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Silicon-lead chalcogenides of the types $Me_4Si_2(E)_2PbPh_2$ and $Ph_2Pb(E)_2Si_2Me_2(E)_2PbPh_2$ (E = S, Se) and related compounds containing tin and antimony

Uwe Herzog [a],*, Gerd Rheinwald [b]

[a] *Institut für Anorganische Chemie, TU Bergakademie Freiberg, Leipziger Straße 29, D-09596 Freiberg, Germany*
[b] *Institut für Chemie, Lehrstuhl Anorganische Chemie, TU Chemnitz, Straße der Nationen 62, D-09111 Chemnitz, Germany*

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Abstract

The reaction of a 1:1 mixture of Ph_2PbCl_2 and $ClSiMe_2$–$SiMe_2Cl$ with H_2S/NEt_3 yielded the mixed silicon–lead sulfide $Me_4Si_2(S)_2PbPh_2$ (**1a**), a bicyclic silicon lead sulfide, $Ph_2Pb(S)_2Si_2Me_2(S)_2PbPh_2$ (**1b**) was obtained by similar treatment of a 2:1 mixture of Ph_2PbCl_2 and Cl_2SiMe–$SiMeCl_2$. The corresponding selenium compounds (**2a**–**b**) were obtained by reactions of mixtures of Ph_2PbCl_2 and methylchlorodisilanes with Li_2Se in THF. All products were characterized by multinuclear (^1H, ^{13}C, ^{29}Si, ^{77}Se and ^{207}Pb) NMR spectroscopy. The molecular structure of **1a** is reported revealing a central five membered ring Si_2S_2Pb in envelope conformation with one sulfur atom (S1) above the plane defined by the atoms Pb1–S2–Si2–Si1. For comparison, the tin compounds $Me_4Si_2(Se)_2SnPh_2$ (**4a**), and $Ph_2Sn(Se)_2Si_2Me_2(Se)_2SnPh_2$ (**4b**) have also been prepared essentially applying the same procedure as for compounds **2a**–**b**. A plot of δ (^{207}Pb) of **1a**–**2b** versus δ (^{119}Sn) of the corresponding tin compounds **3a**–**4b** exhibits a linear correlation with a slope of 4.11 (± 0.17). Attempts to build related cycles containing a Group 15 element led to the isolation of the antimony compounds $Me_4Si_2(E)_2SbPh$ (**5a**: E = S, **5b**: E = Se) starting from $ClSiMe_2$–$SiMe_2Cl$, $PhSbCl_2$ and either H_2S/NEt_3 or Li_2Se. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NMR spectroscopy; Silicon–lead chalcogenides; Antimony; Tin

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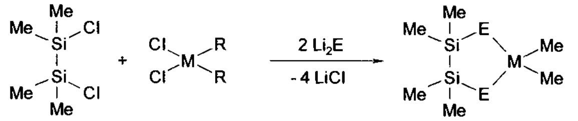
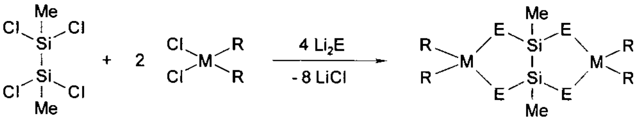
1. Introduction

Recently we have reported on the synthesis of cyclic and bicyclic chalcogenides of the types $Me_4Si_2(E)_2MR_x$ (E = S, Se, Te, MR_x = BPh, $C(CH_2)_5$, $SiMe_2$, SiMePh, $SiPh_2$, $GeMe_2$, $SnMe_2$) [1] and $R_2M(E)_2Si_2Me_2(E)_2MR_2$ (E = S, Se, Te, MR_2 = $C(CH_2)_5$, $SiMe_2$, SiMePh, $SiPh_2$, $GeMe_2$, $SnMe_2$) [2]. For M = B, Si, Ge and Sn these compounds have been prepared by reacting a mixture of the corresponding dichloride and either $ClSiMe_2$–$SiMe_2Cl$ or Cl_2SiMe–$SiMeCl_2$ with lithium sulfide, selenide or telluride Eqs. (1) and (2):



(1)



(2)

In absence of the methylchlorodisilanes the diorganodichlorides of Group 14 elements (Si, Ge, Sn) react with lithium or sodium chalcogenides under formation of trimeric diorganochalcogenides $(R_2ME)_3$ [1,3,4].

A related lead sulfide, $(Ph_2PbS)_3$, was described for the first time in 1887 [5]. Crystal structure analysis of *cis–trans*-$(PhMeSiS)_3$ [6], $(Me_2SnS)_3$ [7,8], $(Me_2SnSe)_3$ [9], $(Me_2SnTe)_3$ [10], $(Ph_2SnS)_3$ [11], $(Ph_2PbS)_3$ [11], (o-$Tol_2PbS)_3$ [12] and (p-$Tol_2PbS)_3$ [12] have been reported revealing non-planar six-membered rings M_3E_3 which adopt a twisted boat conformation.

On the other hand, $ClSiMe_2$–$SiMe_2Cl$ reacts with Li_2E (E = S, Se, Te) under formation of the six membered ring compounds $E(SiMe_2$–$SiMe_2)_2E$. Molecular

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* Corresponding author. Tel.: +49-3731-394343; fax: +49-3731-394058.

E-mail address: uwe.herzog@chemie.tu-freiburg.de (U. Herzog).

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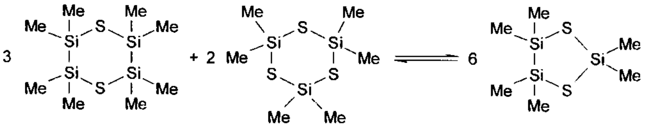
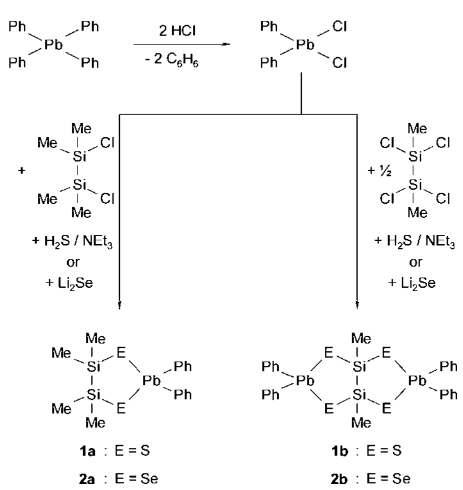
structure analyses for E = S and Se have shown that in these cases the six-membered rings adopt chair conformations [1].

DFT calculations on the system (Eq. (3)):



(3)

revealed that the formation of the five membered ring compound is accompanied by a decrease in the total energy of 36 kJ mol^{-1} in accordance with the observed favorite formation of these five membered rings [13]. So far, molecular structures of such unfused five-membered rings are only known for the dimeric compound $Me_4Si_2(S)_2SiMe-SiMe(S)_2Si_2Me_4$ [1] and the tin compound $Me_4Sn_2(Se)_2SnMe_2$ [14]. While in the first case the five-membered rings adopt twist conformations (very similar to the calculated geometry of $Me_4Si_2(S)_2SiMe_2$ [13]) the latter shows an envelope conformation with the distannane unit and the two selenium atoms in one plane.



Scheme 1.

The aim of this work is to extend these investigations on five membered rings containing a disilane unit as well as another Group 14 element linked by chalcogen atoms towards lead containing cyclic and bicyclic chalcogenides.

2. Results and discussion

A 1:1 molar mixture of diphenyldichloroplumbane, prepared by treatment of a suspension of Ph_4Pb in $CHCl_3$ with HCl, and 1,2-dichlorotetramethyldisilane yielded on treatment with either H_2S-NEt_3 or Li_2Se the new compounds **1a** and **2a** containing a five membered ring Si_2E_2Pb (see Scheme 1). The corresponding bicyclic compounds **1b** and **2b** were observed by similar reactions of a 2:1 molar mixture of Ph_2PbCl_2 and 1,1,2,2-tetrachlorodimethyldisilane (Scheme 1).

The NMR data of **1a**–**2b** are summarized in Table 1. So far the NMR data of the corresponding tin compounds have only been known for E = S (**3a**–**b** [1,2], for E = Se similar compounds with $SnMe_2$ units instead of $SnPh_2$ have been reported, too in [1,2]). Therefore, the tin compounds **4a** and **4b** have also been prepared applying essentially the same procedure as for the lead compounds **2a**–**b**, the NMR data of **3a**–**4b** are given in Table 2.

While the ^{29}Si-NMR chemical shifts of the lead containing cycles and bicycles are close to those of the

Table 1
NMR data of silicon–lead heterocycles (chemical shifts in ppm, coupling constants in Hz)

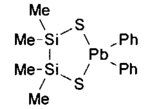
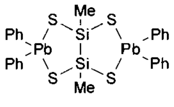
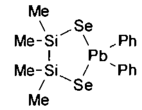
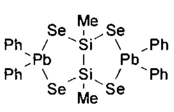
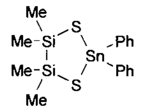
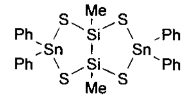
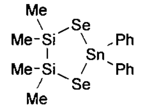
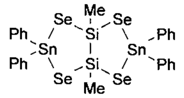
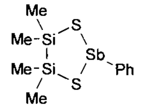
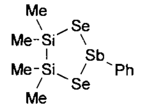
compound		^{77}Se	^{207}Pb	^{29}Si	^{13}C	^{1}H
1a		-	268	11.48 $^2J_{SiPb}$: 7.3 $^1J_{SiC}$: 45.7	Me: 2.65 ($^3J_{PbC}$: 25.3) Ph: i: 157.33 ($^1J_{PbC}$: 581) o: 135.23 ($^2J_{PbC}$: 97.4), m: 130.16 ($^3J_{PbC}$: 115.8) p: 129.78 ($^4J_{PbC}$: 26.8)	Me: 0.373 Ph: o: 7.66, ($^3J_{HH}$: 6.6) m: 7.43 p: 7.30
1b		-	247	32.91 $^2J_{SiPb}$: 4.4 $^1J_{SiC}$: 48.3	Me: 8.80 ($^3J_{PbC}$: 22.2) Ph: i: 157.75 / 157.92 o: 135.30 ($^2J_{PbC}$: 97.4) / 135.56 ($^2J_{PbC}$: 88.9) m: 130.07 ($^3J_{PbC}$: 124.2) / 130.36 ($^3J_{PbC}$: 115.0) p: 129.85 / 129.98	Me: 0.704 Ph: o: 7.65 / 7.67 m: 7.48 / 7.50 p: 7.36
2a		-390	25 $^1J_{PbSe}$: 1544	13.03 $^2J_{SiPb}$: 9.2 $^1J_{SiSe}$: 116.3	Me: 2.26 ($^3J_{PbC}$: 24.5) Ph: i: 155.60 o: 135.30 ($^2J_{PbC}$: 93.6), m: 129.91 ($^3J_{PbC}$: 105.8) p: 129.48 ($^4J_{PbC}$: 23.0)	Me: 0.490 Ph: o: 7.65, ($^3J_{HH}$: 5.1) m: 7.41 p: 7.30
2b		-346	66 $^1J_{PbSe}$: 1477	33.62 $^2J_{SiPb}$: 7.8 $^1J_{SiSe}$: 156.2	Me: 8.70 ($^3J_{PbC}$: 19.9) Ph: i: 156.28 / 157.02 o: 135.37 ($^2J_{PbC}$: 93.6) / 135.52 ($^2J_{PbC}$: 98.2) m: 129.84 ($^3J_{PbC}$: 114.3) / 130.14 ($^3J_{PbC}$: 105.8) p: 129.60 / 129.68	Me: 0.894 Ph: o: 7.65 / 7.67 m: 7.38 / 7.46 p: 7.33

Table 2
NMR data of silicon–tin and silicon–antimony heterocycles $Me_4Si_2(E)SnPh_2$ and $Ph_2Sn(E)_2Si_2Me_2(E)_2SnPh_2$ (E = S, Se (**3a**–**4b**) and $Me_4Si_2(E)_2SbPh$ (**5a**–**b**); chemical shifts in ppm, coupling constants in Hz)

compound	^{77}Se	^{119}Sn	^{29}Si
3a [1] 	-	68	11.66 $^2J_{SiSn}$: 10.2 $^1J_{SiC}$: 45.7
3b [2] 	-	56	31.41 $^2J_{SiSn}$: 8.8 $^1J_{SiC}$: 49.8
4a 	-467 $^1J_{SiSe}$: 110.3 $^2J_{SiSe}$: 8.3	10 $^1J_{SnSe}$: 1266	13.15 $^2J_{SiSn}$: 12.4 $^1J_{SiC}$: 44.7
4b 	-410 $^1J_{SiSe}$: 142.9	16 $^1J_{SnSe}$: 1248	32.40 $^2J_{SiSn}$: 12.6
5a 	-	-	22.09 $^1J_{SiC}$: 46.9
5a 	-239 $^1J_{SiSe}$: 121.5 $^2J_{SiSe}$: 8.3	-	23.96

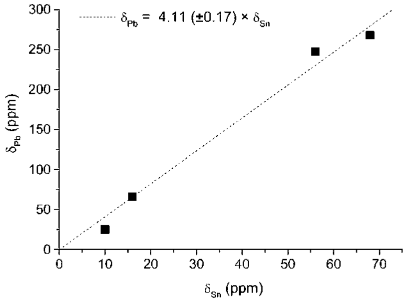


Fig. 1. ^{207}Pb- vs. ^{119}Sn-NMR chemical shifts in $Me_4Si_2(E)_2MPh_2$ and $Ph_2M(E)_2Si_2Me_2(E)_2MPh_2$ (M = Sn, Pb; E = S, Se; **1a**–**4b**).

corresponding tin containing derivatives, the ^{77}Se-NMR chemical shifts of **2a**–**b** are 77 and 64 ppm, respectively, at lower field than those of **4a**–**b**. It has been stated before [15] that in many compounds the ^{207}Pb-NMR chemical shifts parallel the ^{119}Sn-NMR data of the analogous tin compounds by a factor of ca. 3.0. A correlation of the ^{207}Pb- and ^{119}Sn-NMR chemical shifts of **1a**–**4b** is given in Fig. 1, but the slope of the linear fit is with 4.11 somewhat larger. Compared with the six membered ring trimeric diphenyllead sulfide, $(Ph_2PbS)_3$ (δ_{Pb}: 173.4 ppm [11]), the ^{207}Pb-NMR signals of the five membered ring compounds **1a**–**b** are shifted by more than 70 ppm to lower field. This trend has been observed before for δ_{Si} and δ_{Sn} in corresponding silicon and tin compounds [1].

The molecular structure analysis of **1a** (Fig. 2) revealed a central five membered ring PbS_2Si_2 that adopts an envelope conformation. The interplanar angle between the planes formed by Pb(1)–S(2)–Si(2)–Si(1) and Pb(1)–S(1)–Si(1) is 41.65(3)°. The sulfur atom S(1) is 1.032(1) Å out of the plane defined by the atoms Pb(1)–S(2)–Si(2)–Si(1). This may also be the reason for the difference in the angles Pb(1)–S(1)–Si(1) and Pb(1)–S(2)–Si(2) of almost 5°, see Table 3. The bond lengths Pb–S and Pb–C are comparable with the values found in the molecular structure of $(Ph_2PbS)_3$ (average Pb–S: 2.491 Å, Pb–C: 2.191 Å [11]). Due to the smaller ring size the angles S–Pb–S as well as those at the sulfur atoms are smaller than in $(Ph_2PbS)_3$ (average S–Pb–S: 109.4°, Pb–S–Pb: 104.4°).

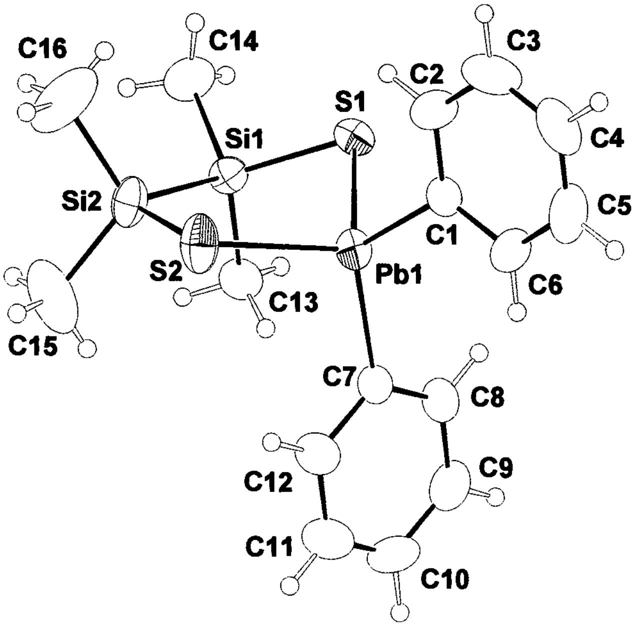


Fig. 2. ORTEP plot of the molecular structure of **1a**.

Table 3
Selected bond distances (Å) bond angles and dihedral angles (°) of **1a**

Atoms	Distances	Atoms	Angles
Si(1)–Si(2)	2.356(2)	S(1)–Pb(1)–S(2)	103.96(4)
Si(1)–S(1)	2.151(2)	Pb(1)–S(1)–Si(1)	95.73(5)
Si(2)–S(2)	2.140(2)	Pb(1)–S(2)–Si(2)	100.48(5)
Pb(1)–S(1)	2.4995(11)	S(1)–Si(1)–Si(2)	108.63(6)
Pb(1)–S(2)	2.4915(11)	S(2)–Si(2)–Si(1)	111.17(6)
Pb(1)–C(1)	2.197(3)	C(1)–Pb(1)–C(7)	120.51(13)
Pb(1)–C(7)	2.204(4)	C(13)–Si(1)–C(14)	110.2(2)
Si(1)–C(13)	1.868(4)	C(15)–Si(2)–C(16)	109.7(3)
Si(1)–C(14)	1.870(5)	Pb(1)–S(2)–Si(2)–Si(1)	−3.28(8)
Si(2)–C(15)	1.877(5)	S(1)–Pb(1)–S(2)–Si(2)	27.73(6)
Si(2)–C(16)	1.859(5)	Si(1)–S(1)–Pb(1)–S(2)	−42.39(5)
		Si(2)–Si(1)–S(1)–Pb(1)	41.00(6)
		S(2)–Si(2)–Si(1)–S(1)	−27.16(9)

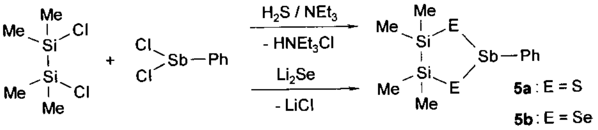
Table 4
Crystal data of **1a** as well as data collection and refinement details

	1a
Empirical formula	$C_{16}H_{22}PbS_2Si_2$
Crystal shape	Plate
Crystal color	Colorless
Crystal size (mm)	0.44 × 0.12 × 0.08
Formula weight	541.83
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.709(2)
b (Å)	11.260(2)
c (Å)	11.607(2)
α (°)	80.754(3)
β (°)	72.789(3)
γ (°)	70.474(3)
V (Å^3)	1022.3(3)
Z	2
D_{calc} (g cm^{-3})	1.760
Linear absorption coefficient (mm^{-1})	8.565
Scan method	ω scans
Absorption correction	Empirical
Max/min transmission	0.5474/0.1166
Measured reflections	11 974
Independent reflections	5769
Observed reflections	4700
R_{int}	0.0356
θ range for collection (°)	1.84–30.88
Index ranges	$-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$
Completeness to θ_{max} (%)	89.3
Final R_1/wR^2 [a] ($I > 2\sigma(I)$)	0.0296/0.0576
Final R_1/wR^2 [a] (all data)	0.0435/0.0610
Goodness-of-fit (S) on F^2 [b]	0.960
H-locating and refining	Geom./constr.
Max/min e-density (e Å^{-3})	1.108/−1.148

[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$, $wR^2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(wF_o^2)]^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$.

[b] $S = [\Sigma w(F_o^2-F_c^2)^2]/(n-p)^{1/2}$, n = used reflections, p = used parameters.

So far no cyclic chalcogenides containing silicon and a Group 15 element are known. The reaction of a 1:1 molar mixture of $ClSiMe_2$–$SiMe_2Cl$ and $PhSbCl_2$ with H_2S in the presence of a tertiary amine yielded the antimony containing cycle **5a** (Eq. (4)):



(4)

The corresponding selenium compound **5b** emerged from $ClSiMe_2$–$SiMe_2Cl$ and $PhSbCl_2$ on treatment with Li_2Se.

The ^{29}Si-NMR shifts of **5a**–**b** are remarkable because they are some 10 ppm downfield from all related compounds $Me_4Si_2(E)_2MR_2$ (E = S, Se) with M constituting a Group 14 element (C, Si, Ge, Sn, Pb) (see Table 2).

3. Experimental

3.1. NMR and GC–MS measurements

All NMR spectra were recorded on a Bruker DPX 400 in $CDCl_3$ solution and with TMS as internal standard for ^{1}H, ^{13}C and ^{29}Si. External Me_4Sn, Ph_4Pb (δ_{Pb} −178 ppm [16]) and Ph_2Se_2 (δ_{Se} 460 ppm [17]) in $CDCl_3$ were used as standards for ^{119}Sn, ^{207}Pb and ^{77}Se.

In order to obtain a sufficient signal-to-noise ratio of ^{29}Si-NMR spectra for resolving $^1J_{SiC}$, $^{1,2}J_{SiSe}$, $^2J_{SiSn}$ or $^2J_{SiPb}$ satellites ^{29}Si INEPT spectra were also recorded. ^{77}Se, ^{119}Sn and ^{207}Pb spectra were determined using an IGATED pulse program.

The assignment of C^{ipso} in phenyl substituents was supported by recording ^{13}C APT spectra. Mass spectra were measured on a Hewlett–Packard 5971 (ionization energy 70 eV, column 30 m × 0.25 mm × 0.25 μm, phenylmethylpolysiloxane, column temperature 80 °C (3 min)/20 K min^{-1}, flow He 0.5 ml min^{-1}).

3.2. Crystal structure analysis

X-ray structure analysis measurements were performed on a Bruker Smart 1k CCD area detector. Crystal data of **1a** as well as data collection and refinement details are given in Table 4.

The unit cell dimensions were determined with the program SMART [18]. For data integration and refinement of the unit cell parameters the program SAINT [10] was used. The space group was determined with the aid of the programs ABSEN [19]. All data were corrected for absorption applying SADABS [20]. The structures were solved using direct methods (SIR97 [21]), refined using least-squares-methods (SHELX-97 [22]) and drawn using ZORTEP [23]. The ellipsoides at the non-hydrogen atoms are at the 50% probability level.

3.3. Starting materials

H_2S, sulfur, selenium, triethylamine, 1 M $LiBEt_3H$ in THF (super hydride), Ph_2SnCl_2, Ph_3Sb, $SbCl_3$ and Ph_4Pb were commercially available. Ph_2PbCl_2 [24] was prepared by treatment of a stirred suspension of Ph_4Pb in $CHCl_3$ with a stream of dry HCl for 2 h. The resulting white solid of Ph_2PbCl_2 was filtered and washed with $CHCl_3$. THF was distilled from sodium potassium alloy prior to use. The other solvents were dried over KOH or sodium wire. All reactions were carried out under argon applying standard Schlenk techniques.

3.4. *5,5-Diphenyl-2,2,3,3-tetramethyl-1,4,2,3,5-dithiadisilaplumbolane (**1a**) and 5,5-diphenyl-2,2,3,3-tetramethyl-1,4,2,3,5-diselenadisilaplumbolane (**2a**)*

Compound **1a**: 0.44 g (1 mmol) Ph_2PbCl_2 and 0.19 g (1 mmol) $ClSiMe_2–SiMe_2Cl$ were dissolved in 15 ml toluene and 0.62 ml (4.5 mmol) NEt_3 were slowly added while H_2S was bubbled through the stirred solution. The reaction mixture turned black (some PbS) and a precipitation of $HNEt_3Cl$ occurred. After filtration, the solvent was removed in vacuo to yield **1a** as colorless crystals, which could be recrystallized from hexane.

Compound **1a**: Anal. Calc. for $C_{16}H_{22}PbS_2Si_2$ (541.85 g mol^{-1}): C 35.47; H 4.09. Found: C 36.02; H 4.43%.

Compound **2a**: 0.44 g (1 mmol) Ph_2PbCl_2 and 0.19 g (1 mmol) $ClSiMe_2–SiMe_2Cl$ were dissolved in 3 ml toluene and this mixture (Ph_2PbCl_2 forms a suspension) was added to a suspension of 2 mmol Li_2Se (prepared from 0.16 g (2 mmol) selenium powder and 4 ml of a 1 M solution of $LiBEt_3H$ in THF). The reaction mixture turned black (some PbSe). After reacting for 30 min the solvents were removed in vacuo and replaced by 10 ml toluene. After filtration the solvent was removed to yield **2a** as a light yellow oil.

3.5. *3,3,7,7-Tetraphenyl-1,5-dimethyl-2,4,6,8-tetrathia-3,7-diplumba-1,5-disilabicyclo[3.3.0]octane (**1b**) and 3,3,7,7-tetraphenyl-1,5-dimethyl-2,4,6,8-tetraselena-3,7-diplumba-1,5-disilabicyclo[3.3.0]octane (**2b**)*

Compound **1b**: 0.44 g (1 mmol) Ph_2PbCl_2 and 0.115 g (0.5 mmol) $Cl_2SiMe–SiMeCl_2$ were dissolved in 15 ml toluene and 0.62 ml (4.5 mmol) NEt_3 were slowly added while H_2S was bubbled through the stirred solution. Work-up as described for **1a** yielded **1b** as a colorless solid soluble in hexane, chloroform and toluene.

Compound **1b**: Anal. Calc. for $C_{26}H_{26}Pb_2S_4Si_2$ (937.31 g mol^{-1}): C 33.32; H 2.80. Found: C 32.98; H 3.23%.

Compound **2b**: 0.44 g (1 mmol) Ph_2PbCl_2 and 0.115 g (0.5 mmol) $Cl_2SiMe–SiMeCl_2$ were dissolved in 3 ml toluene and added to a suspension of 2 mmol Li_2Se as described above for **2a**. An analogous work-up yielded **2b** as a light yellow oil.

3.6. *5,5-Diphenyl-2,2,3,3-tetramethyl-1,4,2,3,5-diselenadisilastannolane (**4a**) and 3,3,7,7-tetraphenyl-1,5-dimethyl-2,4,6,8-tetraselena-3,7-distanna-1,5-disilabicyclo[3.3.0]octane (**4b**)*

Compound **4a**: 0.345 g (1 mmol) Ph_2SnCl_2 and 0.19 g (1 mmol) $ClSiMe_2–SiMe_2Cl$ were dissolved in 1.5 ml THF and added to a suspension of 2 mmol Li_2Se in THF (prepared as described above). After 30 min the solvents were removed in vacuo and replaced by 10 ml hexane. Removal of the solvent from the filtrate yielded **4a** as a light yellow oil.

Compound **4a**: ^{119}Sn-, ^{77}Se- and ^{29}Si-NMR: see Table 2, ^{13}C-NMR: $SiMe_2$ 1.09 ($^3J_{SnC}$: 15.6 Hz), *i* 140.01 ($^1J_{SnC}$: 557.5 Hz), *o* 135.39 ($^2J_{SnC}$: 53.2 Hz), *m* 128.69 ($^3J_{SnC}$: 66.5 Hz), *p* 129.76 ppm ($^4J_{SnC}$: 16.4 Hz); ^{1}H-NMR: 0.53 ($SiMe_2$), 7.65 and 7.36 ppm ($SnPh_2$).

Compound **4b**: 0.345 g (1 mmol) Ph_2SnCl_2 and 0.115 g (0.5 mmol) $Cl_2SiMe–SiMeCl_2$ were dissolved in 1.5 ml THF and reacted with 2 mmol Li_2Se as described above for **4a**. Work-up as for **4a** yielded **4b** as a light yellow solid product.

Compound **4b**: ^{119}Sn-, ^{77}Se- and ^{29}Si-NMR: see Table 2, ^{13}C-NMR: SiMe 6.04 ($^3J_{SnC}$: 15.7 Hz), *i* 139.33/140.03, *o* 135.46 ($^2J_{SnC}$: 53.2 Hz)/135.72 ($^2J_{SnC}$: 45.4 Hz), *m* 128.67 ($^3J_{SnC}$: 68.8 Hz)/128.93 ($^3J_{SnC}$: 67.3 Hz), *p* 129.97/130.08 ppm; ^{1}H-NMR: 1.00 ppm (SiMe), 7.25–7.62 ppm ($SnPh_2$).

Compound **4a** as well as **4b** contained small amounts of $(Ph_2SnSe)_3$, which was proven by NMR spectroscopy.

$(Ph_2SnSe)_3$, ^{119}Sn-NMR: -43.2 ppm (lit. -43.5 ppm [4]) $^1J_{SnSe}$: 1318 Hz, ^{77}Se-NMR: -435 ppm (lit. -452 ppm [4]), ^{13}C-NMR: *i* 139.91, *o* 135.39 ($^2J_{SnC}$: 53.9 Hz), *m* 128.57 ($^3J_{SnC}$: 70.4 Hz), *p* 129.65 ppm ($^4J_{SnC}$: 12.3 Hz).

3.7. *2-Phenyl-4,4,5,5-tetramethyl-1,3,2,4,5-dithiastibadisilolane, $Me_4Si_2(S)_2SbPh$ (**5a**) and 2-phenyl-4,4,5,5-tetramethyl-1,3,2,4,5-diselenastibadisilolane, $Me_4Si_2(Se)_2SbPh$ (**5a**)*

3.7.1. *Phenyldichlorostibane, $PhSbCl_2$*

About 4.56 g (20 mmol) $SbCl_3$ and 3.53 g (10 mmol) $SbPh_3$ were mixed and heated to 100 °C for 3 h yielding an oily product. After cooling to room temperature a NMR spectra of the product proved the formation of $PhSbCl_2$ (^{13}C-NMR (ppm): *i* 151.87, *o* 132.77, *m* 129.43, *p* 131.43; ^{1}H-NMR (ppm): *o* 7.75, *m* 7.47, *p* 7.40) besides small amounts of Ph_2SbCl (^{13}C-NMR (ppm): *i* 144.47, *o* 134.39, m 129.17, *p* 130.06; ^{1}H-NMR (ppm): *o* 7.58, *m* 7.37, *p* 7.40).

3.7.2. *$Me_4Si_2(S)_2SbPh$ (**5a**)*

About 0.27 g (1 mmol) $PhSbCl_2$ and 0.19 g (1 mmol) $ClSiMe_2–SiMe_2Cl$ were dissolved in 20 ml toluene and 0.55 ml (4 mmol) NEt_3 were slowly added while a stream of H_2S was bubbled through the stirred solution. After filtration from the precipitated $HNEt_3Cl$ the solvent was removed in vacuo yielding **5a** as a light yellow oily residue.

Compound **5a**: ^{29}Si-NMR: see Table 2, ^{13}C-NMR (ppm): 3.04/2.24 ($SiMe_2$), *i* 145.10, *o* 134.18, *m* 128.63, *p* 129.33; ^{1}H-NMR: 0.12/0.40 ($SiMe_2$), 7.75 (*ortho*), 7.38 (*meta* + *para*).

GC–MS: 378 (M$^+$, 3), 363 (M − Me, 1), 301 (M − Ph, 1), 290 ($PhSbS_2Si$, 2), 258 (PhSbSSi, 1), 228

(SbS_2SiMe, 4), 198 (PhSb, 9), 165 ($S_2Si_2Me_3$, 10), 135 ($PhSiMe_2$, 100), 121 (Sb, 2), 73 ($SiMe_3$, 22).

3.7.3. $Me_4Si_2(Se)_2SbPh$ (**5b**)

About 0.27 g (1 mmol) $PhSbCl_2$ and 0.19 g (1 mmol) $ClSiMe_2{-}SiMe_2Cl$ were dissolved in 1 ml THF. This mixture was added to a Li_2Se suspension prepared from 2 mmol selenium and 4 ml of a 1 M solution of $LiBEt_3H$ in THF. After stirring for 30 min the solvent was replaced by 10 ml hexane. Filtration and removal of the solvent in vacuo yielded **5b** as a light yellow oily residue.

Compound **5b**: ^{29}Si- and ^{77}Se-NMR: see Table 2, ^{13}C-NMR (ppm): 3.18/1.90 ($SiMe_2$), *i* 139.76, *o* 135.03, *m* 128.50, *p* 128.97; ^{1}H-NMR: 0.20/0.48 ($SiMe_2$), 7.81 (*ortho*), 7.32 (*meta* + *para*).

4. Supplementary material

Crystallographic data (excluding structure factors) for **1a** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no.: CCDC no. 172656. Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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