

Syntheses and structures of $(R_2Bi)_2E$ ($E = S, Te$) and *cyclo*- $(RSbSe)_2[W(CO)_5]_2$ [$R = CH(SiMe_3)_2$]

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Abstract

$(R_2Bi)_2E$ ($E = S$ (**1**), Te (**2**); $R = CH(SiMe_3)_2$) are formed by reaction of R_2BiCl with Na_2S or Na_2Te . The reaction of *cyclo*- $(RSbSe)_n$ [$n = 2, 3$; $R = CH(SiMe_3)_2$] with $W(CO)_5THF$ ($THF =$ tetrahydrofuran) in THF results in trapping of the dimer in *cyclo*- $(RSbSe)_2[W(CO)_5]_2$ (**3**). The crystal structures of **1**, **2**, and **3** are reported.

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Keywords: Bismuth; Antimony selenium; Tellurium; Tungsten complex; X-ray structure

1. Introduction

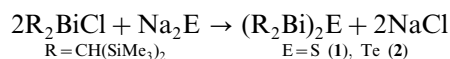
The first bis(diorganobismuth)chalcogenides, $(R_2Bi)_2E$ ($E = O, S, Se, Te$) were prepared 15 years ago by chalcogen insertion into bismuth–bismuth bonds [1–4]; later also reactions between diorganobismuth halides and sodium chalcogenides were used [5]. The only examples with known crystal structures are the mesityl derivatives $(R_2Bi)_2E$ [$E = O, S, Se$; $R = 2,4,6-(CH_3)_3C_6H_2$] [5,6]. We report here on the synthesis and structural characterisation of two novel bis(dialkylbismuth)chalcogenides, $(R_2Bi)_2E$ [$E = S$ (**1**), Te (**2**); $R = CH(SiMe_3)_2$] protected by a bulky alkyl group. The telluride **2** is a heavy atom analogue of cacodyl oxide [7] and the first organometallic molecule with a Bi–Te bond with a known crystal structure [8].

Known organoantimony selenides, *cyclo*- $(RSbSe)_n$ are trimers ($n = 3$; $R = 2,4,6-[(Me_3Si)_2CH]_3C_6H_2$ [9], $2,6-[(Me_3Si)_2CH]_2-4-[(Me_3Si)_3C]C_6H_2$ [10]) and a ring system in a dimer–trimer equilibrium [$n = 2, 3$; $R = CH(SiMe_3)_2$] [11]. We report here on the trapping of the dimer, *cyclo*- $(RSbSe)_2$ as ligand in the binuclear complex *cyclo*- $(RSbSe)_2[W(CO)_5]_2$ (**3**). Complexes with *cyclo*- $(RSbSe)_n$ ligands have not been described before.

The analogous sulphur complex, *cyclo*- $(RSbS)_2- [W(CO)_5]_2$ [$R = CH(SiMe_3)_2$] was also synthesised and characterised by X-ray diffractometry [12]. Related compounds with known crystal structures are *cyclo*- R_2Sb_2Se ($R = 2,6-[(Me_3Si)_2CH]_2-4-[(Me_3Si)_3C]C_6H_2$) [10] and *cyclo*- $(RAsSe)_2[Mn(CO)_2(CH_3C_5H_4)]$ ($R = ^tBu, Bu, Ph, ^cC_6H_{11}$) [13].

2. Results and discussions

The bis(dialkylbismuth) sulfide and telluride **1** and **2** are formed by reaction of $[(Me_3Si)_2CH]_2BiCl$ with Na_2S in water or with Na_2Te in liquid NH_3 , respectively.



The sulfide **1** is a yellow crystalline compound, readily soluble in organic solvents. The solid compound decomposes in air; it is stable only at low temperature in an inert atmosphere. In solution decomposition occurs with formation of R_3Bi [$R = CH(SiMe_3)_2$] and Bi_2S_3 . A similar decomposition pathway was also reported for other bis(diorganobismuth) sulfides [3,5]. Complex **2** is a red–brown solid which is very unstable. Decomposition occurs in solution and in solid state even at low temperature ($-28^\circ C$). The NMR spectra of **1** and **2** in C_6D_6 at $20^\circ C$ show two singlet signals for the trimethylsilyl groups and a singlet for the methine

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protons. Characteristic mass spectra have been obtained by direct chemical ionisation or electron impact techniques.

To establish the solid-state structure of **1** and **2**, X-ray diffraction studies (see Table 1 for details) were carried out on single crystals obtained by cooling concentrated solutions of **1** in petroleum ether and of **2** in THF. The molecular structures are shown in Fig. 1. Selected bond lengths and angles are given in Table 2. The crystals of **1** and **2** consist of discrete molecules with a pyramidal environment around the bismuth centres. The Bi₂E moieties are angular. The Bi–E–Bi angle in **1** [92.48(4)°] is larger than that found in **2** [88.00(7)°]. As a general trend, the Bi–E–Bi angle becomes sharper going from the oxide to the telluride (see Table 3). The Bi–S bond lengths in **1** [255.74(12) and 257.19(12) pm] are comparable with those found in (Mes₂Bi)₂S [252.0(7) and 254.5(6) pm] [5]. The Bi–Te bond lengths in **2** [287.2(3) and 288.9(2) pm] are considerably shorter than the shortest Bi–Te distance found in the crystal of

Bi₂Te₃ [306.6(2) pm] [14]. An interesting aspect of the structures of **1** and **2** is the dissimilarity of the bond angles at bismuth: C–Bi–C = 95.74(14)° and 104.63(15)° in **1**, 97.7(4)° and 105.0(4)° in **2**; C–Bi(1)–E (E = S) 93.56(10)° and 103.19(10)° in **1**, (E = Te) 93.5(3) and 103.9(3)° in **2**. This difference may be a consequence of the steric strain in the molecule, caused by the bulky CH(SiMe₃)₂ substituents. Similar distortions have also been observed in the structures of [(Me₃Si)₂CH]₃Bi [15] and [(Me₃Si)₂CH]₂BiCl [16]. In order to describe the different conformations of bis(diorganobismuth)chalcogenides, the torsion angles φ , Bi–E–Bi–lp, where lp stands for the assumed direction of the lone pair at bismuth and E for the chalcogen atom, are used. With an assignment of the terms *syn* and *anti* to angles of 0 and 180°, the extreme molecular conformations are *syn–syn* and *syn–anti*. As shown in Table 3 all the bis(diorganobismuth)chalcogenides with known crystal structures including **1** and **2** adopt intermediate conformations. They are closer to

Table 1
Crystallographic data and measurements for **1**, **2**, **3**

Compound	1	2	3
Empirical formula	C ₂₈ H ₇₆ Bi ₂ SSi ₈	C ₂₈ H ₇₆ Bi ₂ Si ₈ Te	C ₂₄ H ₃₈ O ₁₀ Sb ₂ Se ₂ Si ₄ W ₂
Formula weight	1087.63	1183.17	1368.02
Colour	Yellow	Light brown	Light brown
Crystal size (mm)	0.4 × 0.4 × 0.3	0.6 × 0.4 × 0.3	0.5 × 0.4 × 0.3
Unit cell dimensions			
<i>a</i> (pm)	1157.4(2)	1173.0(14)	2271.4(5)
<i>b</i> (pm)	1347.6(3)	1363.7(6)	1093.2(2)
<i>c</i> (pm)	1781.6(4)	1758.7(8)	1733.5(3)
<i>α</i> (°)	104.32(3)	75.00(3)	90
<i>β</i> (°)	92.65(3)	88.17(7)	98.00(3)
<i>γ</i> (°)	114.13(3)	65.19(5)	90
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>Z</i>	2	2	4
Diffractometer	Stoe IPDS	Siemens P4	Stoe IPDS
Mo–K α (Å)	0.71073	0.71073	0.71073
Temperature (K)	173(2)	173(2)	173(2)
Reflections collected	34 531	12 768	29 232
Independent reflections	8774	10971	3996
<i>R</i> _{int}	0.0591	0.0341	0.0381
Completeness to θ (%)	92.7	96.9	96.4
Absorption coefficient (mm ⁻¹)	7.510	7.945	8.495
Absorption correction	DIFABS [19]	DIFABS [19]	DIFABS [19]
Final <i>R</i> ^a indices			
[<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0215, <i>wR</i> ₂ = 0.0421	<i>R</i> ₁ = 0.0550, <i>wR</i> ₂ = 0.1178	<i>R</i> ₁ = 0.0168, <i>wR</i> ₂ = 0.0349
<i>R</i> ^a indices (all data)	<i>R</i> ₁ = 0.0350, <i>wR</i> ₂ = 0.0445	<i>R</i> ₁ = 0.0980, <i>wR</i> ₂ = 0.1379	<i>R</i> ₁ = 0.0211, <i>wR</i> ₂ = 0.0356
Goodness of fit on <i>F</i> ²	0.892	1.007	0.986
<i>F</i> (000)	1076	1148	2544
Data/restraints/parameters	8774/0/375	10971/0/379	3996/0/207
Index ranges	4 ≤ <i>h</i> ≤ 14, –16 ≤ <i>k</i> ≤ 16, –21 ≤ <i>l</i> ≤ 21	–15 ≤ <i>h</i> ≤ 1, –16 ≤ <i>k</i> ≤ 15, –22 ≤ <i>l</i> ≤ 22	–27 ≤ <i>h</i> ≤ 27, –12 ≤ <i>k</i> ≤ 12, –21 ≤ <i>l</i> ≤ 21
Largest difference peak and hole (e Å ⁻³)	0.797 and –0.754	1.919 and –2.063	0.900 and –0.753
Refinement method	Full-matrix least-squares on <i>F</i> ² [20]		
Treatment of hydrogen atoms	Refined with a riding model and common isotropic temperature factor		

^a Definition of the *R* values: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{ [w \sum (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)] \}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (\alpha P)^2 + bP$.

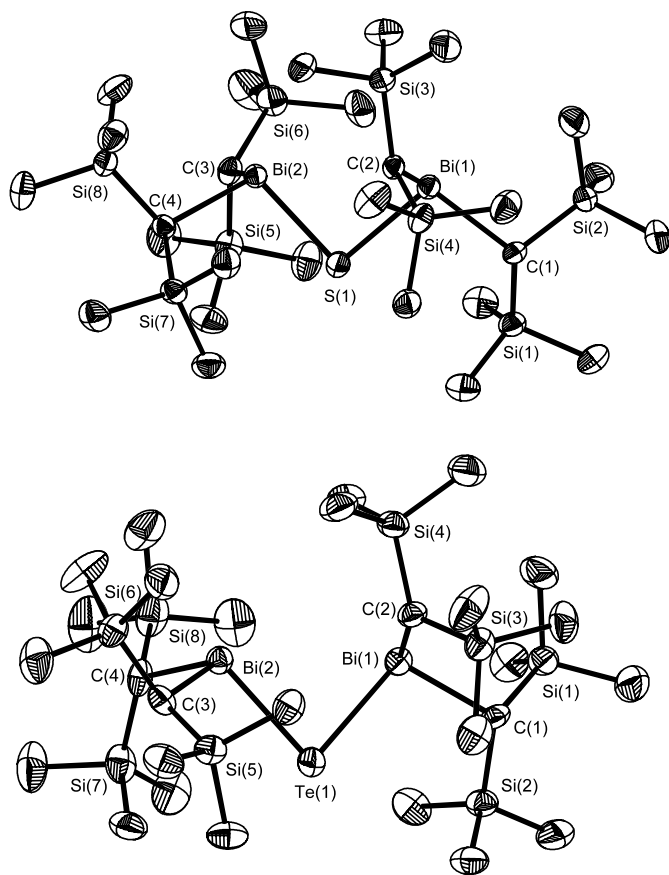
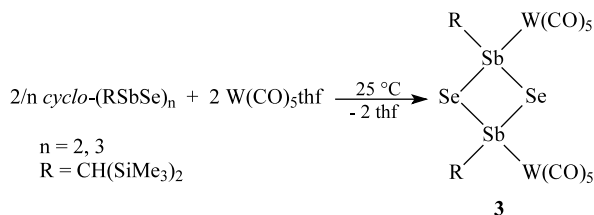


Fig. 1. ORTEP-like representation of **1** and **2** at 50% probability showing the atomic numbering scheme.

syn-syn than to *syn-anti* (Table 3). In **1** and **2** the organic substituents exhibit a *gauche* orientation (Fig. 2) with respect to the Bi...Bi axis.

The ring–ring equilibrium mixture of *cyclo*-(RSbSe)_n (*n* = 2, 3; R = CH(SiMe₃)₂ [11]) reacts with W(CO)₅THF (THF = tetrahydrofuran) to form *cyclo*-(RSbSe)₂[W(CO)₅]₂ (**3**).



Brown crystals of **3** were obtained in 42% yield by cooling petroleum ether solutions to $-28 \text{ }^\circ\text{C}$. They are slightly soluble in aromatic or aliphatic hydrocarbons forming brown air sensitive solutions in THF, dichloromethane or chloroform which decompose slowly at room temperature also in an inert atmosphere. Crystals of **3** are however stable in the air for a short time; they are stable for months when stored under argon at $-30 \text{ }^\circ\text{C}$.

Table 2

Selected interatomic distances (pm) and angles ($^\circ$) in $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Bi}\}_2\text{S}$ (**1**), $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Bi}\}_2\text{Te}$ (**2**), and $[(\text{Me}_3\text{Si})_2\text{CHSb}]_2[\text{W}(\text{CO})_5]_2$ (**3**)

$\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Bi}\}_2\text{S}$ (1)			
Bi(1)–C(1)	230.7(4)	C(1)–Bi(1)–C(2)	104.63(15)
Bi(1)–C(2)	230.9(4)	C(3)–Bi(2)–C(4)	95.74(14)
Bi(2)–C(3)	230.4(4)	Bi(2)–S(1)–Bi(1)	92.48(4)
Bi(2)–C(4)	230.5(4)	C(1)–Bi(1)–S(1)	103.19(10)
Bi(1)–S(1)	257.19(12)	C(2)–Bi(1)–S(1)	93.56(10)
Bi(2)–S(1)	255.74(12)	C(3)–Bi(2)–S(1)	101.07(11)
		C(4)–Bi(2)–S(1)	103.63(9)
$\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Bi}\}_2\text{Te}$ (2)			
Bi(1)–C(1)	230.6(10)	C(1)–Bi(1)–C(2)	105.0(4)
Bi(1)–C(2)	231.6(10)	C(3)–Bi(2)–C(4)	97.7(4)
Bi(2)–C(3)	231.5(10)	Bi(2)–Te(1)–Bi(1)	88.00(7)
Bi(2)–C(4)	231.4(10)	C(1)–Bi(1)–Te(1)	103.9(3)
Bi(1)–Te(1)	288.9(2)	C(2)–Bi(1)–Te(1)	93.5(3)
Bi(2)–Te(1)	287.2(3)	C(3)–Bi(2)–Te(1)	104.6(3)
		C(4)–Bi(2)–Te(1)	101.3(3)
$[(\text{Me}_3\text{Si})_2\text{CHSbSe}]_2[\text{W}(\text{CO})_5]_2$ (3)			
Sb(1)–C(1)	215.5(3)	C(1)–Sb(1)–Se(1)	100.07(7)
Sb(1)–Se(1)	255.86(6)	C(1)–Sb(1)–Se(1)*	104.27(8)
Sb(1)–Se(1)*	255.74(7)	Se(1)*–Sb(1)–Se(1)	90.37(3)
Se(1)–Sb(1)*	255.74(6)	Sb(1)*–Se(1)–Sb(1)	88.56(3)
Sb(1)–W(1)	274.91(5)	Se(1)–Sb(1)–W(1)	114.493(16)
W(1)–C _{ax}	200.2(3)	Se(1)*–Sb(1)–W(1)	111.61(2)
W(1)–C _{eq}	204.2(3)–205.7(4)	C(1)–Sb(1)–W(1)	128.86(8)

Complex **3** was characterised by IR, NMR and by mass spectrometry using the DCI techniques. The NMR spectra of freshly prepared solutions of **3** in C₆D₆ are consistent with the structure established by X-ray diffraction (Fig. 3) and contain the expected two singlet signals for equivalent Me₃Si (0.23 ppm) or CH (0.29 ppm) groups. However, when solutions of **3** in C₆D₆ are exposed to sunlight two new singlet signals at 0.22 (Me₃Si) and 0.28 (CH) ppm appear. They reach a maximum of intensity after 90 min. The photochemical process is reversible and the original spectrum is recovered after 12 h in the absence of light. The most straightforward interpretation for these phenomena is to assume a photochemically induced equilibrium between **3** and the monomer (CO)₅W(R)Sb=Se [R = CH(SiMe₃)₂]. However also the formation of the *trans* isomer of **3** cannot be excluded. Attempts to study the photolysed solutions by mass spectrometry using the ESI technique failed.

The IR spectra of **3** show the common pattern for complexes of the type LW(CO)₅. The structure of **3** as determined by single crystal X-ray diffraction is shown in Fig. 4. The central unit consists of a four-membered Sb₂Se₂ ring (mean deviation from planarity 12.41 pm) with alternating antimony and selenium atoms. The dihedral angles between the Sb–Sb–Se planes is 15.6° and between the Se–Se–Sb planes is 15.8°. In *cyclo*-(RSbS)₂[W(CO)₅]₂, which crystallises also as a *cis* isomer the mean deviation from the planarity is 9.65 pm [12]. In **3** both antimony atoms of

Table 3

Comparative dimensional parameters (interatomic distances, pm, and angles, °) for (R₂Bi)₂E derivatives (R = mesityl, E = O, S, Se and R = bisyl, E = S, Te)

R	E	Conformation φ	Bi–E–Bi–lp		Bi–E–Bi	C–Bi–C	Bi–E	Bi···Bi ^b	Ref.
			φ_1	φ_2					
Mesityl	O		86.51	92.99	124.6(3)	98.3(3) 98.4(3)	206.4(7) 207.5(8)	366.5	[6]
Mesityl	O ^a		84.17	86.46	117.1(8)	97.4(1) 98.3(1)	209.5(2) 211.7(2)	359.5	[5]
Mesityl	S	Near <i>syn–syn</i>	19.47	26.3	98.7(3)	97.4(1) 98.9(9)	252.0(7) 254.5(6)	384.4	[5]
(Me ₃ Si) ₂ CH	S	Near <i>syn–syn</i>	21.39	59.12	92.48(4)	95.74(14) 104.63(15)	255.7(12) 257.2(12)	370.5	^c
Mesityl	Se	Near <i>syn–syn</i>	22.14	22.14	91.2(1)	100.6(3)	265.1(1)	379.1	[5]
(Me ₃ Si) ₂ CH	Te	Near <i>syn–syn</i>	21.33	62.64	88.0(7)	97.69(4) 104.96(4)	287.2(3) 288.9(2)	400.2	^c

^a Crystallised with 0.5 EtOH.^b Intramolecular Bi···Bi distance.^c This paper.

the ring are coordinated to W(CO)₅ units which are in *cis* positions relative to the ring and *trans* to the alkyl groups. The Sb–Se bond lengths [255.74(6) and 255.86(6) pm] in **3** are similar to those found in Sb(SeMe)₃ [256.8(1)–258.8(1) pm] [17]. The endocyclic angles on the antimony and selenium atoms are both close to 90° with Sb(1)–Se(1)–Sb(1)* 88.56(3)° and Se(1)–Sb(1)–Se(1)* 90.37(3)° and describe an almost ideal square. The Sb–W bond length [274.91(5) pm] corresponds to the sum of the covalent radii for Sb and W [278 pm] and is similar to the value found in *cyclo*-(RSbS)₂[W(CO)₅]₂ [273.7(7) pm] [12]. The Me₃Si groups of the *cis* alkyl substituents are directed outwards and together with the W(CO)₅ groups they shield the molecules from each other. Consequently close intermolecular contacts are not observed in the crystals of **3**. A similar orientation of two CH(SiMe₃)₂ groups exists also in *cyclo*-(RSbS)₂[W(CO)₅]₂ [12] and *cyclo*-R₃Sb₃ [R = CH(SiMe₃)₂] [18]. The formation of **3** in the *cis* form contrasts to the *trans* orientation of the organic groups in crystals of *cyclo*-(RSbO)₂ (R = 2,4,6-[(Me₃Si)₂CH]₃C₆H₂) [9].

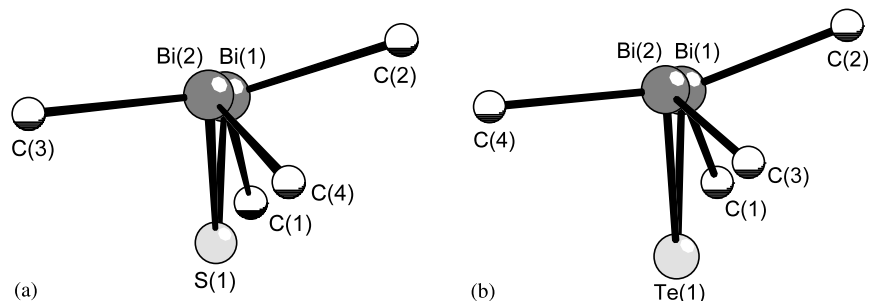
3. Experimental

NMR spectra were run on a Bruker DPX 200 spectrometer. Chemical shifts are reported in δ units (ppm) referenced to C₆D₅H (7.15 ppm, ¹H) and C₆D₆ (128.0 ppm, ¹³C). Mass spectra were recorded on Finnigan MAT CH7 (A) and Finnigan MAT 8222 spectrometers. The pattern of antimony and bismuth-containing ions was compared with theoretical values. For the IR spectra a FT-IR SPEKTRUM 1000 instrument was used. The reactions and manipulations were performed in an atmosphere of dry Ar. *cyclo*-(RSbSe)_n [n = 2–3; R = CH(SiMe₃)₂] [11] and [(Me₃Si)₂CH]₂BiCl [16] were prepared according to reported procedures.

3.1. Synthesis of

bis[*bis*(*bis*(trimethylsilyl)methyl)bismuth]sulfide (**1**)

0.22 g (0.91 mmol) Na₂S·9H₂O in 20 ml water were added to a solution of [(Me₃Si)₂CH]₂BiCl (1 g, 1.7 mmol) in 60 ml Et₂O. After mixing for 1 h the yellow phase was separated and the water phase was washed twice with 50 ml of Et₂O. The organic phases were dried

Fig. 2. Conformation of the C₂Bi–E–BiC₂ fragment in (a) **1** and (b) **2**.

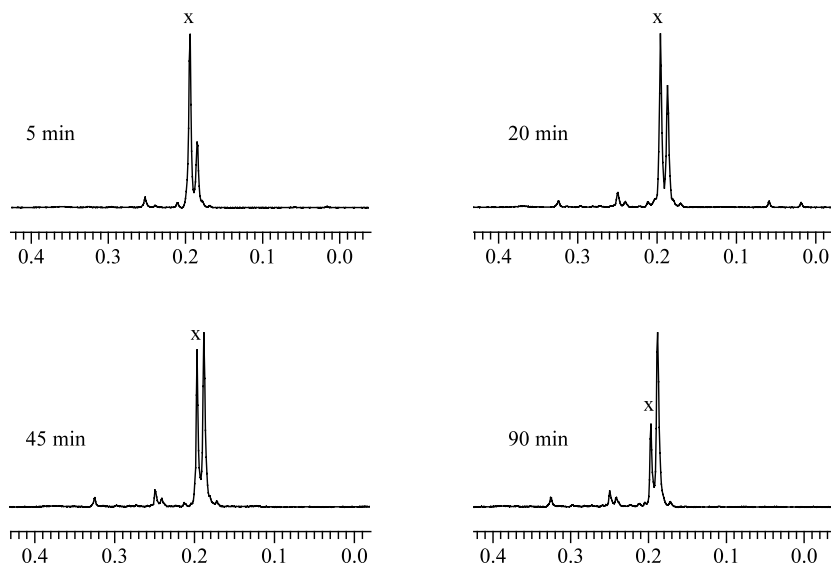


Fig. 3. $^1\text{H-NMR}$ spectra in C_6D_6 of a photolysed solution of **3** (x).

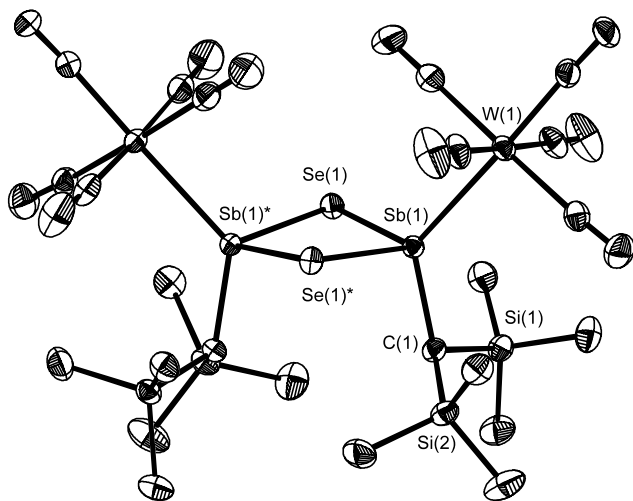


Fig. 4. ORTEP-like representation of **3** at 50% probability showing the atomic numbering scheme.

on CaSO_4 . Removal of the solvent in vacuum gave 0.85 g (88%) of **1** as yellow solid. M.p.: 87°C (dec.). $^1\text{H-NMR}$ (C_6D_6 , 200 MHz): 0.26 (s, 9H, SiCH_3), 0.41 (s, 9H, SiCH_3), 1.30 (s, 1H, CH). $^{13}\text{C-NMR}$ (C_6D_6 , 50 MHz): 4.11 (s, CH_3), 5.74 (s, CH_3), 26.04 (s, CH). MS (EI, 70 eV) m/z (%): 927 (44) [$M^+ - \text{R}$], 559 (6) [R_2BiS^+], 527 (83) [R_2Bi^+], 457 (11) [$\text{R}(\text{MeSiCH}_2)\text{BiS}^+$], 413 (9) [$\text{R}(\text{CH})\text{BiS}^+$], 353 (8) [$\text{RBi}^+ - \text{Me}$], 129 (35) [$\text{R}^+ - 2\text{Me}$], 73 (92) [Me_3Si^+] $\text{R} = \text{CH}(\text{SiMe}_3)_2$.

3.2. Synthesis of bis[bis(bis(trimethylsilyl)methyl)bismuth]telluride (**2**)

1.5 g (2.66 mmol) $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BiCl}$ were added at -60°C to Na_2Te prepared from 0.06 g (2.6 mmol) Na and 0.2 g (1.5 mmol) Te in 60 ml $\text{NH}_3(l)$. The reaction

mixture was stirred at -60°C for 3 h and then the solvent (NH_3) was evaporated. The residue was solved in petroleum ether and a red-brown solution was obtained. The solvent was removed from the petroleum ether solution and 0.84 g (53%) of **2** as a red-brown solid was obtained. M.p.: 83°C (dec.). $^1\text{H-NMR}$ (C_6D_6 , 200 MHz): 0.27 (s, 9H, SiCH_3), 0.40 (s, 9H, SiCH_3), 1.44 (s, 1H, CH). MS (DCI_{pos} , NH_3) m/z (%): 527 (28) [R_2Bi^+], 449 (34) [R_2Te^+], 377 (26) [$\text{R}_2\text{Te}^+ \cdot \text{NH}_3$, $-\text{SiMe}_4$], 306 (20) [$\text{RTe}^+ \cdot \text{NH}_3$], 289 (8) [RTe^+]. MS (DCI_{neg} , NH_3) m/z (%): 653 (46) [R_2BiTe^-], 526 (100) [R_2Bi^-], 454 (49) [R_2Bi^- , $-\text{SiMe}_3$], 289 (82) [RTe^-], 159 (30) [R^-] $\text{R} = \text{CH}(\text{SiMe}_3)_2$.

3.3. Synthesis of cyclo-(RSbSe) $_2[\text{W}(\text{CO})_5]_2$ [$\text{R} = \text{CH}(\text{SiMe}_3)_2$] (**3**)

1.5 g of $\text{cyclo}-(\text{RSbSe})_n$ and $\text{W}(\text{CO})_5\text{THF}$ prepared from 1.46 g (4.14 mmol) $\text{W}(\text{CO})_6$ by irradiation with an UV lamp, in 150 ml of THF were stirred for 4 h at room temperature. Thereafter the solvent was removed under reduced pressure and the remaining brown product was washed twice with 100 ml of petroleum ether. 1.2 g (42%) of **3** was obtained as brown crystals (dec. 134°C) by cooling petroleum ether solutions to -28°C . $^1\text{H-NMR}$ (C_6D_6 , 200 MHz): 0.23 (s, 18H, $(\text{CH}_3)_3\text{Si}$, $^1J_{\text{CH}} = 119.3$ Hz), 0.29 (s, 1H, CH). $^{13}\text{C-NMR}$ (C_6D_6 , 50 MHz): 2.70 (s, $(\text{CH}_3)_3\text{Si}$), 31.94 (s, CH), 196.93 (s, CO_{eq}), 197.32 (s, CO_{ax}). MS (DCI_{pos} , NH_3) m/z (%): 843 (38) [$\text{R}_2\text{Sb}_2\text{SeW}^+ + \text{NH}_3$], 643 (100) [$\text{R}_2\text{Sb}_2\text{Se}^+$]. MS (DCI_{neg} , NH_3) m/z (%): 1281 (5) [$M^- - \text{SiMe}_4$], 1122 (8) [$M^- - \text{SiMe}_4$, $-\text{R}$], 807 (16) [$\text{RSb}_2\text{SeW}(\text{CO})_5^-$], 721 (46) [$\text{R}_2\text{Sb}_2\text{Se}_2^-$], 642 (100) [$\text{R}_2\text{Sb}_2\text{Se}^-$], 324 (52) [$\text{W}(\text{CO})_5^-$] $\text{R} = \text{CH}(\text{SiMe}_3)_2$. IR (petroleum ether): 2072s, 1981s, 1950s cm^{-1} (ν CO).

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 185871 for compound **1**, 185872 for compound **2**, and 185873 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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