligand. A similar effect was noted on comparison of the As–Si bond distances and Si–As–Si angles in compounds **1** and **2** [21].

In conclusion, several homoleptic silyl arsenic(III) and antimony(III) compounds have been synthesised and characterised. Two of the compounds, $As(SiMe_2Cy)_3$ and $Sb(SiPh_3)_3$ were structurally characterised. Complexes **4**–**7** are possible precursors for the preparation of arsenides and antimonides and the reactivity of these complexes is currently being investigated.

3. Experimental

3.1. General procedures

All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a MBraun Unilab glove box. All solvents were distilled from appropriate drying agents prior to use (sodium–toluene and hexanes; potassium–THF; CaH_2 for CH_2Cl_2). All other reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at University College London.

3.2. Physical measurements

NMR spectra were recorded on Brüker AMX300 or DRX500 spectrometers at UCL. The NMR spectra are referenced to CD_2Cl_2 or $CDCl_3$, which were degassed and dried over molecular sieves prior to use; ^1H and ^{13}C chemical shifts are reported relative to $SiMe_4$ (0.00 ppm). Mass spectra (CI) were run on a micromass ZABSE instrument, and IR spectra on a Nicolet 205 instrument. Melting points were obtained in sealed glass capillaries under argon and are uncorrected.

3.3. Preparations

All of the compounds were synthesised by the same general procedures, hence only one example is described in detail below.

3.3.1. Synthesis of compound 4

A mirror of sodium metal is generated on the inner surface of a Schlenk flask by heating and stirring sodium (1.00 g, 43.5 mmol). After cooling to room temperature (r.t.) arsenic powder (1.09 g, 14.5 mmol) and a few crystals of naphthalene were added. THF (40 ml) was added and the resulting black slurry was heated at reflux for 24 h. After cooling to r.t. chlorodimethylcyclohexylsilane (8 ml, 43.2 mmol) was added dropwise with stirring and the reaction mixture was refluxed for a further 12 h. The resulting black slurry was cooled to r.t. and pumped to dryness in vacuo. Toluene (40 ml) was added to the remaining black–grey solid and the mixture was filtered through Celite. The volume of the filtrate was reduced to ca. 15 ml and cooling of this solution to −20°C afforded a 67% yield of colourless crystalline **4**. M.p. 80–82°C. ^1H NMR ($CDCl_3$): δ 0.29 (s, 18H, $SiMe_2$), 0.72–1.83 (m, 33H, SiCy). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.01 ($SiMe_2$), 26.8, 27.7, 28.1, 28.4 (SiCy). CIMS: m/z 499 [M^+], 359 [$M^+ - SiMe_2Cy$]. *Anal.* Calc. for $C_{24}H_{51}AsSi_3$: C, 57.79; H, 10.30. Found: C, 57.48; H, 10.44%.

3.3.2. Compound 5

Yield: 52% of colourless crystalline **5**. M.p. 122–124°C. ^1H NMR (CD_2Cl_2): δ 0.35 (s, 18H, $SiMe_2$), 7.25–7.55 (m, 15H, SiPh). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 1.7 ($SiMe_2$), 127.5 (*m*-C of SiPh), 128.8 (*p*-C of SiPh), 133.7 (*o*-C of $SiPh_3$), *ipso* carbon not detected. CIMS: m/z 481 [M^+]. *Anal.* Calc. for $C_{24}H_{33}AsSi_3 \cdot 0.5CH_2Cl_2$: C, 56.25; H, 6.55. Found: C, 56.25; H, 6.54%.

3.3.3. Compound 6

Yield: 65% of pale yellow crystalline **6**. M.p. 180°C (dec.). ^1H NMR ($CDCl_3$): δ 6.98–7.30 (m, 45H, $SiPh_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 127.2 (*m*-C of $SiPh_3$), 128.8 (*p*-C of $SiPh_3$), 136.2 (*o*-C of $SiPh_3$), *ipso* carbon not detected. CIMS: m/z 853 [M^+], 595 [$M^+ - SiPh_3$]. *Anal.* Calc. for $C_{54}H_{45}AsSi_3$: C, 76.03; H, 5.32. Found: C, 75.98; H, 5.45%.

3.3.4. Compound 7

Yield: 58% of colourless crystalline **7**. M.p. 127°C (dec.). ^1H NMR (CD_2Cl_2): δ 6.87–7.54 (m, 45H, $SiPh_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 126.2 (*m*-C of $SiPh_3$), 128.2 (*p*-C of $SiPh_3$), 135.5 (*o*-C of $SiPh_3$), *ipso* carbon not detected. CIMS: m/z 901 [M^+]. *Anal.* Calc. for $C_{54}H_{45}SbSi_3$: C, 72.07; H, 5.04. Found: C, 72.61; H, 5.08%.

3.4. Structure determinations

Crystals of **4** and **7** were mounted on a glass fibre using silicones grease and cooled on the diffractometer. Crystallographic measurements were carried out with a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo Kα radiation using a combination of ϕ and ω scans with 2° frames and a detector-to-crystal distance of 30 mm. Integration was carried out by the program DENZO-SMN [24]. Data sets were corrected for Lorentz and polarisation effects and for the effects of absorption using the program SCALEPACK [24]. The structure was solved using the

Table 2
Crystallographic data for **4** and **7**

	4	**7**
Empirical formula	$C_{24}H_{51}AsSi_3$	$C_{58}H_{50}ClSbSi_3$
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	6.3863(3)	13.3164(6)
b (Å)	14.2940(6)	21.6196(7)
c (Å)	16.1607(8)	17.6477(8)
α (°)	72.897(3)	90
β (°)	89.005(3)	109.198(3)
γ (°)	88.017(3)	90
V (Å^3)	1409.12(11)	4798.1(3)
D_{calc} (g cm^{-3})	1.176	1.368
Z	2	4
T (K)	100(2)	100(2)
λ (Å)	0.71073	0.71073
Reflections collected	10474	23285
No. unique reflections	6451	9011
Crystal size (mm)	0.80 × 0.15 × 0.10	0.40 × 0.10 × 0.10
θ Range (°)	2.64–27.50	2.48–26.00
R [a] ($I>2\sigma(I)$)	0.0429	0.0519
wR' [b] ($I>2\sigma(I)$)	0.0837	0.1008

[a] $R = \Sigma(\Delta F)/\Sigma(F_o)$.

[b] $wR' = [\Sigma\{w(\Delta F^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$. $w = 1/[\sigma^2(F_o^2)+(aP)^2]$ where $P = [\max(F_o^2)+2(F_c^2)]/3$ and $a = 0.0003$.

direct methods option of SHELXS-97 [25] and developed using conventional alternating cycles of least-squares refinement and difference Fourier synthesis (SHELXL-97) [25] with the aid of XSeed [26]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were fixed in idealised positions and allowed to ride. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. All calculations were carried out on a Silicon Graphics Indy workstation or an IBM-PC compatible personal computer. Crystal data and details of the data collections and refinements are given in Table 2.

4. Supplementary material

Crystallographic data have been deposited with the CCDC and are available on request from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) by quoting the deposition numbers 140720 and 140721.

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