

## Tridecamethyl-1-phospha- and tridecamethyl-1-arsa-2,3,4,5,6,7,8-heptasilabicyclo[2.2.2]octane

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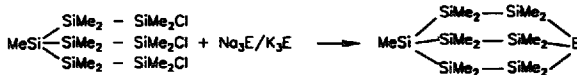
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### Abstract

The octaheterobicyclo[2.2.2]octanes  $\text{MeSi}(\text{SiMe}_2\text{SiMe}_2)_3\text{E}$  (E = P, As) have been prepared in high yields (up to 50%) from the alkali metal phosphide or arsenide  $\text{Na}_3\text{E}/\text{K}_3\text{E}$  and the heptasilane  $\text{MeSi}(\text{SiMe}_2\text{SiMe}_2)_3$



E = P, As

The cages were isolated by crystallization from heptane and the crystal structure of the arsenic compound was determined. The synthesis of the heptasilane  $\text{MeSi}(\text{SiMe}_2\text{SiMe}_2)_3$  is described too. All compounds were characterized by multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{29}\text{Si}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) as well as elemental analysis.

**Keywords:** Silicon; Phosphorus; Arsenic

### 1. Introduction

Just a few bicyclo[2.2.2]octanes composed exclusively of second row elements of Group XIV (Si, Ge, Sn, Pb) and/or Group XV (P, As, Sb, Bi) are known at present.

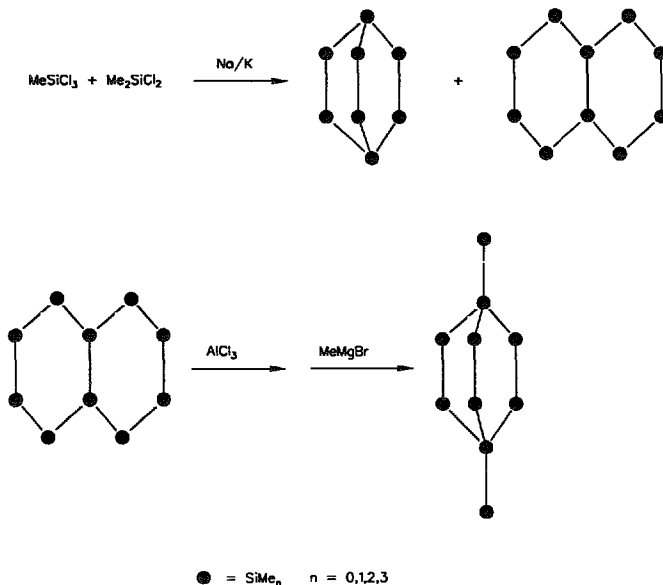
Tetradecamethylbicyclo[2.2.2]octasilane was reported to form in 5% yield in the reaction of Na/K alloy with a mixture of trichloromethylsilane and dichlorodimethylsilane, together with octadecabicyclo[4.4.0]decasilane [1]. The latter rearranges to form a silyl substituted

bicyclo[2.2.2]octasilane [2] (Scheme 1). A detailed and complete review of all cyclic and polycyclic silanes presently known is given in Ref. [3].

When sodium potassium phosphide, arsenide, antimonide or bismuthide  $\text{Na}_3\text{E}/\text{K}_3\text{E}$  (prepared from the elements E and Na/K alloy) react with 1,2-dichlorotetramethyldisilane, the 1,4 diphospha-, diarsa-, distiba- and dibismutha-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octanes are formed [4,5] (Scheme 2). In an analogous manner,  $\text{P}(\text{SnMe}_2\text{SnMe}_2)_3\text{P}$  is formed in the reaction between white phosphorus and 1,1,2,2-tetramethyldistannane [6].

The marked tendency of the heavier elements of Groups XIV and XV to form six-membered ring sys-

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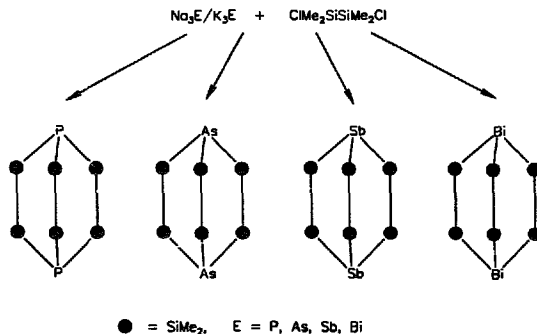
Scheme 1.

tems prompted us to choose the title compounds as synthetic targets.

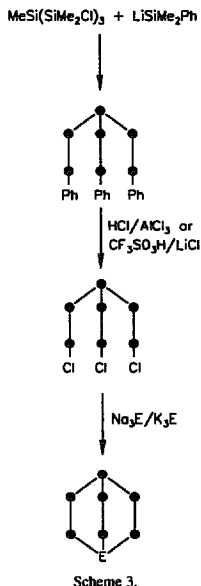
## 2. Syntheses

Starting from methyltri(chlorodimethylsilyl)silane (prepared from  $\text{MeSi}(\text{SiMe}_3)_3$  and  $\text{Me}_3\text{SiCl}$  [7]) and

$\text{PhMe}_2\text{SiLi}$ , we were able to synthesize  $\text{MeSi}(\text{SiMe}_2\text{SiMe}_2\text{Ph})_3$  in reasonable yield (50%). The heptasilane was then easily converted to  $\text{MeSi}(\text{SiMe}_2\text{SiMe}_2\text{Cl})_3$  using  $\text{HCl}/\text{AlCl}_3$  or  $\text{CF}_3\text{SO}_3\text{H}/\text{LiCl}$  (Scheme 3). The subsequent reactions of the trichloroheptasilane with  $\text{Na}_3\text{P}/\text{K}_3\text{P}$  and  $\text{Na}_3\text{As}/\text{K}_3\text{As}$ , carried out in DME, gave the desired



Scheme 2.



cages in astonishingly high yields (48% and 30% respectively).

### 3. Crystal structure of tridecamethyl-1-arsa-2,3,4,5,6,7,8-heptasilabicyclo[2.2.2]octane

Pale yellow single crystals of tridecamethyl-1-arsa-2,3,4,5,6,7,8-heptasilabicyclo[2.2.2]octane suitable for X-ray diffraction analysis were grown in heptane. The data collection was performed under a stream of  $\text{N}_2$  at  $-186^\circ\text{C}$  using a modified STOE four-circle diffractometer and graphite monochromated molybdenum  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal was mounted on the tip of a glass fibre in an inert oil.

Space group  $P2(1)/n$  was chosen and later confirmed by successful structure solution. The structure was solved using xs [8] and refined by full-matrix least-squares with SHELXL-93 [9], minimizing the residuals for  $F^2$ . No absorption correction was applied. Hydrogen atoms were included in the model at their calculated positions. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, isotropic displacement parameters were used for hydrogen atoms. A summary of crystal data, data collection and refinement is given in Table 1.

Table 1

Crystal data, data collection and refinement of tridecamethyl-1-arsa-2,3,4,5,6,7,8-heptasilabicyclo[2.2.2]octane grown in *n*-heptane

empirical formula	$\text{C}_{13}\text{H}_{19}\text{AsSi}_7$
formula weight ( $\text{g mol}^{-1}$ )	466.98
crystal system	monoclinic
space group	$P2(1)/n$
$a$ ( $\text{\AA}$ )	16.327
$b$ ( $\text{\AA}$ )	9.807
$c$ ( $\text{\AA}$ )	16.887
$\alpha$ (deg)	90.00
$\beta$ (deg)	106.39
$\gamma$ (deg)	90.00
volume ( $\text{\AA}^3$ )	2592.5(8)
$Z$	4
temperature (K)	88(2)
wavelength ( $\text{\AA}$ )	0.71073
density (calc) ( $\text{g cm}^{-3}$ )	1.196
absorption coeff. ( $\text{mm}^{-1}$ )	1.63
$F(000)$	992
$2\theta$ range (deg)	2.92 to 22.49
index ranges	$-17 \leq h \leq 17$ ; $-10 \leq k \leq 10$ ; $-18 \leq l \leq 18$
reflections collected	4332
independent reflections	3236 [ $R(\text{int}) = 0.043$ ]
data	2676
parameters	190
goodness of fit on $F^2$	1.041
final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0422$ , $wR_2 = 0.1214$
$R$ indices (all data)	$R_1 = 0.0569$ , $wR_2 = 0.1409$
largest difference peak ( $\text{e \AA}^{-3}$ )	0.49
largest difference hole ( $\text{e \AA}^{-3}$ )	-0.53

Table 2

Fractional coordinates and equivalent isotropic parameters ( $\text{\AA}^2$ ) for the asymmetric unit of tridecamethyl-1-arsa-2,3,4,5,6,7,8-heptasilabicyclo[2.2.2]octane

Atom	$x$	$y$	$z$	$U_{\text{eq}}$
As	0.09171(3)	0.22244(6)	0.46699(3)	0.0183(3)
Si <sub>2</sub>	0.14047(9)	0.31929(15)	0.36021(9)	0.0155(4)
Si <sub>3</sub>	0.28469(9)	0.38316(15)	0.39640(9)	0.0160(4)
Si <sub>4</sub>	0.35866(10)	0.26853(14)	0.51669(9)	0.0147(4)
Si <sub>5</sub>	0.31010(10)	0.3474(2)	0.62596(9)	0.0187(4)
Si <sub>6</sub>	0.16056(10)	0.3596(2)	0.58203(9)	0.0189(4)
Si <sub>7</sub>	0.17388(10)	0.02021(15)	0.49381(9)	0.0184(4)
Si <sub>8</sub>	0.31841(9)	0.03970(15)	0.49583(9)	0.0156(4)
C21	0.1182(4)	0.1909(6)	0.2737(3)	0.0238(13)
C22	0.0728(4)	0.4729(6)	0.3217(4)	0.0271(15)
C31	0.3348(4)	0.3401(6)	0.3110(4)	0.0304(15)
C32	0.2909(4)	0.5751(6)	0.4103(4)	0.0265(14)
C41	0.4776(4)	0.2956(6)	0.5383(4)	0.0249(14)
C51	0.3554(4)	0.5219(6)	0.6578(4)	0.036(2)
C52	0.3461(4)	0.2329(6)	0.7191(3)	0.030(2)
C61	0.1277(4)	0.5424(6)	0.5557(3)	0.0259(14)
C62	0.1165(4)	0.3072(7)	0.6693(4)	0.033(2)
C71	0.1709(4)	-0.0462(6)	0.5977(4)	0.0305(15)
C72	0.1161(4)	-0.1087(6)	0.4150(4)	0.0274(14)
C81	0.3858(4)	-0.0700(6)	0.5813(4)	0.0297(15)
C82	0.3343(4)	-0.0252(6)	0.3961(3)	0.0220(13)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

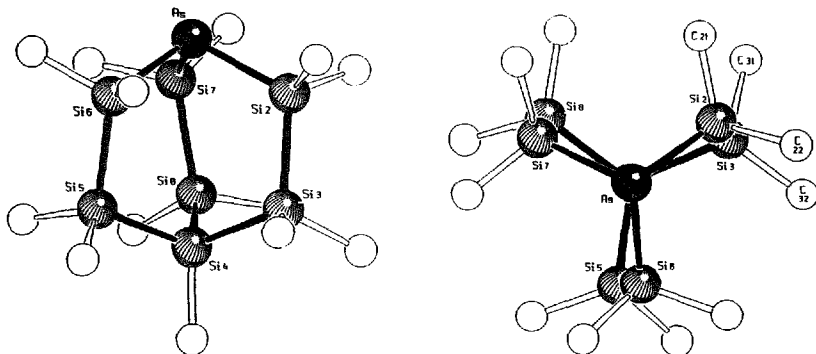


Fig. 1. Molecular structure of tridecamethyl-1-arsa-2,3,4,5,6,7,8-heptasilabicyclo[2.2.2]octane: (a) view perpendicular to the  $C_3$  axis; (b) view in the direction of the  $C_3$  axis.

The space group  $P2_1/n$  is centrosymmetric and characterized by a two-fold screw axis perpendicular to a glide plane. Therefore the unit cell comprises both enantiomers of tridecamethyl-1-arsa-2,3,4,5,6,7,8-heptasilabicyclo[2.2.2]octane. Two molecules of each enantiomer are present in the unit cell.

The molecular structure of the cage and the numbering scheme are shown in Fig. 1. Fractional coordinates and equivalent isotropic thermal parameters for the asymmetric unit are given in Table 2, selected intramolecular angles, torsional angles and distances in Table 3. The estimated standard deviations in parentheses refer to the last digit.

Detailed crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK.

The structure of  $\text{MeSi}(\text{SiMe}_2\text{SiMe}_2)_3\text{As}$  is composed of three  $\text{Si}_5\text{As}$  six-membered rings that adopt a twisted boat conformation with mean torsion angles of

40.57, 20.44,  $-68.34$ , 46.58, 20.44 and  $-64.12^\circ$  (Fig. 1(a)). To a good approximation, the molecule belongs to point group  $C_3$  (Fig. 1(b)). In solution, the average symmetry is  $C_{3v}$ , as deduced from the NMR spectra (see Section 4).

The average SiAs bond length (236.5 pm) compares well with the distances in largely unstrained SiAs compounds such as  $\text{K}_2\text{SiAs}_2$  (237.0 pm [10]),  $\text{As}_7(\text{SiMe}_2)_3$  (239.7 pm [11]) or  $\text{As}(\text{SiH}_3)_3$  (235.2 pm [12]). For strained systems, values as large as 246 pm have been reported [13–15].

The mean SiSi distance of the bonds adjacent to the As atom (234.97 pm) is shorter by 1.34 pm than the mean distance to the apical Si atom (233.63 pm), reflecting the steric repulsions of the nearly staggered methyl groups (torsional angle  $\text{C}21\text{Si}2\text{Si}3\text{C}31$   $18.8^\circ$ ). All SiC bond distances are in the usual range, the average being 188.6(6) pm.

#### 4. NMR spectroscopy

NMR experiments were performed in  $\text{C}_6\text{D}_6$  at  $22^\circ\text{C}$  on a Bruker 300 MSL spectrometer.  $^{29}\text{Si}$  spectra were recorded at 59.6 MHz using INEPT pulse sequences [16] with  $^1\text{H}$  decoupling. The INEPT-INADEQUATE pulse sequence [17] was used for the determination of coupling constants.  $^{31}\text{P}$  spectra were recorded at 121.50,  $^{13}\text{C}$  spectra at 75.47 MHz. Chemical shifts are reported relative to TMS ( $^{29}\text{Si}$ ), 75%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) and TMS ( $^{13}\text{C}$ ). All chemical shifts (ppm) and coupling constants (Hz) are summarized in Table 4.

On the NMR timescale the two carbon atoms on a particular Si atom are equivalent. In solution, the cages thus exhibit the time averaged symmetry  $C_{3v}$ . The corresponding large amplitude motion (essentially a tor-

Table 3  
Selected intramolecular distances (Å) and angles (deg) for tridecamethyl-1-arsa-2,3,4,5,6,7,8-heptasilabicyclo[2.2.2]octane

$\text{AsSi}_6$	2.368(2)	$\text{Si}_4\text{Si}_7\text{As}$	116.49(7)
$\text{AsSi}_7$	2.365(2)	$\text{Si}_5\text{Si}_8\text{As}$	116.17(7)
$\text{AsSi}_2$	2.365(2)	$\text{Si}_1\text{Si}_2\text{Si}_5$	109.43(8)
$\text{Si}_2\text{Si}_3$	2.337(2)	$\text{Si}_4\text{Si}_5\text{Si}_8$	108.80(8)
$\text{Si}_4\text{Si}_5$	2.335(2)	$\text{Si}_7\text{Si}_8\text{Si}_1$	108.53(8)
$\text{Si}_2\text{Si}_8$	2.337(2)	$\text{Si}_1\text{Si}_4\text{Si}_5$	108.63(8)
$\text{Si}_3\text{Si}_8$	2.345(2)	$\text{Si}_1\text{Si}_2\text{Si}_9$	107.05(8)
$\text{Si}_6\text{Si}_5$	2.346(2)	$\text{Si}_3\text{Si}_2\text{Si}_9$	106.07(8)
$\text{Si}_4\text{Si}_7$	2.358(2)	$\text{C}21\text{Si}_2\text{C}22$	107.6(3)
		$\text{C}61\text{Si}_6\text{C}62$	107.3(3)
		$\text{C}71\text{Si}_7\text{C}72$	106.6(3)
$\text{Si}_6\text{AsSi}_7$	102.28(6)	$\text{C}31\text{Si}_1\text{C}32$	107.2(3)
$\text{Si}_8\text{AsSi}_7$	101.94(6)	$\text{C}51\text{Si}_4\text{C}52$	107.4(3)
$\text{Si}_2\text{AsSi}_7$	100.82(5)	$\text{C}81\text{Si}_8\text{C}82$	107.0(3)
$\text{Si}_3\text{Si}_2\text{As}$	115.98(7)		

Table 4  
Chemical shifts [ppm] and coupling constants [Hz] of tridecamethyl-1-phospho- and tridecamethyl-1-arsa-2,3,4,5,6,7,8-heptasilabicyclo[2.2.2]octane

	$\delta(\text{Si})$	$\delta(^{13}\text{C})$	$\delta(^{\circ}\text{Si})$	$\delta(^{13}\text{C})$	$\delta(^{\circ}\text{Si})$	$\delta(^{\circ}\text{C})$	$\delta(^3\text{P})$	$J(\text{P(Si)})$	$J(\text{P}^{\circ}\text{Si})$	$J(\text{Si}^{\circ}\text{Si})$	$J(\text{C}^{\circ}\text{Si}^{\circ}\text{Si})$	$^2J(\text{Si}^{\circ}\text{Si})$
$\text{P(SiMe}_2\text{SiMe}_2)_3 \cdot \text{SiMe}^a$	-18.5	+2.6	-44.5	-2.5	-82.1	-14.7	-238.7	37.0	5.1	66.7	51.4	9.0
$\text{As(SiMe}_2\text{SiMe}_2)_3 \cdot \text{SiMe}^a$	-19.7	+2.2	-44.3	-2.7	-81.0	-14.6				71.9	50.0	6.1
$(\text{PhMe}_2\text{Si}^b \cdot \text{SiMe}_2)_3 \cdot \text{SiMe}^b$	-17.4		-39.7		-71.9					77.4	53.3	7.9
$(\text{TfMe}_2\text{Si}^c \cdot \text{SiMe}_2)_3 \cdot \text{SiMe}^c$	45.6		-39.6		-75.4					78.5	52.5	6.5
$(\text{CfMe}_2\text{Si}^d \cdot \text{SiMe}_2)_3 \cdot \text{SiMe}^d$	26.8		-37.6		-75.9							

$^a \cdot ^2J(\text{PC}) = 17.5$ ;  $^b \cdot ^2J(\text{Si}^{\circ}\text{Si}) = 1.8$ ;  $^c \cdot ^2J(\text{Si}^{\circ}\text{Si}) = 2.4$ ;  $^d \cdot ^2J(\text{Si}^{\circ}\text{Si}) = 2.4$ .

sional vibration) is frozen in the solid state. The two minima of the associated double minimum potential characterize the two enantiomers.

## 5. Experimental details

### 5.1. Techniques

All operations were carried out under a nitrogen atmosphere, solvents were distilled from potassium. The C, H analyses were carried out on a Heraeus Micro U apparatus (tolerances  $\pm 0.3\%$  C,  $\pm 0.2\%$  H). Despite the addition of  $\text{PbBO}_3$  for complete fusion, the measured carbon content of  $(\text{PhMe}_2\text{SiSiMe}_2)_3\text{SiMe}$  fell below the tolerance, presumably due to the formation of silicon carbide.

### 5.2. Synthesis of $(\text{PhMe}_2\text{SiSiMe}_2)_3\text{SiMe}$

25.96 g (95.96 mmol) of  $\text{Me}_2\text{PhSiSiPhMe}_2$  was dissolved in 200 ml of THF and 4.0 g of powdered lithium was added at  $-10^\circ\text{C}$ . The solution turned dark immediately and was stirred overnight at  $-10^\circ\text{C}$ . Excess lithium was then filtered off and the solvent removed in vacuo. The solid residue was suspended in 500 ml of heptane and a solution of 20 g (61.73 mmol) of  $\text{MeSi(SiMe}_2\text{Cl)}_3$  in 500 ml of heptane was added dropwise at  $-20^\circ\text{C}$ . After completion, the reaction mixture was refluxed for 5 h. Subsequently, the salts and solvent were removed by filtration and distillation respectively, and the yellowish oily residue was fractionated in vacuo to give 17.3 g (45%) of a colourless liquid, b.p.<sub>0.05</sub> = 230–240°C.

Anal. Found: C, 58.76; H, 8.84. Calc.: C, 59.73; H, 8.73%.

### 5.3. Synthesis of $(\text{CF}_3\text{O}_2\text{SO}_2\text{SiMe}_2\text{SiMe}_2)_3\text{SiMe}$

10 g (16.04 mmol) of  $(\text{PhMe}_2\text{SiSiMe}_2)_3\text{SiMe}$  was dissolved in 150 ml of pentane. At a temperature of  $-40^\circ\text{C}$ , 7.2 g (48.13 mmol) of  $\text{CF}_3\text{SO}_2\text{H}$  was added quickly. After stirring for another 2 h at  $-40^\circ\text{C}$ , the solvent was removed in vacuo. According to the  $^{29}\text{Si}$  NMR spectra, the residue consists of pure  $(\text{CF}_3\text{SO}_2\text{Me}_2\text{SiSiMe}_2)_3\text{SiMe}$ , which was used immediately for the preparation of  $(\text{CfMe}_2\text{SiSiMe}_2)_3\text{SiMe}$ .

### 5.4. Synthesis of $(\text{CfMe}_2\text{SiSiMe}_2)_3\text{SiMe}$

5.3 g (15.49 mmol) of tris(trifluoromethanesulfonyloxy)heptasilane was suspended in approximately 200 ml of  $\text{Et}_2\text{O}$  and 5 g (18.3 mmol) of  $\text{LiCl}$  was added at  $0^\circ\text{C}$ . After stirring overnight ( $0^\circ\text{C}$ ), the solution was decanted from  $\text{LiCl}$  and the solvent removed in vacuo. The residue was dissolved in heptane and fil-

tered. After removal of the heptane, a semicrystalline solid of pure  $(\text{ClMe}_2\text{SiSiMe}_2)_3\text{SiMe}$  was isolated. Yield 7.3 g (95%).

#### 5.5. Synthesis of $P(\text{SiMe}_2\text{SiMe}_2)_3\text{SiMe}$

0.37 g (12.04 mmol) of white phosphorus was suspended in 50 ml of dimethoxyethane (DME) and 1.08 g (36.11 mmol) of sodium potassium alloy (4:3) was added. After refluxing for 12 h, 6.0 g (12.04 mmol) of  $(\text{ClMe}_2\text{SiSiMe}_2)_3\text{SiMe}$  in 50 ml of DME was added dropwise. The reaction mixture was refluxed for another 18 h. The salts were then filtered by suction and the solvent removed in vacuo. 25 ml of heptane was added and the remaining salts were removed by filtration. Crystallization at  $-70^\circ\text{C}$  yields 2.42 g (48%) of pure  $P(\text{SiMe}_2\text{SiMe}_2)_3\text{SiMe}$  as colourless crystals.

Anal. Found: C, 36.25; H, 9.27. Calc.: C, 36.91; H, 9.29%.

#### 5.6. Synthesis of $\text{As}(\text{SiMe}_2\text{SiMe}_2)_3\text{SiMe}$

0.9 g (12.04 mmol) of powdered arsenic was suspended in 50 ml of DME and 1.08 g (36.11 mmol) of sodium potassium alloy (4:3) was added. The reaction mixture was refluxed for two days. Three times per day, the mixture was activated using an ultrasonic bath. After this time, 6.0 g (12.04 mmol) of  $(\text{ClMe}_2\text{SiSiMe}_2)_3\text{SiMe}$  dissolved in 50 ml of DME was added dropwise without interrupting the reflux. The refluxing was carried on for 12 h, followed by a removal of the salts by filtration and an evaporation of the solvent. Again, 25 ml of heptane was added and the remaining salts were separated by filtration. Crystallization at  $-70^\circ\text{C}$  yields 1.7 g (30%) of yellowish crystals of  $\text{As}(\text{SiMe}_2\text{SiMe}_2)_3\text{SiMe}$ .

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