Organometallics 1993, 12, 3527-3530

Silylated Aminoarsenates with Novel and Conventional Structures

Michael Baier, Martin Paul, and Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Received May 18, 1993®

The reaction of tris(trimethylsilyl) arsenate(V) and heptamethyldisilazane yields hexamethyldisiloxane and a crystalline adduct [$(Me_3SiO)_3AsO{\cdot}(Me_3SiO)_3As{=}NMe$] (2). The crystal structure of 2 features a planar four-membered ring $OAs_2N(Me)$ with two pentacoordinate arsenic atoms bridged symmetrically (point group C_2) by an oxygen atom and the methyl*imino* group. In benzene solution, compound 2 is dissociated into the components $(Me_3SiO)AsO$ and the *imino* compound $(Me_3SiO)_3As{=}NMe$, which isomerizes to give the *amino* isomer $(Me_3SiO)_2AsO[N(Me)SiMe_3]$. $(Me_3SiO)_3AsO$ reacts with (trimethylsilyl)aniline to give again $(Me_3Si)_2O$ and bis(trimethylsilyl) (phenylamino)arsenate(V) (4). In the solid state two crystallographically nonequivalent aminoarsenate molecules $(Me_3SiO)_2AsO[N(H)Ph]$ with tetracoordinate arsenic atoms are associated into dimers via two N—H···O hydrogen bonds.

Introduction

The structural chemistry of arsenic(V) acids is only poorly developed because of the confusing diversity of stoichiometries and structures encountered in all attempts to systematize the experimental data. While standard phosphoric acids are all strictly based on tetrahedrally oxo-coordinated phosphorus, and antimonyl(V) acids on octahedrally oxo-coordinated antimony centers, the corresponding arsenic systems feature not only tetra- *and* hexacoordinate but also pentacoordinate As(V).[1] The modifications of arsenic(V) oxide, As_2O_5, are examples in case, where more than one coordination mode is represented.[2] Although there are a large variety of discrete P_2O_5 phases, none of these contains phosphorus in a coordination number in excess of 4.

Following earlier work on simple silyl arsenates,[3-5] we have recently initiated a series of studies on related condensed systems.[6] The trimethylsilyl derivatives were chosen because of the special properties of the Me_3Si^+ group, which has many functional similarities with the proton H^+. Most notable is its mobility in oxo systems leading inter alia to facile intra- and intermolecular rearrangements ("silyl shifts" vs "proton shifts"). Trimethylsilyl groups are also good leaving groups in substitution reactions and allow transformations under mild conditions. Finally, elimination of hexamethyldisiloxane $(Me_3Si)_2O$ from trimethylsilylated precursor substrates is a preferred mode of condensation, resembling directly the elimination of water (H_2O) from oxo acids.

In previous reports we have described the condensation of tris(trimethylsilyl) arsenate(V) to give a tetrakis(trimethylsilyl) diarsenate(V),[6] which appears as a dimer with tetra-*and* hexacoordinated As(V) centers. From the reactions of these pure oxo systems with disilazanes, related silylated arsazenes with surprisingly stable arsenic/nitrogen ring systems with solely tetracoordinate As(V) could be obtained.[7] In the present paper mixed oxo/aza species with pentacoordinate arsenic(V) are presented, together with a related mononuclear silyl arsonate.

Alkyl/aryl arsenates[8-12] and aminoarsenates[13-15] have been the subject of a number of studies in the past, but the structural chemistry remained virtually unexplored. It was only in very recent investigations that crystal structures have been determined for a few arylated compounds,[16-21] but only one silylated species[19,21] has been included in this work.

Results

The Addition Compound of Tris(trimethylsilyl) Arsenate and Tris(trimethylsilyl) (Methylimino)-arsenate. In an attempt to synthesize silyl derivatives of aminoarsenic acid, $(HO)_2(H_2N)As{=}O$ [or its tautomer: iminoarsenic acid, $(HO)_3As{=}NH$], the oxo analogue $(Me_3SiO)_3As{=}O$ was reacted with *hexa*methyldisilazane (eq 1). Unexpectedly, this condensation reaction led to the cyclic arsazene compound 1 with elimination of hexa-

---

® Abstract published in *Advance ACS Abstracts*, August 15, 1993.

[1] Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, U.K., 1987; pp 900–902.

[2] Jansen, M. *Z. Anorg. Allg. Chem.* **1978**, *441*, 5.

[3] Schmidbaur, H. *Angew. Chem.* **1965**, *77*, 206; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 201.

[4] Schmidt, M.; Ruidisch, I.; Schmidbaur, H. *Chem. Ber.* **1961**, *94*, 2451. Schmidt, M.; Schmidbaur, H. *Angew. Chem.* **1959**, *71*, 553.

[5] Schmidbaur, H.; Arnold, H. S.; Beinhofer, E. *Chem. Ber.* **1964**, *97*, 449.

[6] Baier, M.; Bissinger, P.; Schmidbaur, H. *Chem. Ber.* **1992**, *125*, 373.

[7] Baier, M.; Bissinger, P.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 351.

[8] Crafts, J. M. *Bull. Soc. Chim. Fr.* **1870**, *14*, 99.

[9] Kamai, G. Kh.; Kuz'min, K. J. *Zhur. Khim.* **1955**, 528.

[10] Frøyen, P.; Møller, J. *J. Org. Mass Spectrom.* **1974**, *9*, 132.

[11] Hass, D. *Z. Chem.* **1965**, *5*, 426.

[12] Klepp, M.; Schmid, L. *Monatsh. Chem.* **1968**, *99*, 658.

[13] Winkler, A. *Z. Anorg. Allg. Chem.* **1963**, *322*, 193.

[14] Hass, D. *Z. Anorg. Allg. Chem.* **1965**, *335*, 297.

[15] Gamayurova, V. S.; Daineko, Z. G.; Chernokal'skii, B. D.; Shagidullin, R. R.; Lamanova, I. A.; Avvakumova, L. V. *Zh. Obshch. Khim.* **1974**, *44*, 1537.

[16] Kokorev, G. I.; Litvinov, I. A.; Musin, R. Z.; Naumov, V. A. *Zh. Obshch. Khim.* **1991**, *61*, 2713.

[17] Kokorev, G. I.; Litvinov, I. A.; Naumov, V. A. *Zh. Obshch. Khim.* **1991**, *61*, 450.

[18] Kokorev, G. I.; Litvinov, I. A.; Naumov, V. A.; Yambushev, F. D. *Zh. Obshch. Khim.* **1987**, *57*, 354.

[19] Roesky, H. W.; Bohra, R.; Sheldrick, W. S. *J. Fluorine Chem.* **1983**, *22*, 199.

[20] Bohra, R.; Roesky, H. W.; Lucas, J.; Noltemeyer, M.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1011.

[21] Bohra, R.; Roesky, H. W. *J. Fluorine Chem.* **1984**, *25*, 145.

0276-7333/93/2312-3527$04.00/0

$$6(Me_3SiO)_3AsO + 9(Me_3Si)_2NH \rightarrow 12(Me_3Si)_2O + 3NH_3 + \underset{\mathbf{1}}{2(Me_3SiO)_6As_3N_3} \quad (1)$$

methyldisiloxane and ammonia.[7] In order to avoid this condensation at nitrogen, the same type of reaction has now been carried out with *hepta*methyldisilazane (eq 2).

$$2(Me_3SiO)_3AsO + (Me_3Si)_2NMe \rightarrow (Me_3Si)_2O + \underset{\mathbf{2}}{(Me_3SiO)_3AsO{\cdot}(Me_3SiO)_3AsNMe} \quad (2)$$

The formation of $Me_3SiOSiMe_3$ was again observed (NMR, GC/MS), and the crystalline product isolated from the reaction mixture was indeed found to contain tris(trimethylsilyl) (methylimino)arsenate, $(Me_3SiO)_3As{=}NMe$, but in the form of its 1:1 addition compound with tris(trimethylsilyl) arsenate $(Me_3SiO)_3As{=}O$ (**2**).

Compound **2** is obtained as a colorless crystalline solid in 61% yield. It is stable when stored at low temperature but decomposes when kept at room temperature to give an insoluble, probably polymeric condensation product and hexamethyldisiloxane. The composition of the *solid* material has been confirmed by elemental analysis and CI mass spectral data. Although no molecular ion of the adduct has been observed, several fragment ions exceeding the mass of each of the two components and containing (trimethylsilyl)oxo and both oxo *and* methylimino moieties provide evidence for the association of the two components (**2**).

NMR investigations of benzene solutions have shown, however, that partial dissociation into the components occurs in this solvent (eq 3). Two sets of signals (^1H, ^{13}C)

$$\underset{\mathbf{2}}{(Me_3SiO)_3AsO{\cdot}(Me_3SiO)_3AsNMe} \rightleftharpoons (Me_3SiO)_3As{=}O + \underset{\mathbf{3}}{(Me_3SiO)_2[(Me_3Si)MeN]As{=}O} \quad (3)$$

are detected which can be assigned to $(Me_3SiO)_3As{=}O$, for which reference data are available, and to $(Me_3SiO)_2[NMe(SiMe_3)]As{=}O$ (**3**), the silyl-shifted (O–N) isomer of $(Me_3SiO)_3As{=}NMe$. The structure of the crystalline compound **2** has been determined by single crystal X-ray diffraction.

Crystals of **2** are orthorhombic, acentric space group *Fdd*2, with $Z = 8$ formula units in the unit cell. The lattice is built from dinuclear molecules $(Me_3SiO)_6As_2O(NMe)$. The structure is shown in Figure 1. The complex has a crystallographic 2-fold axis passing through the oxygen and nitrogen atoms bridging the two arsenic atoms to give a four-membered ring (planar by symmetry), and through the *N*-methyl carbon atom. (Again by symmetry, the hydrogen atoms attached to this carbon atom are disordered.)

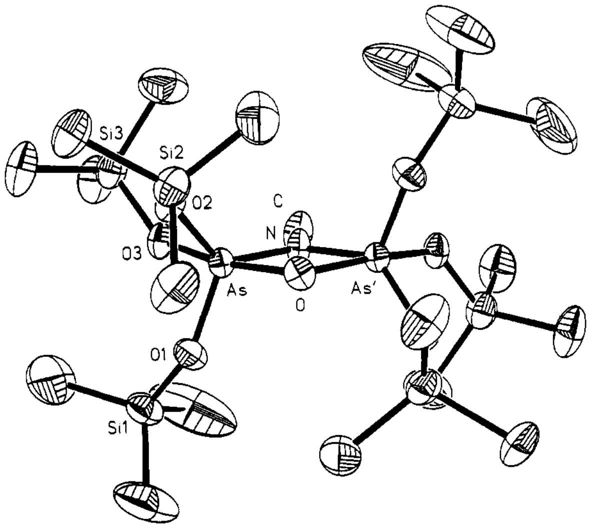

Figure 1. Molecular structure of compound **2** (ORTEP). Hydrogen atoms are omitted for clarity. The molecule has a crystallographic 2-fold axis. Selected bond distances (Å) and angles (deg): As–O1 1.716(2), As–O2 1.730(2), As–O3 1.780(2); As–O 1.819(2), As–N 1.819(2), C–N 1.448(5); Si1–O1 1.646(2), Si2–O2 1.669(2), Si3–O3 1.648(3); N–As–O 79.7(1), As–O–As′ 100.4(1), As–N–As′ 100.3(2), C–N–As 129.8(1); Si1–O1–As 135.3(1), Si2–O2–As 132.3(1), Si3–O3–As 132.2(1).

The two arsenic atoms are pentacoordinated with their five substituents at the vertices of a distorted trigonal bipyramid. One (trimethylsilyl)oxy group (O3) and the bridging oxygen atom (O) occupy axial positions, while the remaining two silyloxy groups (O1, O2) and the nitrogen atom are in equatorial positions. The distance As–O3 (axial) [1.789(2) Å] is significantly longer than the two bonds As–O1 and As–O2 (equatorial) [1.716(2) and 1.730(2) Å]. The As–O distances in the bridge As–O–As [1.819(2) Å] are even longer than any of the three As–O(Si) distances, and the As–O–As′ angle is 100.4(1)°. The coordination at nitrogen is planar (by symmetry) with an As–N–As′ angle of 100.3(2)°. The N–As–O angles are thus compressed to 79.7(1)°, the major origin of the distortion of the trigonal bipyramid at arsenic.

The three (trimethylsilyl)oxy groups have very similar Si–O–As angles and Si–O distances, representing a virtually strain-free situation.

On the basis of this result, compound **2** can, in fact, be identified as an adduct of the two components $(Me_3SiO)_3As{=}O$ and $(Me_3SiO)_3As{=}NMe$, but with a complete transformation of the two double bonds into components of a symmetrical four-membered ring following the representation of a standard [2+2] cycloaddition. Nevertheless, this association appears to be reversible, as shown in the NMR experiments with benzene solutions. This dissociation is accompanied by isomerization of the imino component to give the methyl(trimethylsilyl)*amino*/oxo compound instead of the ((trimethylsilyl)oxy) (methyl*imino*) compound (above).

It is interesting to note that a structure like that now detected for **2** has already been tentatively assigned to the associated alkylimino–alkyl arsenates $(MeO)_6As_2O(N\text{-}i\text{-}Pr)$ and $(MeO)_6As_2O(N\text{-}n\text{-}Bu)$.[22,23] This proposal has now been fully confirmed by the present analysis. Bis(imino)-bridged organoarsenates(V) with As_2N_2 four-membered rings have also been established.[16,19,20,24,25]

***O*,*O*-Bis(trimethylsilyl) (Phenylamino)arsenate [$(Me_3SiO)_2(PhNH)AsO$].** In order to assess the influence of the N substituent on isomerism and the structure of aminoarsenates, the reaction tris(trimethylsilyl) arsenate with *N*-(trimethylsilyl)aniline has also been studied. The two components were found to react smoothly to give hexamethyldisiloxane and bis(trimethylsilyl) (phenylamino)arsenate (**4**).

---

[22] Hass, D. *Z. Chem.* **1967**, *7*, 465.
[23] Preiss, H.; Jancke, H. *Z. Anorg. Allg. Chem.* **1974**, *404*, 199.
[24] Hass, D.; Cech, J. *Z. Chem.* **1969**, *9*, 432.
[25] Hass, D. *Z. Anorg. Allg. Chem.* **1966**, *347*, 123.

$$(Me_3SiO)_3AsO + Me_3SiNHPh \rightarrow (Me_3Si)_2O + (Me_3SiO)_2(PhNH)AsO \quad (4)$$

$$\mathbf{4}$$

Compound 4 was isolated as a colorless crystalline solid, which decomposes at 100 °C. Its composition and structure follows from the elemental analysis, its mass spectrum, its IR absorptions, and its NMR characteristics (Experimental Part). Details of the molecular geometry have been determined by a single crystal X-ray diffraction study.

The compound crystallizes in the monoclinic space group $P2_1/c$ with two independent formula units in the asymmetric unit. The two molecules (A and B) are linked through two N–H···O hydrogen bonds to give dimers (Figure 2). The two monomers (A and B) have very similar structures. The arsenic atoms are in a slightly distorted tetrahedral environment of three oxygen atoms and one nitrogen atom. In both cases one of the oxygen atoms is clearly a double-bonded atom [As1–O13 and As2–O23: 1.626(3) Å]. For comparison, the single-bonded oxygen atoms have significantly longer As–O distances [As1–O11 1.707(2), As1–O12 1.705(3) Å; As2–O21 1.711(3), As2–O22 1.702(3) Å]. The distances As1–N1 and As2–N2 are in the range established for As–N single bonds [1.776(3) and 1.754(4) Å, respectively]. The positions of the N-bound hydrogen atoms have been detected in the structure determination and could be refined satisfactorily such that reliable dimensions can be given for the N–H···O bridges.

The structure of the aryl-substituted compound 4 is thus confirmed to be based on the *amide* form of aminoarsenic acid $(HO)_2(H_2N)As{=}O$, instead of the *imino* isomer $(HO)_3As{=}NH$ found as a component in the alkyl derivative 2. Clearly, the electronic effect of the substituent is governing the isomerization equilibrium in aminoarsenic acid derivatives with hydrogen atoms and silyl groups (mobile as H^+ and Me_3Si^+) as coligands. It should be noted, however, that the free monomeric nitrogen component 3 contained in benzene solutions of 2 also appears in the amino form. The imino isomer seems to be favored only in cases where the N-donor properties allow dimerization or adduct formation (2).[17]

Experimental Part

All experiments were carried out under an atmosphere of dry nitrogen. Solvents were purified, dried, and saturated with nitrogen. Glassware was oven-dried and filled with nitrogen. Instruments: NMR, JEOL GX 400 spectrometer; MS, Varian MAT 311A; IR, Nicolet FX 354.

Reaction of $(Me_3SiO)_3As{=}O$ with $(Me_3Si)_2NMe$. Tris(trimethylsilyl) arsenate[4] (2.26 g, 6.30 mmol) is mixed with heptamethyldisilazane (1.11 g, 6.30 mmol) at room temperature. The mobile liquid mixture slowly becomes more viscous. After 30 min it is heated to 80 °C for 90 min. On cooling, a colorless crystal cake is obtained, which is dissolved in a minimum of hexane. Cooling this solution to −20 °C affords colorless crystals, which are filtered, washed with very little cold hexane, and dried in vacuum; yield 1.4 g (61%). The product (2) slowly decomposes at room temperature but is stable when kept in the refrigerator (−25 °C). ^1H NMR (C_6D_6, 20 °C): δ 0.24 ppm [s, 27H, $(Me_3SiO)_3AsO$], 0.23 [s, 9H, Me_3SiN of 3], 0.28 [s, 18H, Me_3SiO of 3], 2.64 [s, 3H, NMe of 3]. $\{^1H\}^{13}C$ NMR (C_6D_6, 20 °C): δ 1.41 [s, $(Me_3SiO)_3AsO$], 0.31 [s, Me_3SiN of 3], 1.65 [s, Me_3SiO of 3], 30.82 [s, NMe of 3]. MS (CI): m/z 567.4 (1%) [2 − $(Me_3Si)_2O$], 551.4 (2%) [$(Me_3SiO)_4As_2O(NMe)$], 372.3 (35%) [3 + 1], 359.3 (83%) [$(Me_3SiO)_3AsO$ + 1]. Anal. Calcd for $C_{19}H_{57}As_2NO_7Si_6$ (73.02): C, 31.26; H, 7.87; N, 1.92; Si, 23.08. Found: C, 30.96; H, 7.80; N, 1.95; Si, 22.92.

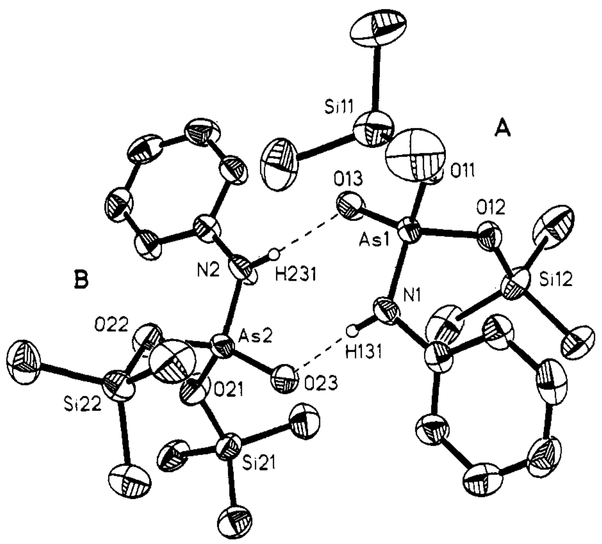

Figure 2. Molecular structure of compound 4. Two crystallographically independent molecules A and B (of very similar structure) are linked through hydrogen bonds. Hydrogen atoms (except hydrogen-bonded cases) are omitted for clarity. Selected bond distances (Å) and angles (deg): As1–N1 1.776(3), As2–N2 1.754(4), As1–O11 1.707(2), As2–O21 1.711(3), As1–O12 1.705(3), As2–O22 1.702(3), As1–O13 1.626(3), As2–O23 1.626(3), O13–H231 1.852(6), O23–H131 2.021(5); Si11–O11–As1 131.3(2), Si21–O21–As2 129.6(2), Si12–O12–As1 131.6(2), Si22–O22–As2 132.0(2), N1–H131–O23 177.9(3), N2–H231–O13 170.6(6).

Table I. Crystal and Structure Solution Data for Compounds 2 and 4

	2	4
formula	$C_{19}H_{57}As_2NO_7Si_6$	$C_{12}H_{24}AsNO_3Si_2$
fw	730.04	361.42
temp (°C)	−65	−46
space group	*Fdd*2	$P2_1/c$
a (Å)	10.100(1)	11.891(1)
b (Å)	43.850(4)	16.708(1)
c (Å)	17.508(2)	18.119(1)
α (deg)	90	90
β (deg)	90	92.54(1)
γ (deg)	90	90
V (Å^3)	7754.0	3598.7
ρ_{calc} (g cm^{-3})	1.25	1.34
Z	8	8
F(000) (e)	3072	1504
μ(Mo Kα) (cm^{-1})	19.4	20.2
diffractometer	CAD4	CAD4
hkl range	+12,+56,±22	+15,+21,±23
no. of measd reflns	4576	8496
no. of unique reflns	4090	6960
R_{int}	0.029	0.020
no. of obsd reflns	3872	5729
$F_o \geq$	$4\sigma(F_o)$	$3\sigma(F_o)$
no. of refined params	160	535
weighting params $1/k$	1/0.00223	1/0
H atoms (found/calc)	−/57	24/−
R (R_w)	0.026 (0.029)	0.034 (0.034)
$\Delta\rho_{fin}$(max/min) (e Å^{-3})	+0.70/−0.92	+0.40/−0.36

Reaction of $(Me_3SiO)_3AsO$ with $Me_3SiNHPh$. Tris(trimethylsilyl) arsenate (2.2 g, 6.14 mmol) is mixed with *N*-(trimethylsilyl)aniline (1.09 g, 6.14 mmol) at room temperature and slowly heated to 90 °C. A small amount of a colorless precipitate is formed. After cooling to room temperature, the viscous reaction mixture is treated with diethyl ether (20 mL) and filtered. The residue is washed with diethyl ether and the solvent is removed from the ether extracts in vacuum. The remaining solid (4) is recrystallized twice from hexane, yield 1.2 g (55%), decomposition temperature 100 °C. ^{1}H NMR (C_6D_6, 20 °C): δ = 0.25 [s, 18H, Me], 6.69–7.60 [m, 5H, Ph]. {^{1}H}^{13}C NMR (C_6D_6, 20 °C): δ 1.42 [s, Me], 142.6, 118.3, 129.4, and 121.5 [s for C1–C4 of Ph]. ^{29}Si NMR (C_6D_6, 20 °C): δ 24.86 [dec, J(Si,H) = 6.85 Hz]. MS (CI): m/z 360.0 (1.4%) [4 − 1], 285.0 (100%) [$(Me_3Si)_2AsO(NH_2)$], 269.3 (4.6%) [$(Me_3SiO)_2AsO$]. Anal. Calcd for $C_{12}H_{24}AsNO_3Si_2$ (361.42): C, 39.88; H, 6.69; N, 3.88; Si, 15.54. Found: C, 39.78; H, 6.72; N, 3.86; Si, 15.50.

Crystal Structure Determination of Compounds 2 and 4. Crystal and structure solution data have been summarized in Table I.

Acknowledgment. This work has been supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. The authors are indebted to Mr. J. Riede for establishing the X-ray data sets.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles (10 pages). Ordering information is given on any current masthead page.

OM930333N