Synthesis of 2,2′,5,5′-Tetraphenyl-1,1′-diarsacalcocene and -strontocene

Matthias Westerhausen,*[a] Christin Birg,[a] and Holger Piotrowski[a]

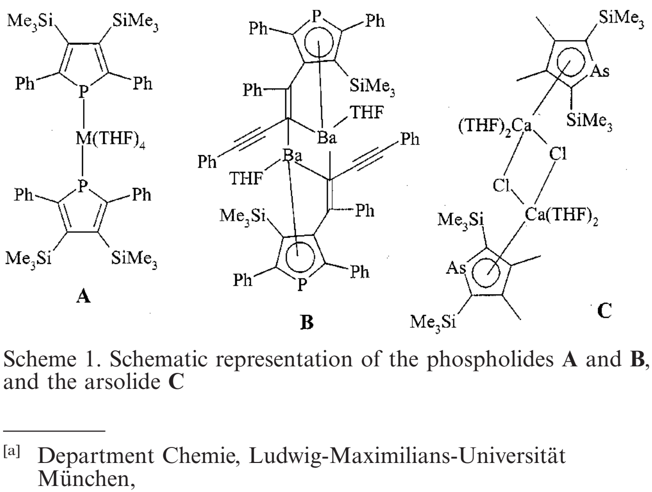
Keywords: Arsenic / As ligands / Calcium / Strontium / Heterocycles / Reaction mechanisms

The metalation of $H_2As{-}Si\mathit{i}Pr_3$ with bis(tetrahydrofuran-*O*)calcium- and -strontium bis[bis(trimethylsilyl)amide] yields tetrakis(tetrahydrofuran-*O*)calcium- (**1a**) and -strontium bis(triisopropylsilylarsanide) (**2a**). These compounds are in equilibrium with their dimers **1b** (Ca) and **2b** (Sr) by elimination of THF. The addition of diphenylbutadiyne to a THF/toluene solution of **1** and **2** gives bis(tetrahydrofuran-*O*)calcium- (**3**) and -strontium bis(2,5-diphenylarsolide) (**4**). The proposed reaction mechanism explains the formation of the $(\mathit{i}Pr_3Si)_2As^-$ and 2,5-diphenyl-3,4-bis(phenylethynyl)arsolide anions based on an intermolecular $H/Si\mathit{i}Pr_3$ exchange reaction. The latter anion was characterized by X-ray crystallography with the binuclear cation $[(THF)_3Ca\{\mu\text{-}As(H)Si\mathit{i}Pr_3\}_3Ca(THF)_3]^+$ (**5**). The arsolide ligands of **3** and **4** are η^5-bonded to the metal centers, whereas **5** crystallizes as a solvent-separated ion pair.

Introduction

The reaction of calcium and strontium bis[bis(trimethylsilyl)phosphanide] with diphenylbutadiyne yields the corresponding alkaline earth metal bis[2,5-diphenyl-3,4-bis(trimethylsilyl)-1-phosphacyclopentadienides] **A** (Scheme 1).[1] The reaction mechanism includes addition as well as 1,3-trimethylsilyl migration steps. The molecular structures of the calcium and strontium derivatives show metal−phosphorus σ-bonds. In contrast to this reaction, the homologous barium bis(phosphanide) $(THF)_4Ba[P(SiMe_3)_2]_2$ reacts differently with diphenylbutadiyne.[2] The main feature besides the central Ba_2C_2 cycle of the formed molecule **B** (Scheme 1) is a η^5-bonded phospholide moiety.

The reduction of 1-chloro-3,4-dimethyl-2,5-bis(trimethylsilyl)arsole yields the corresponding η^5-bonded arsolide **C**.[3] However, only heteroleptic compounds were prepared and no dismutation reactions of 1,1′-dipentelametallocenes have been observed thus far.



Scheme 1. Schematic representation of the phospholides **A** and **B**, and the arsolide **C**

In contrast to these recent examples of pentela-substituted alkaline earth metallocenes, the compounds calcocene[4] and decamethylcalcocene,[5] as well as their strontium analogues,[6,7] are well-known. This topic has been reviewed lately by Hanusa.[8]

We are interested in these 1,1′-dipentelametallocenes in order to investigate the coordination behavior of the anions, as well as the use of these compounds as transfer reagents for phospholide and arsolide ligands. In transition metal phospholides the anions are known to vary between η^1- and η^5- coordination depending on the transition metal fragment, and to obey the 18-electron rule.[9] Recently, a potassium phospholide with a chain structure and η^5-bonded bridging anions was published.[10] The most widely used phospholide transfer reagents are the lithium derivatives prepared by the reduction of 1-phenylphospholes with lithium metal.[9] Here we propose a reaction mechanism for the reaction of calcium- and strontium bis(triisopropylsilylarsanide) with diphenylbutadiyne. The drastically reduced tendency of the $Si\mathit{i}Pr_3$ substituent to show a 1,3-shift leads to a different mechanism than that suggested for the formation of **A** and **B**. This route offers the possibility of preparing trialkylsilyl-free 1,1′-diarsacalcocenes and -strontocenes.

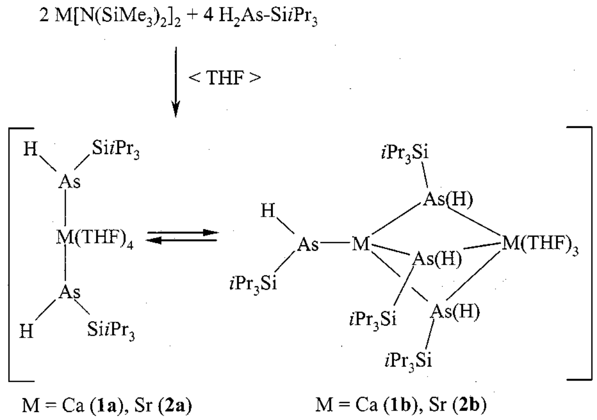
Results and Discussion

The metalation of triisopropylsilylarsane[11] with calcium- and strontium bis[bis(trimethylsilyl)amide][12] yields the corresponding alkaline earth metal bis(arsanides) **1a** and **2a** according to Scheme 2. These monomeric derivatives are expected to be in equilibrium with their dimers **1b** and **2b**, as shown in Scheme 2. This fact leads to broadened resonances (**1a** and **1b**) or a doubling of the signals (**2a** and **2b**). Similar monomer−dimer equilibria are well-known in the chemistry of alkaline earth metal bis(phosphanides)[13] − strontium-[14] and barium bis(triisopropylsilylphosphanide)[15] show this equilibrium even in donor solvents such as THF.

---

[a] Department Chemie, Ludwig-Maximilians-Universität München,
Butenandtstrasse 9 (Haus D), 81377 München, Germany
Fax: (internat.) +49-(0)89/2180-7867
E-mail: maw@cup.uni-muenchen.de

1434−1948/00/1010−2173 $ 17.50+.50/0



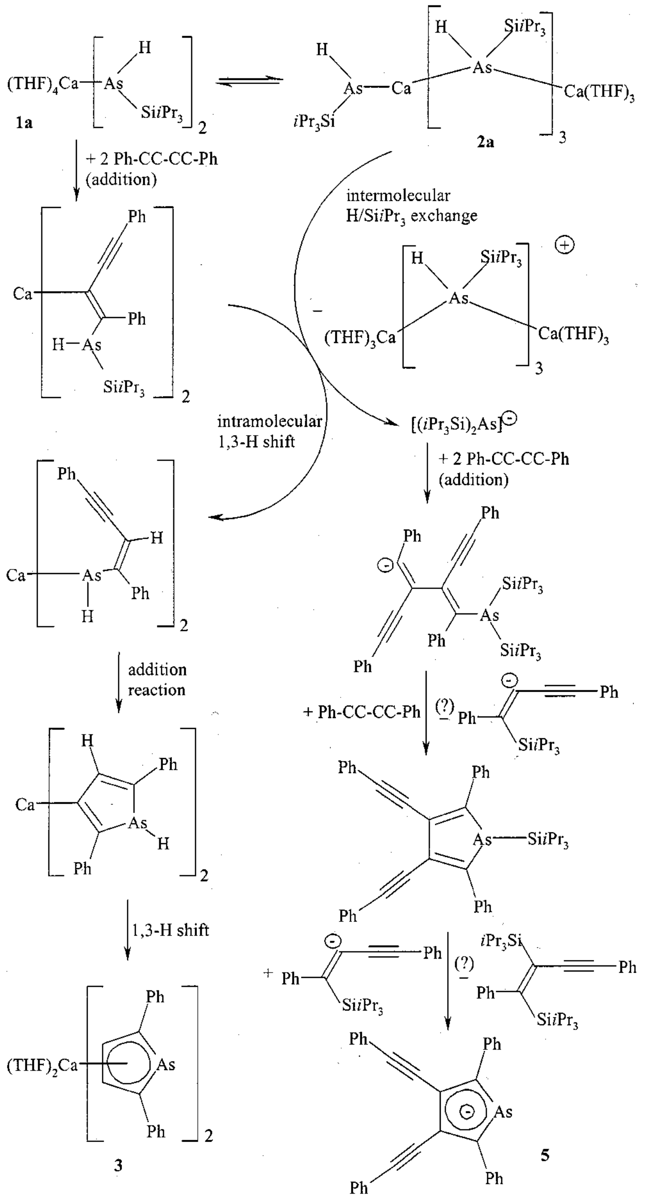
Scheme 2. Synthesis of tetrakis(tetrahydrofuran-*O*)calcium- and -strontium bis(triisopropylsilylarsanide) as well as their monomer-dimer equilibria

Dismutation reactions of alkaline earth metal bis(triisopropylsilylphosphanides) as well as -arsanides) have not been observed thus far. Even after prolonged heating of these compounds in THF or toluene neither bis(triisopropylsilyl)phosphanide and -arsanide anions, nor H_2P^- and H_2As^- ligands were detected.

The reaction of the above described triisopropylsilylarsanides of calcium (**1**) and strontium (**2**) with diphenylbutadiyne in a solvent mixture of toluene and THF gives the poorly soluble bis(tetrahydrofuran-*O*)calcium- (**3**) and -strontium bis(2,5-diphenylarsolide) (**4**). After precipitation of **3** the remaining solution was reduced to a few milliliters. Cooling to 5 °C gave crystalline **5** which was characterized by X-ray crystallography. Methanolysis of the reaction solution and mass spectrometric investigations allowed the identification of $HAs(Si\textit{i}Pr_3)_2$ and $C_{25}H_{31}Si$, a triisopropyl-substituted 1,4-diphenylbutenyne. The proposed mechanism based on these findings is represented in Scheme 3.

The first reaction step is the addition of **1a** and **2a** to a C≡C triple bond, followed by a 1,3-H migration. An intramolecular shift of a triisopropylsilyl substituent seems to be impossible in contrast to the mobility of the trimethylsilyl group.[16] However, an intermolecular H/Si*i*Pr₃ exchange reaction allows a second similar reaction sequence, namely the addition of the alkaline earth metal−arsenic bond to the remaining C≡C bond with a subsequent intramolecular 1,3-H migration. Thus, the 2,5-diphenylarsolide anion is formed (left column of Scheme 3).

This intermolecular $H/Si\textit{i}Pr_3$ exchange yields a bis(triisopropylsilyl)arsanide ligand. The addition of this anion to a diphenylbutadiyne gives a carbanion which attacks another molecule of Ph−C≡C−C≡C−Ph. The elimination of a triisopropylsilanide leaves a 1-triisopropylsilyl-2,5-diphenyl-3,4-bis(phenylethynyl)-1-arsacyclopenta-2,4-diene. The silanide adds to another diphenylbutadiyne; the resulting carbanion abstracts the $\textit{i}Pr_3Si^+$ cation from the arsenic atom and leaves the 2,5-diphenyl-3,4-bis(phenylethynyl)arsolide anion. This would lead to the formation of 1,4-diphenyl-1,2-bis(triisopropylsilyl)but-1-ene-3-yne. The constitution of the anion was confirmed by crystallization as the solvent-separated ion pair **5** with the cation $\{(THF)_3Ca[\mu\text{-}As(H)Si\textit{i}Pr_3]_3Ca(THF)_3\}^+$, and X-ray structure determination, whereas the mass spectrometric investigation of the reaction solution gave fragments which could arise from the triisopropylsilyl-substituted but-1-ene-3-yne. Furthermore, methanolysis of the reaction mixture gave $HAs(Si\textit{i}Pr_3)_2$ which proves the intermolecular $H/Si\textit{i}Pr_3$ exchange reaction. In the course of our investigations, elimination of the already well-known hexakis(triisopropyl)disilane, as well as $HSi\textit{i}Pr_3$, was not observed. However, despite not being able to isolate analytically pure **5**, the formation of this compound supports the reaction mechanism proposed in Scheme 3. Furthermore, Becker and co-workers[17] have investigated the reaction of lithium bis(trimethylsilyl)phosphanide with diphenylethyne in THF. Tetrakis(tetrahydrofuran-*O*)lithium tetraphenylphospholide has been isolated as a solvent-separated ion pair in approximately 60% yield.



Scheme 3. Proposed reaction mechanism for the synthesis of bis(tetrahydrofuran-*O*)calcium- and -strontium bis(2,5-diphenylarsolide)

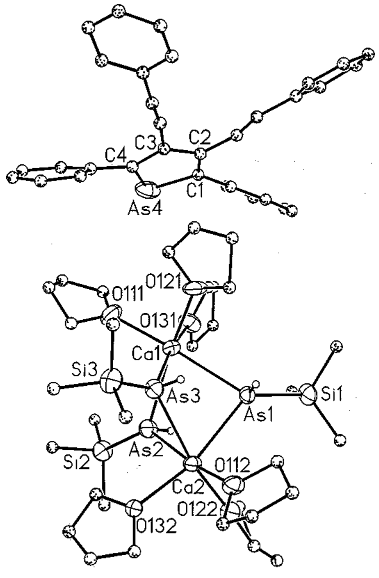


Figure 1. Molecular structure of the ion pair $[(THF)_3Ca[\mu\text{-}As(H)Si\textit{i}Pr_3]_3Ca(THF)_3]^+$ $[2,5\text{-}Ph_2\text{-}3,4\text{-}(Ph{-}C{\equiv}C)_2AsC_4]^-$ (**5**); the carbon atoms are shown with arbitrary radii, the methyl groups and hydrogen atoms, with the exception of the As−H moieties, are omitted for clarity; all other atoms are drawn with 40% ellipsoids; neither of the THF molecules intercalated between the ions are shown for reasons of clarity; selected bond lengths (pm): Ca1−As1 304.5(2), Ca1−As2 307.9(3), Ca1−As3 307.1(2), Ca2−As1 305.3(2), Ca2−As2 306.7(2), Ca2−As3 305.7(3), As1−Si1 232.1(3), As2−Si2 231.3(3), As3−Si3 231.2(3), As4−C1 187.9(14), As4−C4 183.1(15), C1−C2 141(2), C2−C3 141(2), C3−C4 139(2)

However, in this reaction the fate of the trimethylsilyl groups remains unknown.[17]

Figure 1 shows the molecular structure of the solvent-separated ion pair **5**. The rather poor quality of the structure determination results from the disordering within the cation, which is not shown. Furthermore, two THF molecules with high thermal motion of the atoms are incorporated between the ions. The structural data are therefore not discussed in detail. The solvent-separated ion pair **5** consists of a binuclear cation with three bridging triisopropylsilylarsanide substituents; the central fragment is a trigonal Ca_2As_3 bipyramid. The Ca−As bond lengths vary in a very narrow range from 304.4(2) to 307.9(2) pm and are slightly longer than in $(THF)_4Ca[As(SiMe_3)_2]_2$.[18] The coordination spheres of the arsenic atoms As1, As2, and As3 are flattened with the Ca−As−Si and Ca1−As(n)−Ca2 angles ranging from 132.2(1)° to 139.6(1)° and from 84.99(6)° to 85.82(6)°, respectively, and neglecting the hydrogen atoms.

The arsolide cycle shows a delocalization of the anionic charge as expected for an isolated anion. The As−C bond lengths, taking into account the e.s.d. values, are of the same order of magnitude, and are comparable to those found in arsinine (arsabenzene)[19] and 2,3,6-triphenylarsinine.[20] The C−As−C angle in **5** has a value of 87.7(7)°.

NMR Spectroscopy

Table 1. NMR data of bis(tetrahydrofuran-*O*)calcium- (**3**) and −strontium (**4**) bis(2,5-diphenylarsolide)

Compound	**3**[a]	**4**[a]
^1H		
δ(3,4-H)	7.57	7.53
δ(Ph, *o*)	7.21	7.21
δ(Ph, *m*)[b]	7.62	7.59
δ(Ph, *p*)	7.07	7.06
δ(THF)	1.72	1.76
δ(THF)	3.57	3.61
$^{13}C\{^1H\}$		
δ(C-3,4)	125.1	125.1
δ(C-2,5)	163.4	164.5
δ(Ph, *i*)	141.9	141.9
δ(Ph, *o*)[b]	125.1	124.9
δ(Ph, *m*)[b]	128.3	128.4
δ(Ph, *p*)	121.4	121.7
δ(THF)	24.4	24.4
δ(THF)	66.5	66.5

[a] Solvent: $[D_8]$THF, 30 °C. − [b] Assignment to *meta* and *ortho* positions uncertain and probably reversed.

The NMR spectroscopic data of bis(tetrahydrofuran-*O*)calcium- (**3**) and -strontium bis(2,5-diphenylarsolide) (**4**) is summarized in Table 1. Their similarity and hence the lack of influence of the alkaline earth metal on the chemical shifts implies the mainly ionic character of the metal−arsolide interaction. The α-carbon atoms (C2,5) at the arsenic atom show a strong downfield shift. However, similar values are also found for tetrakis(tetrahydrofuran-*O*)calcium bis[2,5-diphenyl-3,4-bis(trimethylsilyl)phospholide] **A**[1] with η^1-bonded phospholide ligands. The chemical shifts of the ^{13}C atoms of the aromatic five-membered cycles are not dependent on either the binding mode, or on the pentele or alkaline earth metal atoms. This observation supports the interpretation of these compounds as mainly ionic.

Molecular Structure of 3

Bis(tetrahydrofuran-*O*)calcium bis(2,5-diphenylarsolide) **3** crystallizes with two crystallographically independent molecules in the asymmetric unit. Figure 2 shows one of the essentially equal molecules and its numbering scheme. The arsolide ligands are η^5-bonded to the calcium centers. The distances between the calcium atoms and the centers of the arsolide cycles lie between 254.1 and 257.5 pm. The Ca−O bond lengths vary in the very narrow and characteristic[13] region of 235.7 and 238.9 pm.

The arsolide ligands show a delocalization of the anionic charge within the five-membered cycle, the C(1*n*)−As(*n*)−C(4*n*) angles are approximately 87 °. The mean As−C bond of 190.5 pm is longer than that in the isolated arsolide anion of **5**. On the other hand, the Ca−As distances are only slightly larger than in the polycyclic cation of **5**. However, these structural parameters are in agreement with those of a calcium-bonded 3,4-dimethyl-2,5-bis(trimethylsilyl)arsolide ligand.[1]

An interaction between the arsolide anion and the phenyl substituents in the 2,5-positions can be excluded. The bond lengths C(1*n*)−C(11*n*) and C(4*n*)−C(14*n*) (*n* = 1, 2, 3, 4) with a mean value of 146.9 pm is characteristic of a C−C single bond between two sp^2 hybridized carbon atoms.[21]

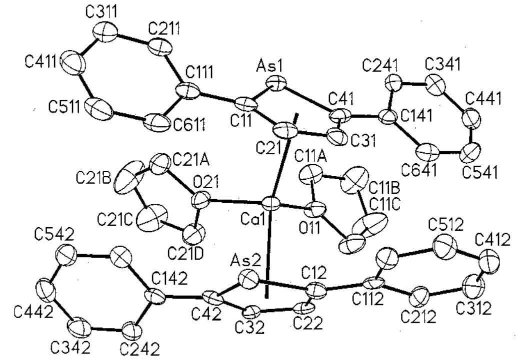


Figure 2. Molecular structure and numbering scheme of bis(tetrahydrofuran-*O*)calcium bis(2,5-diphenylarsolide) **(3)**; only one molecule is shown; hydrogen atoms are omitted for clarity, the ellipsoids represent a probability of 40%; selected bond lengths (pm): Ca1−As1 309.04(9), Ca1−C11 292.2(4), Ca1−C21 285.1(4), Ca1−C31 282.2(4), Ca1−C41 284.7(4), As1−C11 190.9(4), C11−C21 137.2(6), C21−C31 137.8(6), C31−C41 140.1(6), C41−As1 190.6(5), Ca1−As2 307.50(9), Ca1−C12 283.1(5), Ca1−C22 278.9(4), Ca1−C32 282.6(4), Ca1−C42 287.9(3), As2−C12 189.8(4), C12−C22 139.1(5), C22−C32 139.1(6), C32−C42 140.4(5), C42-As2 190.6(4), Ca1−O11 237.8(3), Ca1−O21 235.7(3); selected angles (°): C11-As1−C41 86.1(2), C12-As2−C42 87.1(2), O11−Ca1−O21 82.9(1)

The small angles between the normals of the phenyl planes on the one side and the arsolide plane on the other are rather small (25.2° and 20.4°); however, this orientation is a consequence of the intramolecular steric repulsion between the substituents and the packing of the molecules in the crystal.

Conclusion

The substitution pattern of the alkaline earth metal bis(arsanides) influence the mechanism of their reactions with diphenylbutadiyne. The migration of the sterically demanding triisopropylsilyl groups is avoided, instead an intermolecular H/Si*i*Pr$_3$ exchange reaction is observed. As a consequence of this reaction two different arsolide substituents have been characterized by X-ray crystallography: the 2,5-diphenylarsolide and the 2,5-diphenyl-3,4-diphenylethynylarsolide anion. The latter was not isolated as a diarsacalcocene, as the bulky binuclear cation [(THF)$_3$Ca[μ-As(H)Si*i*Pr$_3$]$_3$Ca(THF)$_3$]$^+$ was necessary for stabilization and crystallization.

The 1,1′-diarsacalcocene **3** and -strontocene **4** are available in high purity due to their poor solubility in toluene. However, these compounds have a limited use as synthons for arsolide transfer reactions because of a rather poor yield with regard to the alkaline earth metal or the arsenic atoms.

Experimental Section

General Remarks: All experiments and manipulations were carried out under argon purified by passage through a BTS catalyst and P$_4$O$_{10}$. Reactions were performed by using standard Schlenk techniques and using dried, thoroughly deoxygenated solvents. The starting materials (THF)$_2$Ca[N(SiMe$_3$)$_2$]$_2$,[12,22,23] (THF)$_2$Sr[N(SiMe$_3$)$_2$]$_2$,[12,22,23] and H$_2$AsSi*i*Pr$_3$[11] were prepared according to literature procedures. NMR spectra were recorded on Jeol GSX270 and EX400 spectrometers. A Perkin−Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra; solid substances were examined as Nujol mulls between KBr plates (vs: very strong, s strong, m: medium, w: weak, vw: very weak, sh: shoulder). The frequencies in the region of the Nujol vibrations were not listed.

Tetrakis(tetrahydrofuran-*O*)calcium Bis(triisopropylsilylarsanide) (1): Triisopropylsilylarsane (1.17 g, 4.98 mmol) was added at room temp. to a solution of of bis(tetrahydrofuran-*O*)calcium bis[bis(trimethylsilyl)amide] (0.96 g, 1.90 mmol) in 20 mL of THF. The volume of the reaction mixture was reduced to approximately a quarter of the original volume. At 4 °C a precipitate of **1** was obtained as air- and moisture-sensitive colorless crystals, yield: 1.03 g (1.30 mmol), 68%. − Dec. above 140 °C without melting. − ^{1}H NMR ([D$_8$]toluene, 30 °C): δ = 1.03 (d, ^3J = 6.0 Hz, 18 H, CH$_3$), 0.97 (sept, ^3J = 6.0 Hz, 3 H, CH), 1.55 and 3.50 (THF). − ^{13}C{^{1}H} NMR ([D$_8$]toluene, 30 °C): δ = 15.1 (CH), 18.7 (CH$_3$), 25.4 and 67.4 (THF). − ^{29}Si{^{1}H} NMR ([D$_8$]toluene, 30 °C): δ = 31.1. − IR: $\tilde{\nu}$ = 2091 vs [ν(AsH)], 1293 w, 1260 w, 1249 w, 1232 sh, 1178 vw, 1159 vw, 1093 sh, 1071 s, 1036 s, 1016 s, 992 s, 967 w, 954 m, 918 s, 882 vs, 833 m, 803 w, 743 w, 672 s, 653 s, 609 s, 573 s, 560 s, 502 s, 464 s, 445 m, 420 m, 385 m, 363 sh cm^{-1}. − MS (70 eV); *m*/*z* (%): 59 (89) [SiC$_2$H$_7$], 61 (7), 73 (83) [SiC$_3$H$_9$], 75 (15) [As], 87 (54) [SiC$_4$H$_{11}$], 103 (11), 115 (100) [SiC$_6$H$_{15}$], 131 (16), 157 (24) [SiC$_9$H$_{21}$], 158 (21) [HSiC$_9$H$_{21}$], 207 (30), 300 (19) [Si$_2$C$_{17}$H$_{40}$], 390 (7) [CaAs$_2$Si$_2$C$_{10}$H$_{24}$]. − C$_{18}$H$_{44}$As$_2$CaSi$_2$ (506.6, THF-free): calcd. C 42.67, H 8.75; found C 43.16, H 8.84.

Tetrakis(tetrahydrofuran-*O*)strontium Bis(triisopropylsilylarsanide) (2): Triisopropylsilylarsane (1.17 g, 4.98 mmol) was added to a solution of bis(tetrahydrofuran-*O*)strontium bis[bis(trimethylsilyl)amide] (1.05 g, 1.90 mmol) in 10 mL of THF. All volatile materials were removed under vacuum and the remaining yellowish powder dried until a pressure of 0.01 Torr was reached. Yield: 1.43 g (1.70 mmol), 89%. − Dec. above 140 °C without melting. − ^{1}H NMR ([D$_8$]toluene, 30 °C):δ = 1.28 (d, ^3J = 6.4 Hz, 18 H, CH$_3$), 1.27 (sept, ^3J = 6.4 Hz, 3 H, CH), 1.48 and 3.56 (THF). − ^{13}C{^{1}H} NMR ([D$_8$]toluene, 30 °C): δ = 15.4 (CH), 20.3 (Me), 25.5 and 67.6 (THF). − ^{29}Si{^{1}H} NMR ([D$_8$]toluene, 30 °C): δ = 31.2. − IR: $\tilde{\nu}$ = 2052 s [ν(AsH)]; 1295 vw, 1249 sh, 1225 w, 1179 vw, 1071 s, 1036 vs, 1015 s, 968 w, 953 w, 917 s, 882 vs, 663 s, 646 vs, 593 s, 575 vs, 558 s, 503 s, 462 m, 424 vw, 386 w, 360 vw cm^{-1}. − C$_{18}$H$_{44}$As$_2$Si$_2$Sr (554.2, THF-free): calcd. C 44.71, H 8.66; found C 42.18, H 8.30.

Bis(tetrahydrofuran-*O*)calcium Bis(2,5-diphenylarsolide) (3): **1** (1.12 g, 1.41 mmol) in 3 mL of THF, and diphenylbutadiyne (0.30 g, 1.41 mmol) were combined in 20 mL of unstirred toluene. After 7 days the NMR spectroscopic control measurements showed the complete consumption of diphenylbutadiyne. The brown reaction mixture was reduced to two thirds of the original volume. At 4 °C crystals of **3** precipitated. Washing of the solid with small portions of toluene left analytically pure **3** (0.31 g, 0.42 mmol, 30% with regard to calcium). The mother liquor and the toluene washing were combined. After reduction of the volume and cooling to 4 °C crystals of **3** and bis[tris(tetrahydrofuran-*O*)calcium] tris(μ-triisopropylsilylarsanide) 2,5-diphenyl-3,4-bis(phenylethynyl)arsolide (**5**) [m. p. 115 °C (dec.); ^{1}H NMR: δ = 1.16 (CH$_3$ and CH), 6.78−7.66 (phenyl), 1.77 and 3.64 (THF)], precipitated, however, analytically pure **5** was not obtained from this reaction. − Physical data of **3**: dec. above 250 °C without melting. − NMR data see Table 1. − IR: $\tilde{\nu}$ = 1315 vw, 1295 vw, 1267 s, 1249 w, 1202 vw, 1277 w, 1156 w, 1137 vw, 1105 vw, 1073 s, 1026 vs, 1019 vs, 999 w, 984 vw, 968 vw, 953 vw, 903 m, 875 s, 841 sh, 802 vs, 756 vs, 693 vs, 672 w, 666 w, 653 w, 620 vw, 590 vw, 554 w, 525 w, 514 vw, 452 w, 430 s, 299 vw, 291 vw cm^{-1}. − $C_{40}H_{40}As_2CaO_2$ (742.7): calcd. C 64.69, H 5.43; found C 63.09, H 5.78.

Bis(tetrahydrofuran-*O*)strontium Bis(2,5-diphenylarsolide) (4): Tetrakis(tetrahydrofuran-*O*)strontium bis(triisopropylsilylarsanide) (**2**) (1.60 g, 1.90 mmol) was dissolved in a mixture of 5 mL of THF and 15 mL of toluene. Diphenylbutadiyne (0.39 g, 1.9 mmol) was added to this yellowish solution which turned brown within a few hours. After two days stirring at room temp., the reaction mixture was concentrated to half its volume and **4** precipitated. Washing with toluene left an almost colorless powder of **4** (0.55 g, 0.7 mmol, 37% with regard to strontium). - Dec. above 250 °C without melting. − NMR data see Table 1. − IR: $\tilde{\nu}$ = 1316 vw, 1293 vw, 1265 s, 1185 vw, 1175 vw, 1157 w, 1099 m, 1073 s, 1029 s, 1023 s, 999 w, 982 vw, 970 vw, 902 m, 878 m, 847 w, 840 w, 800 s, 756 vs, 693 s, 666 vw, 620 vw, 589 vw, 554 w, 524 vw, 510 vw, 497 vw, 453 vw, 431 m, 422 vw, 405 vw, 396 vw cm^{-1}. − $C_{40}H_{40}As_2O_2Sr$ (790.2): calcd. C 60.80, H 5.10; found C 59.03, H 5.39.

Structure Determinations: Single crystals of **3** and **5** were covered with oil[24] and mounted on a STOE IPDS diffractometer with graphite monochromated Mo-K_α radiation (λ = 71.073 pm). Crystallographic parameters and details of data collection are summarized in Table 2. The structures were solved by direct methods and refined with the software packages SHELXL-93 and SHELXL-97.[26] Neutral scattering factors were taken from Cromer and Mann[27] and for the hydrogen atoms from Stewart et al.[28] For **3** neither absorption nor extinction corrections were applied.

Table 2. Crystallographic data of **3** and **5,** as well as details of the structure solution and refinement procedures

Compound	**3**	**5**
Formula	$C_{40}H_{40}As_2CaO_2$	$C_{91}H_{150}As_4Ca_2O_8Si_3$
Formula mass [gmol^{-1}]	742.67	1836.26
T [K]	200(2)	200(2)
Space group[25]	$P2_1/n$	$P\bar{1}$
a [pm]	1637.19(8)	1403.5(1)
b [pm]	1739.82(8)	1675.8(1)
c [pm]	2417.54(13)	2434.5(2)
α [°]	90	108.166(9)
β [°]	94.354(6)	96.771(9)
γ [°]	90	90.934(9)
V [nm^3]	6866.3(6)	5394.2(7)
Z	8	2
$d_{calcd.}$ [gcm^3]	1.4369	1.1306(2)
μ [mm^{-1}]	2.130	1.401
F(000)	3056	1948
Scan range [°]	$3.6 < 2\theta < 48.1$	$3.3 < 2\theta < 47.9$
Collected data	23605	31005
Unique data	10103	15766
Data with $I > 2\sigma(I)$	5965	5868
Parameters	811	803
Restraints	0	312
wR_2[a] (all data, on F^2)	0.0580	0.2398
wR_2[a] [$I > 2\sigma(I)$]	0.0517	0.2062
R_1[a] [$I > 2\sigma(I)$]	0.0338	0.0805
GOF[b] on F^2	0.779	0.897
Residual density [eÅ^{-3}]	0.348/-0.280	1.017/-0.439

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

The non-hydrogen atoms of **3** were refined anisotropically. The H-atoms were considered with a riding model under restriction of ideal symmetry at the corresponding atom. The asymmetric unit contains two molecules.[29] The structure of **5** consists of a solvent-separated ion pair with two additional THF molecules in the cavities. Whereas the non-hydrogen atoms of the anion were refined anisotropically, all other C atoms were considered isotropically. The isopropylsilyl groups and part of the THF ligands show a two-site disorder. All hydrogen atoms were refined using a riding model with ideal geometry at the corresponding carbon and arsenic atoms.

Acknowledgments

This work was financially supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Prof. Dr. P. Klüfers for his kind support. Furthermore, C. Birg wishes to express her gratitude to the State of Bavaria, Germany for a Ph. D. scholarship granted.

---

[1] M. Westerhausen, M. H. Digeser, H. Nöth, W. Ponikwar, T. Seifert, K. Polborn, *Inorg. Chem.* **1999**, *38*, 3207−3214.

[2] M. Westerhausen, M. H. Digeser, H. Nöth, T. Seifert, A. Pfitzner, *J. Am. Chem. Soc.* **1998**, *120*, 6722−6725.

[3] M. Westerhausen, M. H. Digeser, C. Gückel, H. Nöth, J. Knizek, W. Ponikwar, *Organometallics* **1999**, *18*, 2491−2496.

[4] R. Zerger, G. Stucky, *J. Organomet. Chem.* **1974**, *80*, 7−17.

[5] R. A. Anderson, J. M. Boncella, C. J. Burns, R. Blom, A. Haaland, H. V. Volden, *J. Organomet. Chem.* **1986**, *312*, C49−C52.

[6] [6a] E. O. Fischer, G. Stölzle, *Chem. Ber.* **1961**, *94*, 2187−2193. − [6b] B. G. Gowenlock, W. E. Lindsell, B. Singh, *J. Chem. Soc., Dalton Trans.* **1978**, 657−664.

[7] R. Blom, K. Faegri, H. V. Volden, *Organometallics* **1990**, *9*, 372−379.

[8] [8a] T. P. Hanusa, *Chem. Rev.* **1993**, *93*, 1023−1036. − [8b] See also: P. Jutzi, N. Burford, *Chem. Rev.* **1999**, *99*, 969−990 and literature cited therein.

[9] [9a] D. L. Kershner, F. Basolo, *Coord. Chem. Rev.* **1987**, *79*, 279−292. − [9b] F. Mathey, *Chem. Rev.* **1988**, *88*, 429−453. − [9c] F. Mathey, *Coord. Chem. Rev.* **1994**, *137*, 1−52. − [9d] J. F. Nixon, *Coord. Chem. Rev.* **1995**, *145*, 201−258.

[10] F. G. N. Cloke, P. B. Hitchcock, J. F. Nixon, D. J. Wilson, *Organometallics* **2000**, *19*, 219−220.

[11] M. Westerhausen, M. Wieneke, W. Schwarz, *J. Organomet. Chem.* **1999**, *572*, 249−257.

[12] [12a] M. Westerhausen, *Inorg. Chem.* **1991**, *30*, 96−101. − [12b] see also: M. Westerhausen, *Trends Organomet. Chem.* **1997**, *2*, 89−105.

[13] M. Westerhausen, *Coord. Chem. Rev.* **1998**, *176*, 157−210.

[14] M. Westerhausen, C. Birg, M. Krofta, P. Mayer, T. Seifert, H. Nöth, A. Pfitzner, T. Nilges, H.-J. Deiseroth, *Z. Anorg. Allg. Chem.* **2000**, *626*, in press.

[15] M. Westerhausen, M. H. Digeser, M. Krofta, N. Wiberg, H. Nöth, J. Knizek, W. Ponikwar, T. Seifert, *Eur. J. Inorg. Chem.* **1999**, 743−750.

[16] See for example: [16a] M. Westerhausen, M. H. Digeser, W. Schwarz, *Inorg. Chem.* **1997**, *36*, 521−527. − [16b] M. Westerhausen, M. H. Digeser, W. Schwarz, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1237−1242.

[17] G. Becker, G. Ditten, K. Hübler, U. Hübler, K. Merz, M. Niemeyer, N. Seidler, M. Westerhausen, Z. Zheng, *Organosilicon Chemistry II: From Molecules to Materials*, (Eds.: N. Auner, J. Weis), VCH, Weinheim, **1996**, p. 161−186.

[18] M. Westerhausen, W. Schwarz, *Z. Naturforsch.* **1995**, *50b*, 106−114.

[19] T. C. Wong, L. S. Bartell, *J. Mol. Struct.* **1978**, *44*, 169−175.

[20] P. Jutzi, *Angew. Chem.* **1975**, *87*, 269−283; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 232−246.

[21] J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 3rd Ed., J. Wiley, New York, **1985**, p. 18−20.

[22] M. Westerhausen, M. Hartmann, N. Makropoulos, B. Wieneke, M. Wieneke, W. Schwarz, D. Stalke, *Z. Naturforsch.* **1998**, *53b*, 117−125.

[23] D. C. Bradley, M. B. Hursthouse, A. A. Ibrahim, K. M. Abdul Malik, M. Motevalli, R. Möseler, H. Powell, J. D. Runnacles, A. C. Sullivan, *Polyhedron* **1990**, *9*, 2959−2964.

[24] [24a] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615–619. – [24b] D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171–178.

[25] *International Tables for Crystallography*, Vol. A, *Space Group Symmetry*, 2nd Ed., (Ed.: T. Hahn), D. Reidel, Dordrecht, **1984**.

[26] G. M. Sheldrick *SHELXL-93*, Universität Göttingen, **1993**; *SHELXL-97*, Universität Göttingen, **1997**.

[27] D. T. Cromer, J. B. Mann *Acta Crystallogr.* **1968**, *A24*, 321–324.

[28] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175–3187.

[29] Crystallographic data (excluding structure factors) for the structure of **3** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141345. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

Received March 7, 2000
[I00088]