Bismuthanides and Bismuthanediides − Synthesis and Structural Characterization of $[R_2Bi]^-$ and $[(RBi)_{12}Na_{21}]^{3-}$ Salts with Bulky Silyl Substituents

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Dedicated to Prof. Dr. Gottfried Huttner on the occasion of his 65th birthday

Keywords: Bismuth / Lithium / Sodium / Silicon / Cluster compounds

The reaction of bismuth trihalides with the bulky alkali metal silanides $[(THF)_3LiSi(SiMe_3)_3]$ and $[(THF)_2NaSi(CMe_3)_3]$ affords the cyclotetrabismuthanes $(RBi)_4$ **1** and **3**, the alkali metal bismuthanides $[Li(THF)_4][Bi\{Si(SiMe_3)_3\}_2]$ (**2**) and $Na(THF)_3[Bi\{Si(CMe_3)_3\}]_2$ (**4**) and the bismuthanediide $Na_3(THF)_{14}[Na_{21}\{BiSi(CMe_3)_3\}_{12}]$ (**5**). Compound **2** features a two-coordinate bismuth atom. The core of **5** is a Bi_{12} icosahedron which is face-capped by 20 sodium atoms. The cluster is filled with a sodium atom. All structures were confirmed by single crystal X-ray crystallography. In addition, the bismuthanides and bismuthanediides were investigated by quantum chemical calculations.

Introduction

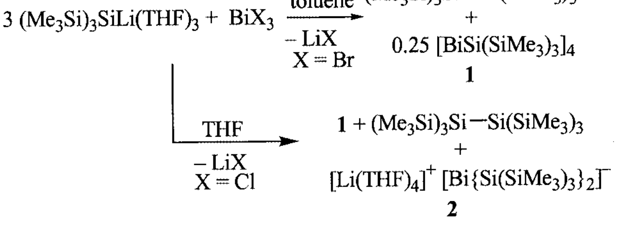
Alkali metal amides, phosphides and arsanides are common reagents, and their structural chemistry, especially that of the heavier homologous, has been explored recently.[1] This interest focused mainly on lithiated species and, consequently, relatively little is known about heavier alkali metal derivatives.[2] The structural chemistry of doubly metalated phosphanes and arsanes M_2PR revealed a high diversity of cluster compounds.[3,4]

Metalated bismuthanes have been known for 60 years, when the synthesis of $MBi(C_6H_5)_2$ (M = Li, Na, K) by reduction of $(C_6H_5)_2BiI$ with alkali metals in liquid ammonia was described.[5] About 40 years later, the first lithium bismuthanide $[(dme)LiBi(SiMe_3)_2]$ was structurally characterized.[6] MER_2 and M_2ER (E = P, As) compounds are normally prepared by metalation of phosphanes and arsanes and the lack of stable hydrogen compounds of bismuth might have caused the low interest in metalated bismuthanes;[7] only very recently was the first stable diarylbismuthane reported.[8] We report here on the reduction of bismuth halides with alkali metal silanides resulting in cyclotetrabismuthanes[9] and bismuthanides and bismuthanediides. The reaction of $SbCl_3$ with $NaSi(CMe_3)_3$ leads to the isolation of the cyclotetrastibane $[(Me_3C)_3SiSb]_4$.[10]

Results and Discussion

Reactions

The reaction of $BiBr_3$ with three equivalents of $[(THF)_3LiSi(SiMe_3)_3]$ in toluene affords the cyclotetrabismuthane **1** in good yields [Equation (1)].[9] If $BiCl_3$ in THF is used instead, **1** forms as the main product of the reaction, too. Initially a green solution is observed during warming of the reaction mixture from −78 °C to ambient temperatures. On stirring at room temperature the color changes to brown. Workup allows isolation of **1** as pentane soluble red crystals. The green component is soluble in THF. The dark green crystals obtained proved to be **2** [Equation (1), nonstoichiometric]. If $NaSi(CMe_3)_3$ dissolved in THF is reacted with $BiBr_3$ [Equation (2), nonstoichiometric] the reaction proceeds similarly to Equation (1).



$$3\,(Me_3Si)_3SiLi(THF)_3 + BiX_3 \xrightarrow[-\,LiX,\ X = Br]{toluene} (Me_3Si)_3Si{-}Si(SiMe_3)_3 + 0.25\,[BiSi(SiMe_3)_3]_4\ \mathbf{1}$$

$$\xrightarrow[-\,LiX,\ X = Cl]{THF} \mathbf{1} + (Me_3Si)_3Si{-}Si(SiMe_3)_3 + [Li(THF)_4]^+\,[Bi\{Si(SiMe_3)_3\}_2]^-\ \mathbf{2} \quad (1)$$

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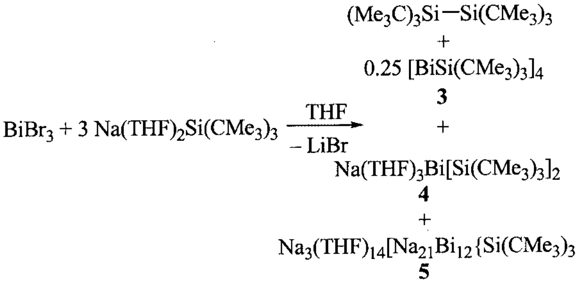
Table 1. Data for the X-ray structure determinations of **2**, **3**, **4** and **5**.

Compound	**2**	**3**·2THF	**4**	**5**
Chemical formula	$C_{34}H_{86}BiLiO_4Si_8$	$C_{48}H_{108}Bi_4Si_4 \cdot 2C_4H_8O$	$C_{36}H_{78}BiNaO_3Si_2$	$C_{200}H_{436}Bi_{12}Na_{24}O_{14}Si_{12}$
Molecular weight	999.7	1777.8	847.1	6462.1
T [K]	190	210	203	210
Crystal system	monoclinic	monoclinic	trigonal	trigonal
Space group	$P2_1/c$	$C2/c$	$P3_1$	$R\bar{3}$
a [pm]	1928.4(2)	2379.0(5)	1252.8(2)	2255.8(3)
b [pm]	1494.2(2)	1328.0(3)	1252.8(2)	2255.8(3)
c [pm]	1882.1(2)	2410.6(5)	2413.3(5)	4893(1)
β [°]	91.053(2)	112.28(3)	–	–
V [nm^3]	422(1)	7.05(1)	3.2809(1)	21.56(1)
Z	4	4	3	3
Density (calcd.) [g cm^{-3}]	1.225	1.676	1.286	1.497
Absorption coefficient [mm^{-1}]	3.457	10.059	4.124	7.445
F(000)	2080	3456	1320	9576
Crystal color	green	red	red	black
Crystal size [mm]	0.3 × 0.24 × 0.12	0.3 × 0.3 × 0.15	0.25 × 0.25 × 0.15	0.35 × 0.35 × 0.3
Scan type	CCD area detection	image plate area detection	ω-scan	image plate area detection
2θ-range [°]	4.0–49.5	3.6–48.0	3.6–50.0	3.6–48.0
Abs. corr.	multi-scan	numerical	-	numerical
Min/max. transm.	0.346/1.00	0.062/0.437	-	0.169/0.249
Refl. collected	9671	26501	2265	18194
Independent reflections	9265	5543	2258	7340
Observed refl. [$I > 2\sigma(I)$]	5765	4233	1811	3477
x (weighting scheme)	0.1035	0.0126	0.120	0.0291
y (weighting scheme)	0.1073	468.3614	5.6147	0
Parameters	454	316	227	508
$R1$ [$F > 4\sigma(F)$]	0.064	0.064	0.072	0.051
wR_2 (all data)	0.189	0.168	0.199	0.117
$R1$ (all data)	0.116	0.082	0.103	0.123
GOOF	1.023	1.239	1.166	0.766
Largest difference peak/hole [e·nm^{-3}]	2540/–2100 (near Bi)	2170/–2080	1220/–1110	1040/–1050



$$\mathrm{BiBr_3 + 3\,Na(THF)_2Si(CMe_3)_3} \xrightarrow[-\,\mathrm{LiBr}]{\mathrm{THF}} \mathrm{(Me_3C)_3Si{-}Si(CMe_3)_3} + \underset{\mathbf{3}}{0.25\,[\mathrm{BiSi(CMe_3)_3}]_4} + \underset{\mathbf{4}}{\mathrm{Na(THF)_3Bi[Si(CMe_3)_3]_2}} + \underset{\mathbf{5}}{\mathrm{Na_3(THF)_{14}[Na_{21}Bi_{12}\{Si(CMe_3)_3\}_{12}]}} \quad (2)$$

The cyclotetrabismuthane **3** is formed predominantly. In addition, the bismuthanide **3** and the bismuthanediide **4** can be isolated. Compound **4** is the first example of a bismetalated bismuthane and a highly aggregated structure is expected as alkali metal phosphanediides and arsanediides form a large variety of cage compounds.[3]

Crystal Structure Analysis

The molecule structure of **3** resembles that of **1**.[9] The tetrabismuthane **3** crystallizes in the monoclinic space group $C2/c$ (Table 1, Figure 1) together with two molecules of THF. No direct intermolecular contacts are observed. The molecule of **3** with a folded Bi_4 core resides on a crystallographic twofold axis (angle between Bi_3 planes: 150°). This folding angle is even flatter than in **1** (angle between Bi_3 planes 138°). $[(Me_3Si)_2CHBi]_4$ [11] with less bulky substituents than **1** and **3** has a more folded Bi_4 core (angle between Bi_3 planes: 113°). The Bi–Bi–Bi bond angles are near 90°, as expected. The Bi–Bi–Si angles are wider, and

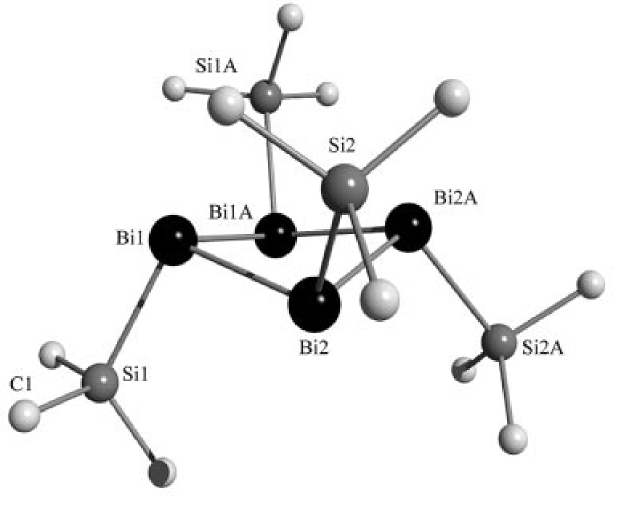


Figure 1. View of a molecule of **3**; disordered methyl groups are omitted from the plot for clarity; selected bond lengths [pm] and angles [°]: Bi(1)–Bi(2) 301.3(1), Bi(1)–Bi(1A) 303.1(2), Bi(2)–Bi(2A) 303.8(2), Bi(1)–Si(1) 275.0(6), Bi(2)–Si(2) 276.5(5); Bi(1)–Bi(2)–Bi(2A) 87.97(2), Bi(2)–Bi(1)–Bi(1A) 88.10(2), Bi(2)–Bi(1)–Si(1) 100.3(1), Bi(1A)–Bi(1)–Si(1) 101.4(1), Bi(1)–Bi(2)–Si(2) 108.9(1), Bi(2A)–Bi(2)–Si(2) 105.8(1)

range from 100° to 109° due to the steric demand of the substituents.

The Bi−Bi distances [($d_{Bi\text{-}Bi}$ = 301.3(1)−303.8(2) pm)] are similar to those in **1**. $[(Me_3Si)_2CHBi]_4$ has more alternating Bi−Bi bonds [$d_{Bi\text{-}Bi}$ = 297.0(5)−304.4(2) pm]. The Bi−Si bond lengths (d_{BiSi} = 275.8 pm on average) are longer than those in **1** by approx. 5 pm. This difference is typical for the substituents under consideration and is observed in other cases, too.[12] This difference in the Bi−Si bond lengths and the increasing flattening of the Bi_4 cores in the known cyclotetrabismuthanes is due to the increased steric demand of the substituents.

Compound **2** crystallizes in the monoclinic space group $P2_1/a$. In this $LiBiR_2$ compound, the ions are separated. The lithium cation is coordinated by four THF molecules in a distorted tetrahedral manner. The BiR_2 anion (Figure 2) has a two-coordinate Bi atom. The shortest nonbonding intramolecular distances (except H) are 390 pm (for Bi−C_{methyl}), and the nearest Bi atom of a neighboring anion is 1100 pm away. The Bi−Si distances [$d_{Bi\text{-}Si}$ = 267 pm on average] are shorter than those in **1** by 4 pm. This is due to the lower coordination number at the Bi atom. The Si−Bi−Si angle (114.4°) is larger than 90°, the usual angle observed in BiR_3 compounds. The wide range for the Si−Si−Si and Si−Si−Bi angles observed makes the distortion of the hypersilyl group obvious.

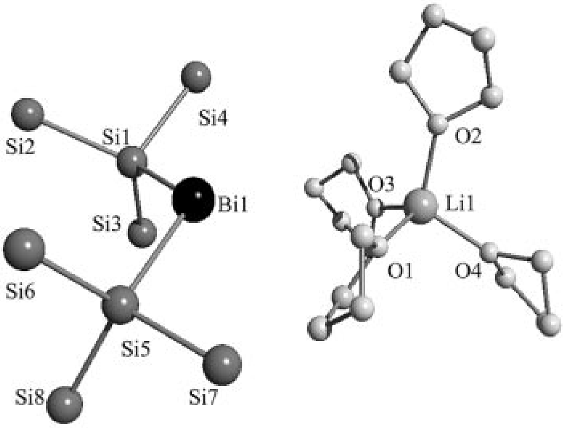


Figure 2. View of a molecule of **2**; disordered methyl groups are omitted from the plot for clarity; selected bond lengths [pm] and angles [°]: Bi(1)−Si(1) 266.8(5), Bi(1)−Si(5) 267.2(4), Si(1,5)−Si 234.2 (aver.); Si(1)−Bi(1)−Si(5) 112.2(1), Si−Si(1,5)−Si 103.1(3)−110.1(3), Bi(1)−Si(1)−Si(4) 123.1(3), Bi(1)−Si(1)−Si(3) 113.1(3), Bi(1)−Si(1)−Si(2) 99.5(2), Bi(1)−Si(5)−Si(6) 115.2(2), Bi(1)−Si(5)−Si(7) 120.6(2), Bi(1)−Si(5)−Si(8) 92.8(2)

For $[Bi(SiH_3)_2]^-$ an Si−Bi−Si angle of 93.4° is calculated by MP2 calculations.[13] This angle is nearly unaffected by the coordination of a lithium or sodium atom to the bismuth atom (see Table 2, Figure 3).[13] $[(dme)LiBi(SiMe_3)_3]$[6] is the only structurally characterized lithium bismuthanide so far. In this polymeric structure the Bi atom is tetracoordinated by two Si and two Li atoms, with an Si−Bi−Si angle of 91.8(4)°.

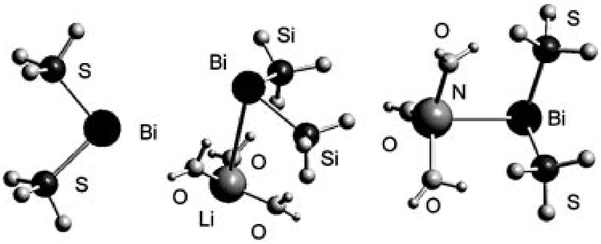


Figure 3. Calculated structures of $[(H_3Si)_2Bi]^-$ and $[(H_3Si)_2Bi\text{-}M(OH_2)_3]$ (M = Li, Na)

Compound **4** crystallizes in the trigonal space group $P3_1$ with Z = 3. Here, unlike **2**, a separated ion pair is not present. The alkali metal ion is coordinated by three THF molecules and the fourth coordination site is occupied by the Bi atom of the $BiSi_2$ unit. Thus, the Bi atom in **4** (Figure 4) is three-coordinated by two Si atoms (d_{BiSi} = 271.7 pm on average) and a sodium atom [$d_{Bi\text{-}Na}$ = 311(1) pm]. Similar to the differences in **1** and **2**, the Bi−Si distances in **4** are

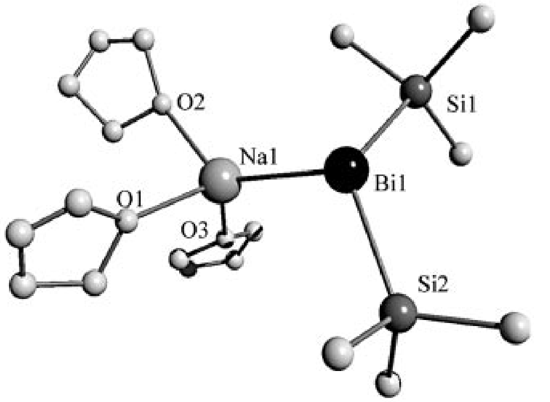


Figure 4. View of a molecule of **4**; disordered methyl groups are omitted from the plot for clarity; selected bond lengths [pm] and angles [°]: Bi(1)−Si(1) 272.6(10), Bi(1)−Si(2) 270.7(8), Bi(1)−Na(1) 311(1); Si(1)−Bi(1)−Si(2) 122.3(2), Na(1)−Bi(1)−Si(1) 113.7(4), Na(1)−Bi(1)−Si(2) 98.6(3)

Table 2. Results of MP2 calculations on bismuthanides

	d(Bi-Si) [pm]	*d*(Bi−M) [pm]	Si−Bi−Si [°]	M−Bi−Si [°]	M−Bi/Si−Bi−Si [°]
$[(H_3Si)_2Bi]^-$	267.8	–	93.4	–	
$(H_3Si)_2BiLi(OH_2)_3$	267.1	308.2	92.7	81.0, 88.4	85
$(H_3Si)_2BiNa(OH_2)_3$	267.4	367.3	92.7	74.9, 85.0	80
for comparison: crystal structure of $(Me_3Si)_2BiLi(dme)$[6] (c.n. Bi and Li = 4)	263 (1)	292(3)	91.8	96(1), 106(1)	

shorter than those in **3** by 4 pm. The Si−Bi−Si angle is even wider (122.3°) than that in **2**. Here, the higher steric demand of the $Si(CMe_3)_3$ group compared to the $Si(SiMe_3)_3$ group becomes obvious again. The line Bi(1)−Na(1) is not orthogonal to the Si_2Bi plane, as might be expected, and as proposed by the quantum chemical calculations (Table 2). The angle of the line Bi(1)−Na(1) to the Si_2Bi plane is 143.8°, which means that the Bi atom is only 82 pm above the Si_2Na plane.

Compound **5** crystallizes in the trigonal space group $R\bar{3}$ with $Z = 3$, and is the sodium salt of an RBi^{2-} ion, which means that a highly aggregated structure can be expected. In fact, **5** forms an RBi dodecamer (Figure 5a) in which 12 bismuth atoms and 20 sodium atoms form a ball-like cage. Of the remaining four sodium atoms two show up as $[Na(THF)_4]^+$ and one as $[Na(THF)_6]^+$. In the structural model applied, the fourth is in a disordered position in the center of the $Bi_{12}Na_{20}$ cage. The disordered sodium atom takes the positions of an internal icosahedron.

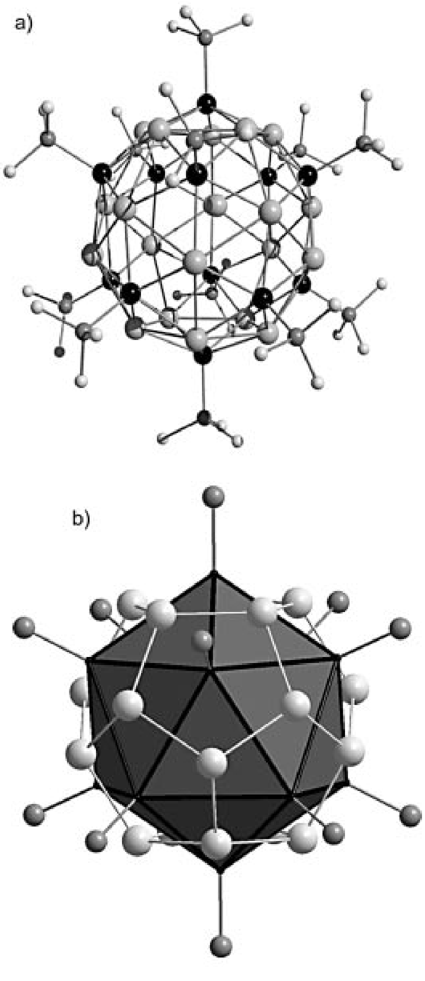


Figure 5. View of the cluster anion of **5**: a) showing only one position of the disordered central sodium atom (methyl groups are omitted for clarity); b) polyhedral representation of the Bi_{12} icosahedron with capping sodium atoms in pentagon dodecahedral arrangement; only the silicon atoms are shown for the $Si(CMe_3)_3$ substituents; selected bond lengths [pm] and angles [°] Bi(1)−Si(1) 263.0(4), Bi(2)−Si(2) 264.4(4), Bi−Na 317.2(6)−324.4(6); Si(1)−Bi(1)−Na 106.8(1)−113.5(1)

In the cage, 12 Bi atoms form an icosahedron (d_{BiBi} = 527−536 pm), whose faces are capped by 20 sodium atoms (Figure 5b). These sodium atoms themselves form a pentagonal dodecahedron ($d_{Na\text{-}Na}$ = 351−363 pm). All Bi atoms are bonded to the central silicon atom of a $Si(CMe_3)_3$ substituent (d_{BiSi} = 263.7 pm on average), which is severely disordered, as usual. The Bi−Si bond is even shorter than in **3** and **4**, which is expected in the series $R{-}BiX_2$, R_2Bi^- and RBi^{2-}. The $(RBi)_{12}Na_{20}$ cage is unique in the chemistry of bismuth, although $(R'P)_{12}Li_{20}$ and $(R'As)_{12}R_{20}$ (R = Li, Na) clusters with an analogous arrangement of the pnicogen and alkali metal atoms as in **5** are known.[3] These clusters are filled, too. In most cases M_nO (n = 2,6) units are present in the center of the cages. RI-DFT calculations[14] were performed on an empty $[(HBi)_{12}Na_{20}]^{4-}$ shell (Figure 6a). The resulting structure was quite similar to the observed structure of **5**. If a sodium cation is placed in the center of this $[(HBi)_{12}Na_{20}]^{4-}$ shell, the final position for this cation is out of the center of the shell and in a position similar to that of one position for the disordered encapsulated sodium atom. Adding this additional positive charge inside the cage results in a shrinking of the cage. This means the diameter of the $Bi_{12}Na_{20}$ shell decreases from 1044 pm to 1020 pm (Figure 6b). The Bi−Na interactions in **5**, as well as the Bi-(Li, Na) contacts in **2** and **4**, are mostly ionic, as is revealed by Aldrich−Heinzmann population analyses.[15] This is expressed in the shared electron numbers, which are as low as 0.22 to 0.29 for the Bi−Na interactions.

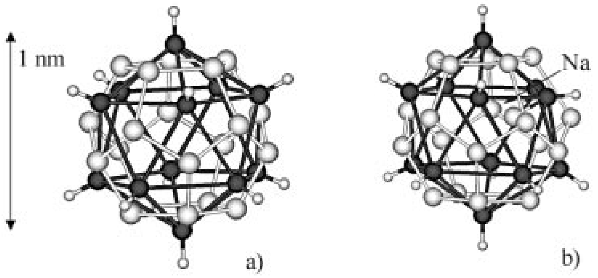


Figure 6. View of a) $[(HBi)_{12}Na_{20}]^{4-}$ and b) $[(HBi)_{12}Na_{21}]^{3-}$ as derived from RI-DFT calculations; average selected bond lengths [pm] a) Bi−Na 330.7, Bi−H 184.5, Bi···Bi 548.0, Na···Na 364.0; b) Bi−Na 328.6, Bi−H 184.0, Bi···Bi 545.0, Na···Na 361.6

Conclusion

The reaction of bismuth halides with bulky silanides has proved to be a valuable entry to the chemistry of bismuth ring compounds as well as for the synthesis of anionic bismuthanides R_2Bi^- and RBi^{2-}. In particular, the latter opens a novel field for bismuth. Whether these compounds are useful for synthetic applications will depend on their improved availability.

Experimental Section

General: All experiments were performed under purified nitrogen or in vacuo with Schlenk techniques. All yields are referenced to

BiX_3. Chemical analysis for **3** gave unreliable results, due to the partial loss of THF from the crystals, and for the ionic species **2**, **4** and **5** due to their sensitivity. NMR: Bruker ACP 250; Mass spectra: Varian MAT 711; X-ray crystallography: Suitable crystals were mounted with a perfluorinated polyether oil on the tip of a glass fiber and cooled immediately on the goniometer head. Data collections were performed with Mo-K_α radiation on a Bruker AXS (**2**), STOE IPDS (**3**, **5**) or a STOE STADI4 diffractometer (**4**). Absorption correction was performed numerically with XRED (STOE) for **3**,**5** and empirically using equivalent reflections for **2**. Structures were solved and refined with the Bruker AXS SHELXTL 5.1 program package. Refinement in full-matrix against F^2. All hydrogen atoms were included as a riding model with fixed isotropic U values in the final refinement. For further data see Table 1. The structures of **4** and **5** are influenced by disorder of the CMe_3 groups. In part, we attempted to describe this by a split model. The crystal structure of **4** was refined as a merohedral twin (BASF 0.49, Flack parameter −0.03). The low parameter/data ratio and the lack of an absorption correction due to decomposition of the crystal together with the severe disorder of the silyl groups allows no detailed discussion of the structure.

CCDC-174922 (**2**), -174923 (**3**) -174924 (**4**) and -174925 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Compounds 1 and 2: A solution of [$(THF)_3LiSi(SiMe_3)_3$][16−18] (2.58 g, 5.49 mmol) in 20 mL THF was added dropwise to a stirred solution of $BiCl_3$ (0.58 g, 1.84 mmol) in 20 mL THF at −78 °C within 10 min. The dark-colored mixture was stirred for an additional 10 min at low temperature and was then quickly warmed to ambient temperature. After stirring for 1 h the dark green solution was stripped down. The residue was extracted with 50 mL of pentane in several portions. After filtration an orange-red solution was obtained, from which **1** was isolated as tiny red crystals by cooling to −20 °C. The solid, dark colored residue after the pentane extraction was treated with 15 mL of THF. After filtration a dark green solution of **2** (pure by NMR spectroscopy) was obtained. Upon cooling to −20 °C, green crystals of **2** formed; yield: 0.92 g (51%; with reference to Bi).

1:[9] ^1H NMR (250 MHz, C_6D_6): $\delta = 0.49$ ppm. ^{13}C NMR: $\delta = 5.6$ ppm. ^{29}Si NMR: $\delta = -124$ (Si) −2.2 ($SiMe_3$).

2: ^1H NMR (250 MHz, C_6D_6): $\delta = 0.64$ (s, 54 H, $SiMe_3$), 1.66 (m, 16 H, CH_2), 3.40 (m, 16 H, OCH_2) ppm. ^{13}C NMR: $\delta = 5.9$ ($SiMe_3$), 26.0 (CH_2), 68.9 (OCH_2), ppm. ^{29}Si NMR: $\delta = -110$ (Si) −8.6 ($SiMe_3$) (approx. 6% **1** as impurity, as indicated by ^1H NMR integration).

Compounds 3, **4 and 5:** [$NaSi(CMe_3)_3$] (6.80 mmol),[10] dissolved in 10 mL THF, was added dropwise with a syringe into a stirred solution of $BiBr_3$ (1.02 g, 2.27 mmol) in 40 mL of THF at −78 °C. The dark-colored solution was stirred for an additional 30 min at −78 °C. The THF was removed in vacuo before ambient temperature was reached. The residue was extracted with 50 mL of pentane and 20 mL of THF. The pentane solution was reduced to a volume of 10 mL. Upon cooling to −20 °C red crystals of **3** were isolated [yield: 0.30 g (32%)]. From the THF solution dark-red crystals of **4** were isolated, which were accompanied by traces of **3** and several nearly dark black crystals of **5**. Attempts to purify **4** by recrystallization resulted in decomposition of **4** to **3**.

3: ^1H NMR (250 MHz; C_6D_6): $\delta = 1.15$ ppm. ^{13}C NMR: $\delta = 30.9$ ppm. MS (EI, 70 eV): *m*/*z* (%) = 816 (5) [$Bi_2\{Si(CMe_3)_3\}_2$]$^{+\cdot}$, 607 (4) [$Bi\{Si(CMe_3)_3\}_2$]$^+$, 550 (2) [$Bi\{Si(CMe_3)_3\}\{Si(CMe_3)_2\}$]$^{+\cdot}$, 408 (5) [$BiSi(CMe_3)_3$]$^{+\cdot}$, 57 (100) [$C(CMe_3)_3$]$^+$.

4: $C_{36}H_{78}BiNaO_3Si_2$ (847.2): calcd. C 51.04, H 9.28; found C 56.53, H 11.30. ^1H NMR (250 MHz; C_6D_6): $\delta = 1.41$ (m, 12 H, CH_2), 1.49 (s, 54 H, CMe_3), 3.56 (m, 12 H, OCH_2) ppm. ^{13}C NMR: $\delta =$ 25.8 (CH_2), 34.6 (CMe_3), 67.9 (OCH_2).

5: $C_{200}H_{436}Bi_{12}Na_{24}O_{14}Si_{12}$ (6462.2): calcd. C 37.17, H 6.80; found C 36.96, H 7.94.

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