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Journal of Organometallic Chemistry 614–615 (2000) 70–73

Journal of Organometallic Chemistry

Communication

Homoleptic triisopropylsilylarsandiides of magnesium and divalent tin

Matthias Westerhausen *, Nikolaos Makropoulos, Holger Piotrowski,
Marcus Warchhold, Heinrich Nöth

Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 9 (Haus D), D-81377 München, Germany

Dedicated to Professor Sheldon Shore on the occasion of his 70th birthday.

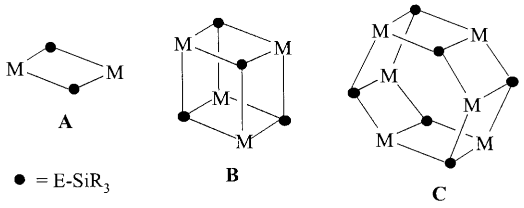
Abstract

The magnesiation of $H_2As–Si^{i}Pr_3$ yields the tetramer $[(THF)MgAsSi^{i}Pr_3]_4$ (**1**) with a central Mg_4As_4 heterocubane moiety. The reaction of $Sn[N(SiMe_3)_2]_2$ with triisopropylsilylarsane gives the hexamer $[SnAsSi^{i}Pr_3]_6$ (**2**) with an inner hexagonal Sn_6As_6 prism. The molecular structures of both these compounds have been determined. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Arsenic; Cage compounds; Magnesium; Metalations; Tin

1. Introduction

Homoleptic metal imides and phosphandiides of divalent metals of the type $[(L)_mM{=}ER]_n$ are not monomeric but form oligomers and cage compounds. The reaction of AlCp* with triisopropylsilylazide yields $[Cp^*Al–NSi^{i}Pr_3]_2$ [1] with an Al_2N_2 cycle ($n = 2$, **A**) whereas the monomeric species ($n = 1$) with an M=E double bond is still unknown. The structure **B** with a central M_4E_4 heterocubane moiety was observed for compounds with steric demanding substituents. Examples from the nitrogen chemistry include molecules such as a wide variety of tin imides [2] whereas homoleptic magnesium imides [3] adopt structures of the type **C**. The phosphorus containing heterocubane structures include molecules such as $[(THF)Mg–PSiR_3]_4$ with R as isopropyl [4] and *tert*-butyl [5] and $[Sn–PSi^{t}Bu_3]$ [6]. Solvent-free magnesium tri(*tert*-butyl)silylphosphandiide crystallizes hexameric with a slightly distorted hexagonal Mg_6P_6 prism [7]. In addition, hexameric $[SnPSi^{i}Pr_3]_6$ [8] as well as compounds of the type $[HM–ESi^{i}Pr_3]_6$ (M = Al, E = P, As; M = Ga, E = As [9]) also show distorted hexagonal M_6E_6 prisms (Scheme 1).



Scheme 1. Schematic structures derived from $M{=}E–SiR_3$ ($M = M^{II}$, $R'M^{III}$; E = pnictogen): dimer $[ME–SiR_3]_2$ (**A**) with a M_2E_2 cycle, tetramer $[ME–SiR_3]_4$ (**B**) with a M_4E_4 heterocubane moiety, hexamer $[ME–SiR_3]_6$ (**C**) with a hexagonal M_6E_6 prism.

Investigations dealing with molecules which contain magnesium or tin arsenic bonds are up to the present quite rare. The magnesiation of bis(trimethylsilyl)arsane in THF yields $(THF)_2Mg[As(SiMe_3)_2]_2$ with a mean Mg–As bond length of 259 pm [10]. Depending on the steric demand of the substituents monomeric [11] and dimeric tin(II) bis(arsanides) [12] are well-known. Here we report the arsandiides of magnesium and divalent tin with metal–arsenic cages.

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* Corresponding author. Tel.: + 49-89-5902638; fax: + 49-241-5902578.

E-mail address: maw@cup.uni-muenchen.de (M. Westerhausen).

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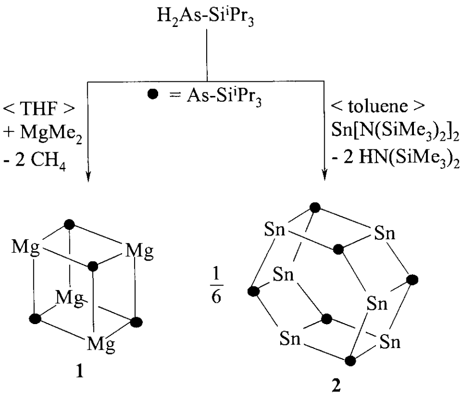
PII: S0022-328X(00)00631-8

2. Synthesis

The magnesisation of triisopropylsilylarsane [13] with dimethylmagnesium in THF yields quantitatively the tetramer $[(THF)MgAsSi^{i}Pr_3]_4$ (**1**) with a central Mg_4As_4 heterocubane fragment (Scheme 2). The reaction of tin(II) bis[bis(trimethylsilyl)amide] with $H_2AsSi^{i}Pr_3$ in toluene gives a deep red solution. After reduction to a few milliliters, blue–violet crystals of $[SnAsSi^{i}Pr_3]_6$ (**2**) with a hexagonal Sn_6As_6 prism precipitate.

Both these compounds have no melting points; at temperatures above 250°C the substances turn dark and decompose. Furthermore, the NMR parameters of the isopropyl substituents seem not to be dependent on the metal or the oligomerization degree. Therefore, the molecular structures of **1** and **2** were determined by X-ray crystallography.



Scheme 2. Synthesis of (tetrahydrofuran)magnesium triisopropylsilylarsandiide (**1**) and tin(II) triisopropylsilylarsandiide (**2**).

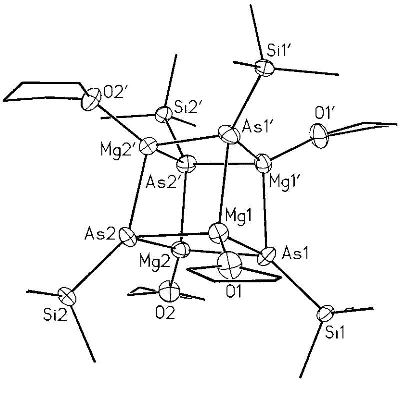


Fig. 1. Molecular structure of **1**. The ellipsoids of non-carbon and non-H atoms represent a probability of 40%, the methyl groups are omitted for clarity reasons. Selected bond lengths [pm]: Mg1–As1 260.1(2), Mg1–As2 261.3(2), Mg1–As1′ 262.2(2), Mg1–O1 202.9(4), Mg2–As1 260.8(2), Mg2–As2 261.3(2), Mg2–As2′ 262.2(2), Mg2–O2 203.7(4), As1–Si1 227.2(2), As2–Si2 227.7(1).

3. Molecular structures

The molecular structure of **1** and the numbering scheme are represented in Fig. 1. The molecule exhibits crystallographic C_2 symmetry, atoms generated by this symmetry operation are marked with apostrophes. The magnesium atoms are coordinated distorted tetrahedrally with AsMgAs angles between 97.0 and 100.3°. The Mg–O distances with values of 203 pm lie in the characteristic range [14].

The Mg–As bond lengths in **1** of approximately 262 pm are slightly elongated compared to those in $(THF)_2Mg[As(SiMe_3)_2]_2$ with values of 259 pm. This is a consequence of the coordination number of four at the arsenic atom in **1** and the bulkiness of the triisopropylsilyl group. In contrast to this fact, the As–Si bonds of 227.5 pm are shorter than those in the above mentioned monomeric magnesium bis(arsanide) with a mean value of 232.4 pm. The elongation of the Mg–As bonds on the one hand and the reduction of the As–Si distances on the other hand are a result of electrostatic repulsion between the dianions and electrostatic attraction between the dianionic arsenic and the positively charged silicon atoms.

The molecular structure of **2** and the numbering scheme are shown in Fig. 2. This molecule adopts crystallographic C_{2v} symmetry with an inversion center in the center of the slightly distorted hexagonal Sn_6As_6 prism. The atoms generated by the mirror plane (x, y, z) are marked with apostrophes (‘), those produced by the inversion center $(-x, -y+1, -z)$ are marked with two apostrophes (“), whereas the atoms generated by applying of the C_2 symmetry $(-x, -y+1, z)$ are marked with a number symbol (#).

The tin atoms show a pyramidal coordination sphere, the arsenic atoms are surrounded distorted tetrahedrally. The As–Si bond lengths (235.5 pm) are greater than found in **1** but similar to those observed in dimeric

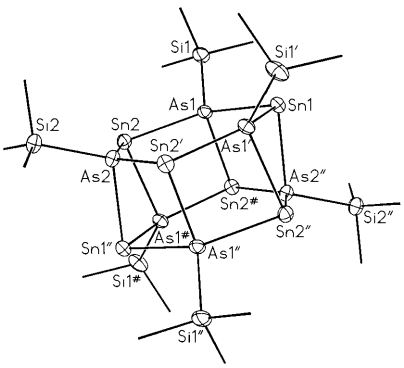


Fig. 2. Molecular structure of **2**. The ellipsoids of all heavier atoms represent a probability of 40%, methyl groups and hydrogen atoms are not drawn for clarity reasons. Selected bond lengths [pm]: Sn1–As1 270.83(9), Sn1–As1′ 270.83(9), Sn1–As2″ 272.9(1), Sn2–As1 270.36(9), Sn2–As2 271.35(6), Sn2–As1# 274.22(9), As1–Si1 235.4(2), As2–Si2 235.6(3).

$Sn[As(SiMe_3)_2]_2$ [12]. The higher covalency of the Sn–As bonds reduces the charge on the arsenic atoms and as a consequence also the electrostatic attraction between the arsenic and silicon atoms. The Sn–As distances of **2** are similar to those of the terminal arsanide ligands in $\{Sn[As(SiMe_3)_2]_2\}_2$ whereas the Sn–As^b bond lengths of the bridging arsanide substituents are elongated by approximately 6 pm [12].

4. Summary

The magnesiation of triisopropylsilylarsane in THF yields tetrameric (tetrahydrofuran)magnesium triisopropylsilylarsandiide (**1**). The metalation of $H_2As–Si^iPr_3$ with tin(II) bis[bis(trimethylsilyl)amide] gives hexameric tin triisopropylsilylarsandiide (**2**). The homologous metal phosphorus cages show similar geometries. Although both the tin compounds show very similar hexagonal Sn_6E_6 prisms, $[SnPSi^iPr_3]_6$ crystallized in the centrosymmetric triclinic space group $P\bar{1}$ with the inversion center in the center of the molecule and the homologous arsenic derivative precipitated in the tetragonal space group $P4_2/m$. Here the Sn_6As_6 cage contains an additional mirror plane and a C_2 axis, the molecule adopts crystallographic C_{2v} symmetry.

5. Experimental

5.1. General

All experiments and manipulations were carried out under an atmosphere of argon. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The starting $H_2AsSi^iPr_3$ was prepared by a literature procedure [13]. NMR spectra were recorded on JEOL spectrometers GSX270 and EX400. A Nicolet 520 FT-IR spectrophotometer was used to record the IR spectra; solid substances were measured in Nujol between KBr plates (vs, very strong; s, strong; m, medium strong; w, weak; vw, very weak; sh, shoulder). The low carbon values at the elemental analysis result from carbide and carbonate formation as well as loss of neutral coligands during handling and combustion of the compounds.

5.2. *Tetrakis[(tetrahydrofuran)-magnesium-triisopropylsilylarsandiide]* (**1**)

In 25 ml of toluene 1.11 ml of $H_2AsSi^iPr_3$ (5.25 mmol) were dissolved and cooled to 0°C. A 1 M solution of dimethylmagnesium in tetrahydrofuran was added slowly. The evolution of methane is observed immediately. The reaction solution was concentrated to a few milliliters. At 0°C 1.69 g of colorless crystals of **1** (98%) precipitated, m.p. (dec.) at 360°C. ^1H-NMR (toluene-d_8): δ 1.22 [sept, $^3J(H,H) = 6.7$ Hz, 12H, CH], 1.37 [d, $^3J(H,H) = 6.7$ Hz, CH_3], 1.52 and 4.16 (m, THF). $^{13}C\{^1H\}$-NMR: δ 16.05 (CH), 20.69 (CH_3), 25.00 and 69.77 (THF). $^{29}Si\{^1H\}$-NMR: δ 30.08. IR (Nujol, cm^{-1}): 1295 s, 1261 m, 1236 s, 1219 s, 1176 s, 1154 s, 1072 m, 1027 vs, 1011 vs, 982 m, 916 s, 880 vs, 803 m, 676 sh, 646 m, 629 m, 576 m, 554 m, 503 vs, 461 m, 421 s, 394 m, 330 sh, 305 m. MS [70 eV, *m/z*, (%)]: 1204 (1), 1056 (2), 908 (4), 760 (8), 612 (10), 464 (17), 316 (26), 168 (100). Elemental analysis (THF-free molecule, $C_{36}H_{84}As_4Mg_4Si_4$, 1026.3): Anal. Calc.: C, 42.12; H, 8.25. Found C, 41.48; H, 8.24%.

5.3. *Hexakis[tin(II)-triisopropylsilylarsandiide]* (**2**)

At 0°C, 2.77 ml of $Sn[N(SiMe_3)_2]_2$ (7.1 mmol) were dropped slowly to a solution of 1.5 ml $H_2AsSi^iPr_3$ (7.1 mmol) in 25 ml of toluene. The solution turned deep red. After stirring at room temperature (r.t.) for several

Table 1
Crystallographic data of **1** and **2** as well as details of the structure solution and refinement procedures

Compound	**1**	**2**·C_6H_6
Empirical formula	$C_{52}H_{116}As_4Mg_4O_4Si_4$	$C_{60}H_{132}As_6Si_6Sn_6$
Formula weight (g mol^{-1})	1314.72	2183.99
Temperature (K)	183(2)	200(3)
Crystal size (mm)	0.20 × 0.20 × 0.05	0.16 × 0.06 × 0.06
Space group [16]	$I2/a$ (no. 15)	$P4_2/m$ (no. 84)
Unit cell dimensions		
a (Å)	24.084(2)	13.9006(8)
b (Å)	12.635(1)	13.9006(8)
c (Å)	25.507(3)	22.0283(13)
β (°)	115.4450(1)	90
V (Å^3)	7009.2(10)	4256.5(4)
Z	4	2
ρ_{calc} (g cm^3)	1.246	1.704
λ (Å)	0.71073	0.71073
μ (cm^{-1})	2.031	4.164
Absorbance corrections	Semi-empirical	Numerical
T_{min}/T_{max}	0.6767/0.8622	0.7138/0.7949
Unique data (R_{int})	4701 (0.0606)	3444 (0.0677)
Parameters	319	112
wR_2 [a] (all data on F^2)	0.1041	0.1033
R_1 [a] (all data)	0.0757	0.0639
Observed data ($I > 2\sigma(I)$)	3413	2415
R_1 [a] ($I > 2\sigma(I)$)	0.0442	0.0423
Goodness-of-fit s [b] on F^2	1.017	0.934
Residual density (e Å^{-3})	0.406/−0.351	1.117/−0.724
CCDC-no. [17]	CCDC-145503	CCDC-145600

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

[b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

hours, the solution was concentrated to a few milliliters. At r.t., 2.3 g of **2** (89%) precipitated; m.p. (dec.) at 250°C. ^{1}H-NMR (benzene-d_6): δ 1.08–1.57 (m, broad). ^{13}C{^{1}H}-NMR: δ 17.55 (CH), 20.07 (CH_3, broad). MS [70 eV], m/z (%)]: 2137 (1), 2062 (1.5), 1989 (1.5), 1913 (2.0), 1839 (3.0), 1765 (3.5), 1690 (4.5), 1616 (5.5), 1542 (4.5), 1468 (5.0), 1394 (5.0), 1320 (4.0), 1246 (3.5), 1172 (3.0), 1098 (2.5). Elemental analysis ($C_{60}H_{132}As_6Si_6Sn_6$, 2105.81): Anal. Calc.: C, 30.79: H, 6.03. Found C, 31.28; H, 6.65%.

5.4. Crystal structure determinations

Data was collected on a Siemens P4 diffractometer with a Siemens SMART-CCD area detector (**1**) or on a STOE-IPDS (**2**) with graphite monochromated Mo–K_α radiation ($\lambda = 71.073$ pm) using oil-coated rapidly cooled single crystals [15]. Crystallographic parameters, details of data collection and refinement procedures are summarized in Table 1 [16,17].

The structures were solved by direct methods (SIR97 [18]) and refined with the software packages SHELXL-93 and SHELXL-97 [19]. Neutral scattering factors were taken from Cromer and Mann [20] and for the hydrogen atoms from Stewart et al. [21]. All non-hydrogen atoms were refined anisotropically. The H-atoms were considered with a riding model under restriction of ideal symmetry at the corresponding carbon atoms. The single crystal of **2** was extremely small (Table 1). One isopropyl group shows a two-site disorder; all isopropyl carbon atoms of **2** were refined isotropically.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft, Bonn, and the Fonds der Chemischen Industrie, Frankfurt/Main, for generous financial funding. We thank Professor Dr P. Klüfers for his kind support.

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[17] Crystallographic data (excluding structure factors) for the structures of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 145503 for **1** and 145600 for **2**. Copies of the data can be obtained on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk www: http://www.ccdc.cam/ac.uk].

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