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Monomeric and Dimeric Tetrahydrofuran Complexes of Barium Bis[bis(dimethyl-*tert*-butylsilyl)arsanide][†]

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The metathesis reaction of (dme)$LiAsH_2$ with $ClSiMe_2{}^tBu$ allows the isolation of bis(dimethyl-*tert*-butylsilyl)arsane **1** in a rather poor yield. The inversion barrier of 64 kJ·mol^{-1} for **1** can be deduced from dynamic ^{1}H and ^{13}C{^{1}H} NMR experiments. The metalation of **1** by bis(tetrahydrofuran)barium bis[bis(trimethylsilyl)amide] in tetrahydrofuran leads to the formation of tetrakis(tetrahydrofuran)barium bis[bis(dimethyl-*tert*-butylsilyl)arsanide] **2**. The coordination sphere of the metal center is best described as a pentagonal bipyramid with the arsanide ligands in apical positions; however, one equatorial position remains unoccupied due to the steric shielding by the demanding trialkylsilyl groups. Recrystallization of **1** from toluene leads to the loss of tetrahydrofuran coligands and the formation of dimeric (tetrahydrofuran)barium bis[bis(dimethyl-*tert*-butylsilyl)arsanide] **3**. The barium atom shows the small coordination number of 4, and therefore, extremely short terminal Ba−As bonds of 319 pm are observed. Crystallographic data: **2**, monoclinic, $C2/c$, $a = 1981.8(7)$ pm, $b = 1137.4(3)$ pm, $c = 2445.9(7)$ pm, $\beta = 93.71(4)°$, $Z = 4$, wR2 = 0.1193; **3**, monoclinic, $P2_1/c$, $a = 3077.91(1)$ pm, $b = 1165.53(1)$ pm, $c = 2611.67(1)$ pm, $\beta = 93.58(1)°$, $Z = 4$, wR2 = 0.1358.

Introduction

The alkaline earth metal chemistry experiences a vastly growing interest due to unexpected structures as for example the bent monomeric halogenides,[1] hydroxides,[2] and amides[2] and the dimeric hydrides[3] of the type X−M(μ-X)$_3$M as predicted by ab initio SCF calculations. Furthermore, the easy access of appropriate synthons, the alkaline earth metal bis[bis(trimethylsilyl)amides],[4] started a fruitful preparative chemistry of molecular alkaline earth metal compounds. During the past few years numerous novel derivatives have been characterized by X-ray structure determinations such as complexes with Ca−C[5,6] and Ca−Sn σ bonds[7] as well as alkaline earth metal thiolates[8,9] (sulfanides), selenolates[9] (selanides), and tellurolates[10] (tellanides). Compounds with bonds between the alkaline earth metals and the heavier pentele[11] atoms attract increasing attention due to monomer−dimer equilibria in aromatic hydrocarbons and unique structures in the crystalline state. Trialkylsilyl-substituted alkaline earth metal bis(phosphanides) with small alkyl groups contain a trigonal M_2P_3 bipyramid with the metal atoms in apical positions.[12,13] The enhancement of the bulkiness of the trialkylsilyl substituents leads to the formation of monocyclic derivatives of the type $R_2P{-}M(L)_n[\mu\text{-}PR_2]_2M{-}(L)_n{-}PR_2$ with neutral coligands L such as tetrahydrofuran or 1,2-dimethoxyethane.[14] In toluene solution not only is the monomer−dimer equilibrium observed, but also the intramolecular phosphanide ligand exchange between the terminal and bridging sites.

Far less attention has been given to the homologous arsanides. The tetrahydrofuran complexes of magnesium,[15] calcium, and strontium bis[bis(trimethylsilyl)arsanide][16] are published; how-

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[†] Dedicated to Professor Heinrich Nöth on the occasion of his 70th Birthday.

[‡] X-ray structure analysis.

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(11) The expression “pentele” is recommended by the IUPAC for the group 15 elements (nitrogen group) due to the misleading meaning of the word “pnicogen” (which comes from the Greek “πνικτός”, best translated as “suffocate”); see: IUPAC. *Nomenklatur der anorganischen Chemie*; VCH Verlagsgesellschaft: Weinheim, 1994; p 52.

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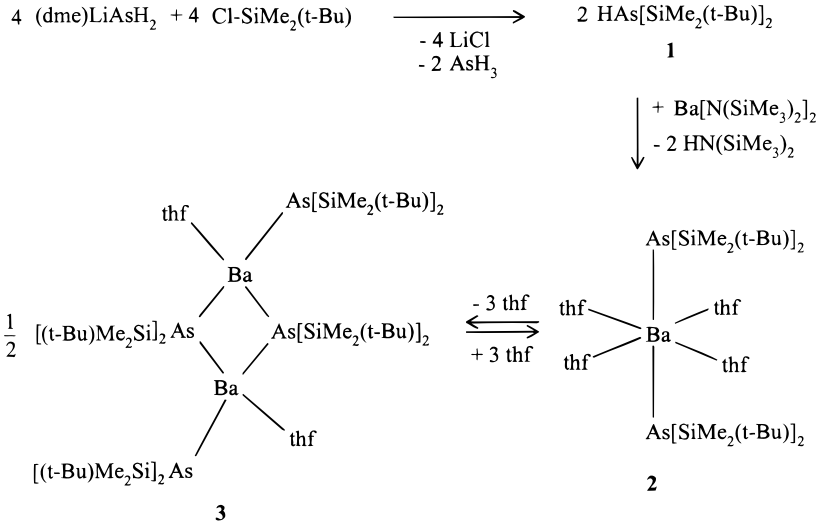
Scheme 1



ever, no barium bis(arsanide) is described thus far. Here we report the synthesis and solid-state structures of monomeric and dimeric, monocyclic tetrahydrofuran adducts of barium bis[bis(dimethyl-*tert*-butylsilyl)arsanide] as well as the dynamic behavior of bis(dimethyl-*tert*-butylsilyl)arsane.

Results and Discussion

Preparation. (1,2-Dimethoxyethane-*O,O′*)lithium arsanide (dme)$LiAsH_2$[17] proved to be a suitable synthon for the preparation of bis(trialkylsilyl)arsanes. The metathesis reaction with chlorodimethyl-*tert*-butylsilane allows the isolation of bis(dimethyl-*tert*-butyl)arsane **1** in a rather poor yield according to Scheme 1. The metalation of **1** with bis(tetrahydrofuran)barium bis[bis(trimethylsilyl)amide] yields quantitatively colorless tetrakis(tetrahydrofuran)barium bis[bis(dimethylsilyl-*tert*-butylsilyl)arsanide] **2**. Recrystallization from concentrated toluene solutions leads to the loss of neutral coligands and to the formation of dimeric monocyclic bis(tetrahydrofuran)barium bis[bis(dimethylsilyl-*tert*-butylsilyl)arsanide] **3**. Scheme 1 shows the monomer−dimer equilibrium; however, the NMR parameters of both the compounds **1** and **2** show only small differences and the prove of the coexistence of monomers and dimers in toluene solution is not unequivocally possible by ^{1}H, ^{13}C, or ^{29}Si NMR spectroscopy.

Molecular Structure of 2. The molecular structure of the C_2 symmetric molecule and the numbering scheme of **2** are shown in Figure 1. The barium atom is coordinated distorted pentagonal bipyramidically with a vacant coordination site in the equatorial plane. As a consequence the Ba−As bonds are tilted toward the coordination gap, and the As−Ba−As′ moiety is bent with an angle of 140.8°. The Ba−O distances of approximately 276 pm are in the range of the values observed for the barium bis(amides) $(thf)_2Ba[N(SiMe_3)_2]_2$[18] and the dimer $\{(thf)Ba[N(SiMe_3)_2]_2\}_2$[18] (273 and 277 pm, respectively) as well as the barium bis(phosphanides) $(thf)_4Ba[P(SiMe_3)_2]_2$[19] and $(thf)_4Ba[P(SiMe_2{}^{i}Pr)_2]_2$[14] (272 and 275 pm, respectively), whereas slightly longer Ba−O bonds are realized for $(dme)_3Ba[P(SiMe_2CH_2)_2]_2$[13] (283 pm) with an 8-fold coordinated metal center. The higher coordination number of the last-mentioned barium bis(phosphanide) affects more clearly the Ba−P bond lengths, which amount 333 pm, whereas the other phosphanides with a 6-fold coordinated metal center display Ba−P values of approximately 319 pm. The Ba−As bond length of 330 pm is even shorter than the barium pentele distance in the highly coordinated barium bis(phosphanide).

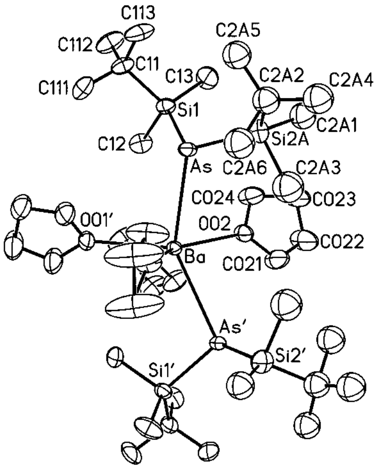


Figure 1. Molecular structure and numbering scheme of **2**. The ellipsoids represent a 50% probability. The hydrogen atoms are omitted for clarity. The atoms of the symmetry-related half of the molecule are marked with an apostrophe. The disordering within the arsanide ligand is not shown.

One of the dimethyl-*tert*-butylsilyl groups is disordered on two sites (Si2a and Si2b) with a population ratio of 0.483(9): 0.517(9). This overlying of one of the trialkylsilyl substituents leads to different angle sums of the arsenic atom of 331.1 and 350.5° for the fragments Ba/As/Si1/Si2a and Ba/As/Si1/Si2b, respectively. In both of these cases, the bis(trialkylsilyl)arsanide anion fills the same space (Figure 2). This observation clearly shows that the intramolecular steric and electrostatic arguments dominate the structure of this highly ionic molecule, thus allowing a wide tolerance for the angle sum due to easily possible tilt movements.

Intermolecular interaction is limited on van der Waals forces. Due to the shielding of the coordination gap the barium atoms of **2** show no close contacts to neighboring molecules. There-

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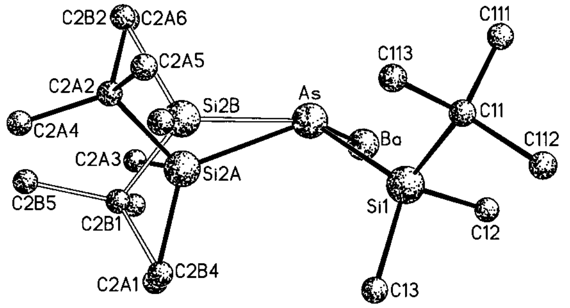

Figure 2. Representation of the disordering of one of the dimethyl-*tert*-butylsilyl substituents of **2**. The atoms are drawn with arbitrary radii, and the hydrogen atoms are omitted for clarity.

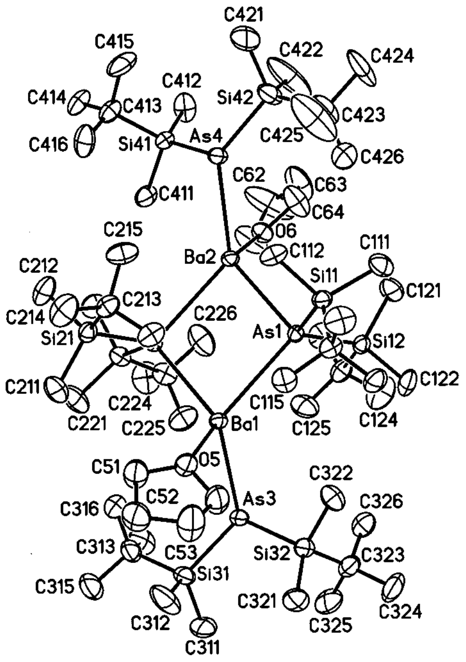

Figure 3. Molecular structure and numbering scheme of dimeric **3**. The ellipsoids represent a 50% probability. The hydrogen atoms are omitted for clarity.

fore, the crystal structure is best described as a hexagonal closest packing of molecules distorted due to the ellipsoid shape of the molecules.

Molecular Structure of 3. The molecular structure of **3** is displayed in Figure 3. The barium atoms Ba1 and Ba2 are coordinated distorted tetrahedrally by two bridging and one terminal arsanide substituent as well as one tetrahydrofuran molecule. The distortion results from the small endocyclic As1−Ba−As2 angles of approximately 81°, which leads to a widening of the exocyclic As−Ba−As angles up to 124.3°. In Table 1 selected structural parameters are listed. Due to the rather small coordination number of four of the metal centers, the Ba−O distances are slightly shortened.

The structural parameters of compound **3** are surprisingly similar to the corresponding values of the dimer $\{(thf)_2Ba[P(SiMe_2{}^iPr)_2]_2\}_2$[14] with Ba−P bond lengths to the terminal and bridging bis(dimethylisopropylsilyl)phosphanide ligands of 316 and 332 pm, respectively; however, the coordination number of the barium atoms in the phosphanide is raised to 5. Similar Li−E bond lengths are also observed for $[(dme)LiE(SiMe_3)_2]_2$ with E as P[20] (256 pm) and As[21] (259 pm) with quadruply coordinated lithium and pentele atoms even though the larger van der Waals radius influences the E−Si distances (for E = P, 221 pm;[20] for E = As, 231 pm[21]).

Table 1. Selected Bond Lengths (pm) and Angles (deg) of Dimeric (Tetrahydrofuran)barium Bis[bis(dimethyl-*tert*-butylsilyl)arsanide] **3**

n	1	2	3	4
Ba1−As(n)	332.83(7)	332.36(7)	318.90(7)	
Ba2−As(n)	330.27(6)	333.58(7)		318.88(7)
As(n)−Si(n1)	233.0(2)	232.5(2)	230.4(2)	231.0(2)
As(n)−Si(n2)	232.6(2)	232.3(2)	231.1(2)	231.8(2)
Ba(n)−O5/O6	273.9(4)	269.1(4)		
As1−Ba1−As(n)		80.92(2)	121.06(2)	
As1−Ba2−As(n)		81.11(2)		118.63(2)
As2−Ba1−As(n)			121.31(2)	
As2−Ba2−As(n)				124.33(2)
Si(n1)−As(n)−Si(n2)	106.03(7)	100.78(7)	105.29(7)	105.59(8)
Ba1−As(n)−Si(n1)	114.64(5)	104.22(5)	118.80(6)	
Ba1−As(n)−Si(n2)	119.70(5)	124.09(5)	104.34(5)	
Ba2−As(n)−Si(n1)	108.24(5)	118.33(5)		92.54(5)
Ba2−As(n)−Si(n2)	108.21(5)	111.80(5)		129.73(8)
O5−Ba1−As(n)	125.1(1)	119.7(1)	92.3(1)	
O6−Ba2−As(n)	115.8(1)	124.0(1)		95.1(1)

Table 2. Chemical ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ Shifts of Bis(dimethyl-*tert*-butylsilyl)arsane **1** as Well as the Monomeric and Dimeric Barium Bis(arsanides) **2** and **3**

compound	**1**	**2**	**3**
solvent	benzene-d_6	thf-d_8	toluene-d_8
	^1H NMR		
δ(SiMe)	0.21, 0.31	0.17	0.51
δ(^{t}Bu)	0.99	0.90	1.18
δ(AsH)	−0.19	−	−
	$^{13}C\{^1H\}$ NMR		
δ(SiMe)	−1.85, 0.74	3.65	3.39
δ(CMe_3)	18.58	19.87	26.35
δ(CMe_3)	26.68	26.79	28.15
	$^{29}Si\{^1H\}$ NMR		
δ(Si)	16.08	20.12	16.19

The As−Si bond lengths show a small dependency from the coordination number of the arsenic atom whether the arsanide ligand is bridging (mean value 232.6 pm) or terminally bonded (231.1 pm). These values lie in the expected range for arsanides,[15,16,21] whereas the As−Si bond lengths of dimeric bis[bis(trimethylsilyl)arsanyl]stannylene[22] and the arsanes such as $(Me_3Si)_2As-As(SiMe_3)_2$[23] amount to approximately 236 pm.

Another point of interest is the angle sum at the pentele atom of the terminally bonded arsanide ligand. For the alkaline earth metal bis[bis(trimethylsilyl)arsanides] these values vary strongly between 309° and a planar coordination sphere of the As-atom. The atoms As3 and As4 display with angle sums of approximately 328° pyramidal coordination spheres. The differences observed for the distal and proximal endocyclic As(*n*)−Ba1−As3 and As(*n*)−Ba2−As4 angles are a consequence of steric intramolecular repulsion between the bulky arsanide substituents and the coordinated tetrahydrofuran molecules.

Spectroscopic Data. Table 2 summarizes the NMR data of arsane **1** as well as of compounds **2** and **3**. The trialkylsilyl groups of the bridging and terminal arsanide ligands of **3** are not distinguishable by NMR spectroscopy. A similar observa-

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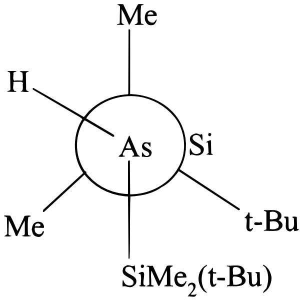

Figure 4. Newman projection along the As−Si bond in **1**. The nonequivalence of the two silicon-bonded methyl groups is clearly shown.

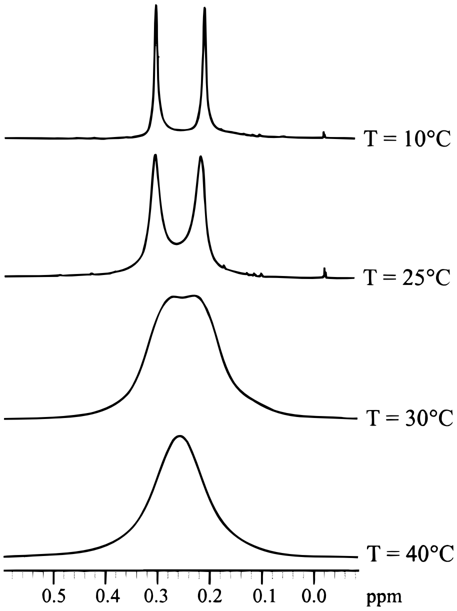

Figure 5. Dynamic ^1H NMR studies of the silicon-bonded methyl groups of bis(dimethyl-*tert*-butylsilyl)arsane **1** (see text). Experimental data: solvent benzene-d_6, 399.785 MHz.

tion was made for the bis(trimethylsilyl)amide ligands of the dimeric barium bis[bis(trimethylsilyl)amides]. Due to the high ionicity of these compounds only small effects if any are to be expected on the NMR experiments. Special attention has to be drawn to the arsane **1**. Provided that the arsenic atom is surrounded trigonal pyramidically, the two methyl groups bonded to the silicon atom are diastereotopic and magnetically inequivalent. This is best demonstrated by a Newman projection along the As−Si bond (Figure 4). This fact enables us to calculate the inversion barrier of **1**. The inversion of amines, phosphanes, and arsanes has been a point of interest for more than thirty years.[25] Figure 5 shows the temperature dependency of the ^1H resonances of the silicon bonded methyl groups. On the basis of the Gutowsky−Holm equation,[26] an inversion barrier of 64 $kJ\cdot mol^{-1}$ is deduced. A verification succeeded by the interpretation of the dynamic $^{13}C\{^1H\}$ NMR spectra. This value is very small considering the inversion barriers of ammonia (24.5 $kJ\cdot mol^{-1}$), trimethylamine (31.4 $kJ\cdot mol^{-1}$), and of phosphane PH_3 (155 $kJ\cdot mol^{-1}$).[27] On the other hand silyl substituents lower the inversion barrier and lead to increased SiESi bond angles. Trisilylamine is planar,[28] whereas trisilylphosphane and -arsane display Si−E−Si-bond angles of 96.8[29] and 94.1°,[29] respectively. Due to the bulky trialkylsilyl groups, further reduction of the energy barrier and enlargement of the Si−E−Si angles is realized as can be seen from the comparison of $P(SiH_3)_3$[29] and $P(SiMe_3)_3$ (105.2° [30]).

Conclusion

The tetrahydrofuran complexes of the barium bis[bis(dimethyl-*tert*-butylsilyl)arsanides] are mainly ionic compounds. Electrostatic interactions (anion−cation attraction, anion−anion repulsion) as well as steric interligand repulsion dominate the structural parameters such as the bond lengths and the angle sums of the arsenic atoms. Furthermore, the electrostatic nature levels out the chemical shifts as well as the coupling constants of the terminal and bridging arsanide substituents of the monomeric and dimeric barium bis(arsanides).

Experimental Section

All experiments and manipulations were carried out under argon purified by passage through BTS catalyst and P_4O_{10}. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The starting materials (1,2-dimethoxyethane-*O,O′*)lithium arsanide[17] and barium bis[bis(trimethylsilyl)amide][18,24,31] were prepared by literature procedures. NMR spectra were recorded on the Bruker spectrometers AM200, AC250, and AM400 or JEOL spectrometers GSX270 and EX400. A Perkin-Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra; solid substances were measured in Nujol between CsBr windows (vs, very strong; s, strong; m, medium strong; w, weak; vw, very weak; sh, shoulder). The frequencies in the region of the Nujol vibrations are not listed.

Caution: *Arsenic compounds are extremely toxic and may be absorbed by inhalation and through the skin. During the synthesis of **1**, arsane AsH_3 is formed.*

Synthesis of Bis(dimethyl-*tert*-butylsilyl)arsane, 1. At −10 °C a solution of 15.1 g of $ClSiMe_2{}^tBu$ (100 mmol) in 40 mL of 1,2-dimethoxyethane was dropped slowly to 200 mL of a 0.5 M 1,2-dimethoxyethane solution of $(dme)LiAsH_2$. After complete addition, the reaction mixture was stirred at room temperature for 48 h before all volatile materials such as solvents and $H_2AsSiMe_2{}^tBu$ were removed in a vacuum. The residue was dissolved in 80 mL *n*-pentane and filtered to separate the precipitated LiCl. The distillation in a vacuum yields, at 65 °C/5 × 10^{-2} Torr, 3.58 g of $HAs(SiMe_2{}^tBu)_2$, **1** (11.7 mmol; 23%) as a colorless liquid, which solidified slowly at room temperature. Mp: 36−38 °C. NMR data are summarized in Table 2. MS (70 eV, sample temperature 300 K): 306 (3, M), 249 (2, $HAsSi_2Me_4{}^tBu$), 115 (15, $SiMe_2{}^tBu$), 75 (100, As), 73 (68, $SiMe_3$), 59 (10). IR (CsBr): 2950 s, 2926 s, 2894 m, 2882 m, 2854 m, 2709 vw, 2083 m (νAsH), 1464 vs, 1415 m, 1387 w, 1361 s, 1256 s, 1244 s, 1006 m, 937 w, 836 vs, 819 m, 799 m, 767 s, 688 m, 672 s, 630 w, 573 w, 531 w, 405 w, 375 w, 337 w, 284 vw, 261 w. RE (single crystal): 2964 sh, 2952 s, 2926 s, 2894 vs, 2881 sh, 2855 s, 2767 vw, 2708 sh, 2703 w, 2081 vs (νAsH), 1258 sh, 1247 w, 1203 m, 1182 m, 1004 w, 938 m, 835 sh, 817 m, 770 w, 689 m ($\nu_{as}SiC_2$), 672 s ($\nu SiC'$), 577 vs (ν_sSiC_2), 529 w, 410 s, 393 w, 338 m (ν_sAsSi_2), 301 vw, 266 sh, 233 w, 202 s (δ_sSiC_2C'),

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168 w, 148 sh, 120 w. Anal. Found (calcd for $AsSi_2C_{12}H_{31}$, 306.47 g·mol^{-1}): C, 46.79 (47.03); H, 9.98 (10.20)

Synthesis of Tetrakis(tetrahydrofuran)barium Bis[bis(dimethyl-*tert*-butylsilyl)arsanide], 2. A 3.08 g amount of **1** (10.0 mmol) dissolved in 5 mL of tetrahydrofuran was dropped at −60 °C to a solution of 3.03 g of bis(tetrahydrofuran)barium bis[bis(trimethylsilyl)-amide] (5.02 mmol) in 25 mL of tetrahydrofuran. After warming to room temperature and stirring for additional 12 h, the solution was concentrated to a few milliliters. At −30 °C 3.5 g of crystalline **2** (3.53 mmol, 70%) precipitated. Mp: 76−80 °C (dec). NMR data are listed in Table 2. IR (Nujol, CsBr): 1401 w, 1354 m, 1293 w, 1240 s, 1228 s, 1184 w, 1073 w, 1038 vs, 1005 s, 936 m, 910 sh, 879 s, 818 vs, 789 vs, 741 s, 669 s, 650 vs, 570 s, 413 vs, 384 s, 379 s, 332 w. Anal. Found (calcd for $C_{40}H_{92}As_2BaO_4Si_4$, 1036.68 g·mol^{-1}): C, 43.78 (46.34); H, 8.82 (8.95).

Synthesis of Dimeric (Tetrahydrofuran)barium Bis[bis(dimethyl-*tert*-butylsilyl)arsanide], 3. A 1.1 g amount of **2** (0.98 mmol) was dissolved in 2 mL of toluene. The solution is filtered if any solid material is present. After removal of the volatile amount of tetrahydrofuran and concentration to an oil the toluene solution is slowly cooled from +50 to +7 °C. Slightly reddish crystals of **3** precipitate nearly quantitatively. Mp: 89−90 °C (dec). NMR data are summarized in Table 2. IR (Nujol, CsBr): 1403 m, 1360 m, 1294 vw, 1245 vs, 1201 w, 1183 w, 1073 vw, 1037 s, 1005 s, 935 s, 876 m, 670 s, 658 s, 571 s, 526 vw, 408 s, 375 s, 334 vw, 302 vw. Anal. Found (calcd for $Ba_2As_4Si_8C_{56}H_{136}O_2$, 1640.65 g·mol^{-1}): C, 39.77 (40.99); H, 7.86 (8.36).

X-ray Structure Analysis. Suitable single crystals of the derivatives **2** and **3** were covered with Nujol and sealed in thin-walled capillaries. The crystal structure analysis of **2** was performed on the diffractometer Siemens P4; three standard reflections were measured periodically as a check of crystal and instrument stability and showed no decay. The data of **3** were collected on a Siemens P4 equipped with a SMART area detector. Graphite-monochromated Mo Kα radiation was used in both cases. For the two compounds a semiempirical absorption correction (ψ scan) was applied. The crystallographic data as well as details of the structure solution and refinement procedures are summarized in Table 3.

The crystal structures were solved by direct methods with the program SHELXTL Plus.[34] The refinement of the structures succeeded with the program packages SHELXL-93[33] and SHELXTL PC, version 5.03,[34] where the function $\sum[w(F_o^2 - F_c^2)^2]$ was minimized. The displacement parameters of all non-hydrogen atoms were treated anisotropically. For all calculations the atom form factors of the neutral atoms Ba, As, Si, O, and C[35] as well as hydrogen[36] were used. The H atoms were taken into account in idealized positions with fixed U values and C−H distances of 96 pm.

Table 3. Crystallographic Data of **2** and **3** as Well as Details of the Structure Solution and Refinement Procedures

compound	**2**	**3**
empirical formula	$C_{40}H_{92}As_2$-BaO_4Si_4	$C_{65}H_{145}As_4$-$Ba_2O_2Si_8$
fw (g mol^{-1})	1036.68	1757.89
temp T (°C)	193	183
space group[32]	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
unit cell dimens		
a (pm)	1981.8(7)	3077.91(1)
b (pm)	1137.4(3)	1165.53(1)
c (pm)	2445.9(7)	2611.67(1)
β (deg)	93.71(4)	93.58(1)
V (nm^3)	5.502(3)	9.35076(9)
Z	4	4
ρ_{calcd} (g cm^3)	1.252	1.249
λ (nm)	71.073	71.073
μ (mm^{-1})	2.034	2.377
R indices[a] with $I > -\sigma(I)$ (data)	5289	18676
wR_2	0.1193	0.1358
R_1	0.0570	0.0771
R indices[a] with $I > 2\sigma(I)$ (data)	4445	15971
wR_2	0.1137	0.1295
R_1	0.0438	0.0587
goodness-of-fit s^b on F^2	1.048	1.184
residual density (e nm^{-3})	880; −1065	2339; −586

[a] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$. [b] Definition of the R indices: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.[33]

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Supporting Information Available: An X-ray crystallographic file in CIF format is available on the Internet. Ordering and access information is given on any current masthead page.

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