Notes

Synthesis and Crystal Structure of the Tetraaluminatetrahedrane Al₄[Si(*t*-Bu)₃]₄, the Second Al₄R₄ Compound

Andreas Purath, Carsten Dohmeier, Achim Ecker, and Hansgeorg Schnöckel*

*Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstrasse,
Geb. 30.45, D-76128 Karlsruhe, Germany*

Kerstin Amelunxen, Thomas Passler, and Nils Wiberg*

*Institut für Anorganische Chemie, Universität München,
Meiserstrasse 1, D-80333 München, Germany*

Received November 17, 1997

Summary: The reaction of (AlI·NEt₃)₄ with donor-free t-Bu₃SiNa in toluene at −78 °C leads to the generation and crystallization of Al₄[Si(t-Bu)₃]₄, which—after Al₄-Cp*₄− is the second structurally characterized Al₄R₄ compound. The obtained experimental data were compared with results of ab initio calculations.

Introduction

AlX molecules (X = Cl, Br, I) are well-known high-temperature species which have been studied extensively by means of spectroscopic methods.[1,2] A few years ago we developed a method to generate AlX molecules on a synthetic scale and to obtain metastable AlX solutions from which the first room-temperature-stable, donor-stabilized AlX compounds could be crystallized.[3] Such solutions as well as the pure compounds are suitable starting materials for the generation of further Al(I) derivatives: e.g., the first Al(I) organic compound, AlCp* (**1**),[4a] which forms tetrameric units in the solid state with relatively weak Al−Al bonds within the tetrahedron (d(AlAl) = 2.770(5) Å). The weak Al−Al bonds in **1** were confirmed by means of quantum chemical calculations[5] and consequently, upon increasing the temperature, monomeric AlCp* could be ob-
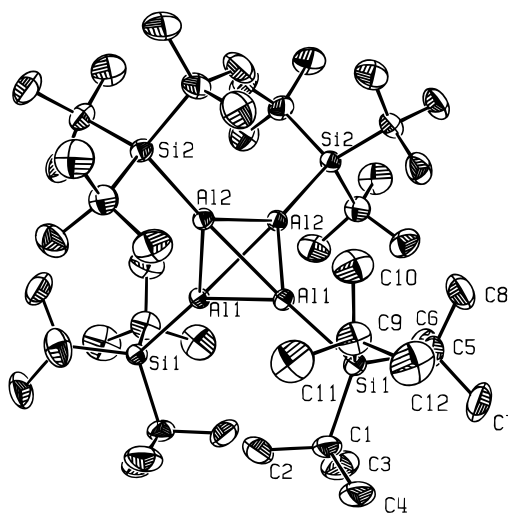
* To whom correspondence should be addressed: H.S., Tel. +49 721 6082981; fax +49 721 6084854; e-mail hg@achpc9.chemie.uni-karlsruhe.de; N.W., fax +49 089 5902578.

(1) Klemm, W.; Voss, E.; Geigersberger, K. *Z. Anorg. Chem.* **1948**, *256*, 15.
(2) (a) Schnöckel, H. *Z. Anorg. Allg. Chem.* **1976**, *424*, 203. (b) Schnöckel, H. *Z. Naturforsch.* **1976**, *31B*, 1291. (c) Schnöckel, H. *J. Mol. Struct.* **1978**, *50*, 267. (d) Schnöckel, H. *J. Mol. Struct.* **1978**, *50*, 275. (e) Ahlrichs, R.; Zhengyang, L.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1984**, *519*, 155.
(3) (a) Mocker, M.; Robel, C.; Schnöckel, H. *Angew. Chem.* **1994**, *106*, 1860; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1754. (b) Ecker, A.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 149.
(4) (a) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem.* **1991**, *103*, 594; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564. (b) Dohmeier, C.; Passler, T.; Schnöckel, H.; Wiberg, N.; In *Frontiers of Organosilicon Chemistry*; (Bassindale, A. R., Gaspar, P. P., Eds.; The Royal Society of Chemistry: Cambridge, U.K., 1991; pp 263−270.
(5) Gauss, J.; Schneider, U.; Ahlrichs, R.; Dohmeier, C.; Schnöckel, H. *J. Am. Chem. Soc.* **1993**, *115*, 2402.

Figure 1. ORTEP drawing of **2**, showing 50% probability ellipsoids (H atoms not shown). Selected bond lengths (Å): Al1−Al2 = 2.6004(12), Al1−Al1A = 2.612(2), Al2−Al2A = 2.603(2), Al1−Si1 = 2.5014(10), Al2−Si2 = 2.4966(11).

tained in solution as well as in the gas phase.[6] The structure of monomeric AlCp* was determined by gas-phase electron diffraction. The second Al₄R₄ compound that we prepared, even before **1**, was Al₄[Si(*t*-Bu)₃]₄ (**2**).[4b] In contrast to **1**, strong Al−Al bonds were predicted for this compound by theoretical calculations.[7] Supporting experimental evidence for this was given by its high thermal stability: **2** could be sublimed without decomposition under high vacuum (10⁻⁵ mbar) at about 180 °C. However, crystals of **2** suitable for a structural analysis could not be obtained at the time. We report here a successful method for the preparation of crystalline **2** and its structural data (Figure 1).

(6) Haaland, A.; Martinsen, K.-G.; Shlykov, S. A.; Volden, H. V.; Dohmeier, C.; Schnöckel, H. O*rganometallics* **1995**, *14*, 3116.
(7) Schneider, U.; Ahlrichs, R.; Horn, H.; Schäfer, A. *Angew. Chem.* **1992**, *104*, 327; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 353.

Table 1. Data for the X-ray Structural Study of 2

formula	(AlSi-*t*-Bu$_3$)$_4$·C$_7$H$_{16}$
emp form	C$_{55}$H$_{108}$Al$_4$Si$_4$
cryst size, mm	1.03 × 0.85 × 0.77
cryst syst	monoclinic
space group	*C*2/*c*
fw	1005.9
a, Å	23.743(5)
b, Å	12.729(3)
c, Å	25.120(5)
α, deg	90
β, deg	115.92(3)
γ, deg	90
V, Å^3	6827.9(23)
Z	4
D(calcd), g cm^{-3}	0.979
F(000)	2184
μ, mm^{-1}	0.167
2θ range, deg	3.60−50.00
scan width, deg	1.2, ω-scan
no. of collcd rflns	11 044
no. of unique rflns	6009
no. of obsd rflns	4870
GOF	1.149
wR2 (all data)	0.1641
R1	0.0486
largest diff peak, e Å^{-3}	0.907
deepest diff peak, e Å^{-3}	−0.510

Table 2. Comparison of Al−Al and Al−Si Distances of 2 Obtained by Experiment and by *ab Initio* Calculations

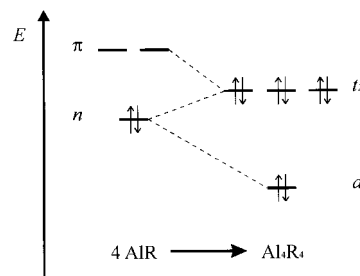|	exptl	SCF[5]	DFT
d(Al−Al), Å	2.604	2.638	2.655
d(Al−Si), Å	2.498	2.594	2.566

Results and Discussion

Solid (AlI·NEt$_3$)$_4$ (**3**) and donor-free *t*-Bu$_3$SiNa[8] were suspended in toluene at −78 °C, and when the reaction mixture was warmed to room temperature, a violet solution was obtained. After separation of NaI and evaporation of toluene a violet solid was isolated. Recrystallization from heptane at −30 °C gave crystals of **2**. The structure of **2** was determined by X-ray crystallography. Data for the X-ray study are given in Table 1. Its most important structural features are the Al−Al and the Al−Si bonds, which are summarized, together with the results of *ab initio* calculations, in Table 2. The Al−Al bond length is 2.604(4) Å, which is 0.17 Å shorter than that in **1** and 0.06 Å shorter than that expected for a "normal" Al−Al bond in R$_2$Al−AlR$_2$ (R = CH(SiMe$_3$)$_2$).[9] This reduced bond strength in the R$_2$Al−AlR$_2$ compound is mainly based on the repulsion between the positively polarized Al atoms.[10] The Al−Si bonds are about 2.50 Å, which is the average of the aforementioned normal Al−Al bonds and Si−Si bonds, as for example in Si(SiMe$_3$)$_4$ (2.346(1) Å).[11] Therefore, the short Al−Si bonds in **2** are most remarkable, but they are in line with results of *ab initio* calculations. Consequently, this strong bonding is equivalent to a large tetramerization energy (Δ*E*$_{tetra}$) of AlSi(*t*-Bu)$_3$, which is extrapolated to be −600 kJ/mol.[7] This value

Figure 2. Section of the qualitative MO diagram of the Al$_4$R$_4$ tetrahedron.

has been confirmed by DFT calculations. Furthermore, this is in line with experimental data: monomers are not observed in solution by NMR spectroscopy or in the gas phase above the heated solid by mass spectroscopy. In contrast, the Δ*E*$_{tetra}$ value for AlCp* is only −160 kJ/mol.[5] By the tetramerization of AlR the four lone-pair orbitals of the aluminum atoms are combined into a low-lying a$_1$ orbital and a high-lying set of t$_2$ orbitals. Δ*E*$_{tetra}$ depends on the stabilization by interaction of the t$_2$ orbitals with π orbitals which are unoccupied in the monomers (Figure 2). For the monomer of **1** there is strong π (back)bonding from Cp* to the empty p orbitals of the aluminum atom, which is equivalent to a large HOMO−LUMO gap. Consequently, the t$_2$ orbitals of the tetramer are hardly lowered. In contrast, backbonding within the monomers of **2** is not possible and therefore a small HOMO−LUMO gap results. The t$_2$ orbitals are strongly lowered in energy, and Δ*E*$_{tetra}$ should be high. Furthermore, a high HOMO−LUMO gap for **1** and a small one for **2** is in line with the yellow color of **1** and the violet color of **2**. Since, as deduced from a detailed theoretical study, there is a strong correlation between the HOMO−LUMO gap and the tetramerization energy, the different behavior of **1** and **2** seems plausible.

A further experimental confirmation of different Al−Al bond strengths in **1** and **2** should be evident from the ^{27}Al NMR shifts. The observed large high-field shift for **1** (−80.8 ppm) is in line with the prediction of *ab initio* calculations.[5] However, in spite of many efforts we have not been able to obtain a ^{27}Al NMR spectrum of **2**, which, because of the different HOMO−LUMO gap, should resonate at very low field. Obviously, this resonance is too broad to be observed, which is not unexpected for aluminum compounds.

By crystallization of pure **2** a further problem could be solved. The sample of **2** obtained a few years ago exhibited a mass spectrum which could not be interpreted. Besides the mass peak of **2**$^+$ at *m*/*z* 904 there was an additional peak at *m*/*z* 911 of 40% intensity with respect to the former. The origin of the additional peak is now clear. The difference of 7 *m*/*z* units is a result of a missing C(CH)$_3$ group (*m*/*z* −57) and the addition of four oxygen atoms (*m*/*z* +64). The explanation for this observation of unexpected oxygen is simple. In solution **2** is very sensitive to O$_2$ and therefore, in analogy to the formation of Al$_4$Se$_4$R$_4$ and Al$_4$Te$_4$R$_4$ from (AlCp*)$_4$ and Se and Te,[12] the heterocubane-like species Al$_4$O$_4$-

(8) Wiberg, N.; Amelunxen, K.; Lerner, H.-W.; Schuster, H.; Nöth, H.; Krossing, I.; Schmidt-Amelunxen, M.; Seifert, T. *J. Organomet. Chem.* **1997**, *542*, 1.

(9) Uhl, W. *Z. Naturforsch.* **1988**, *B43*, 1113.

(10) Ecker, A.; Baum, E.; Friesen, M. A.; Junker, M. A.; Üffing, C.; Köppe, R.; Schnöckel, H. *Z. Anorg. Allg. Chem.*, in press.

(11) . Heine, A.; Herbst-Irmer, R.; Sheldrick, G. M.; Stahlke, D. *Inorg. Chem.* **1993**, *32*, 2694.

(12) Schulz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stahlke, D.; Kuhn, A. *Angew. Chem.* **1993**, *105*,1828; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1729.

[Si(*t*-Bu)$_3$]$_4$ is formed.[13] This could be confirmed by carrying out a reaction of $^{18}O_2$ with a solution of **2**. The colorless solid obtained after removal of solvent exhibited a mass spectrum with the highest mass peak at *m/z* 919. The difference of 8 *m/z* units from the peak of *m/z* 911 is caused by the mass difference between four ^{16}O atoms and four ^{18}O atoms. In contrast to its solution, solid **2** is much more stable toward the attack of O_2, as experiments with single crystals on the diffractometer have shown. The results presented here have again convincingly demonstrated that the supersilyl group has a marked ability to stabilize reactive species.

Experimental Section

General Considerations. All experiments were carried out under dry argon in a glovebox (MBRAUN MB150-GI) or under dry nitrogen using standard Schlenk techniques. Solvents were dried over potassium and degassed prior to use. Raman spectra were recorded on a XY Dilor 800 (in C_6D_6 solution, λ(excitation) = 514.53 nm) and NMR spectra by means of a Bruker AC 250 (^{1}H) or a Bruker AMX 300 spectrometer (^{27}Al, ^{29}Si). Chemical shifts are reported in δ units (ppm) referenced to C_6D_5H (7.16 ppm, ^{1}H), C_6D_6 (128.8 ppm, ^{13}C), external [Al(H$_2$O)$_6$]$^{3+}$ (0.5 M, 0 ppm, ^{27}Al), or external SiMe$_4$ (0 ppm, ^{29}Si). Electron impact mass spectra were obtained on a Varian MS 8230.

Synthesis of (Al$_4$[Si(*t*-Bu)$_3$]$_4$ (2). A solid mixture of 73 mg (0.29 mmol) of AlI·NEt$_3$ and 64 mg (0.29 mmol) of *t*-Bu$_3$SiNa was prepared and suspended in 5 mL of toluene at −78 °C. Slow warming to room temperature afforded a violet solution. After filtration from solid NaI, toluene was removed. Addition of 10 mL of heptane to the violet solid residue gave a violet solution and a gray-brown, voluminous precipitate of unknown composition. This solid−liquid mixture was filtered via cannula, and subsequently the filtrate was concentrated to 5 mL. From this solution were obtained violet crystals suitable for structural analysis after 12 h at −30 °C.

Yield: 20 mg, 30%. Mp: could not be obtained (**2** sublimed at about 180 °C at 10^{-5} mbar). Raman: 445.7 cm^{-1} (ν_{A1}(Al$_4$)). MS (*m/z*, ion, relative intensity; 230 °C): 904 [M]$^+$ 100%; 705.4 [M − Si-*t*-Bu$_3$)]$^+$ 89.1%.

^{27}Al NMR (C_6D_6): no signal detected. ^{1}H NMR (C_6D_6): 1.37 (s). ^{13}C{^{1}H} NMR (C_6D_6): 32.75; 25.78. ^{29}Si NMR (C_6D_6): 15.2.

X-ray Analysis. For details of the crystal structure determination and the refinement, see Table 1. Data were collected on a Stoe Stadi IV diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). For this purpose the crystal was mounted on a glass fiber and cooled under a nitrogen stream to 210 K. Calculations were carried out with the SHELXL program system. The structure was solved by direct methods. Hydrogen atoms were included in the refinement at calculated positions. All non-hydrogen atoms were refined with anisotropic thermal parameters, except for the heptane carbon atoms, which were refined isotropically.

Computational Details. The *ab initio* calculations were carried out using the TURBOMOLE program.[14] The DFT calculations were performed with the recently developed RI-*J* DFT turbo: 95 version. For the density functional we selected the B-P parameterization (a combination of Becke exchange,[15] Vosko, Wilk, and Nusair correlation,[16] and Perdew correlation[17] functionals). Open-shell systems were treated using the spin-unrestricted formalism. We employed the split valence basis set of Schäfer, Horn, and Ahlrichs[18] augmented with polarization functions for non-hydrogen atoms and auxiliary basis sets for fitting the electron density from ref 19.

Supporting Information Available: Tables of crystal data and structure refinement details, atom coordinates and *U* values, bond distances and angles, and anisotropic thermal parameters and ORTEP diagrams (11 pages). Ordering information is given on any current masthead page.

OM971015H

(13) The investigation concerning the preparation and the constitution of {Al$_4$O$_4$[Si(*t*-Bu)$_3$]$_4$} is under way: Amelunxen, K.; Ecker, A.; Nöth, H.; Schwenk, H.; Schnöckel, H.; Wiberg, N. To be submitted for publication.

(14) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.
(15) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.
(16) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
(17) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822.
(18) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
(19) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283.