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Adamantane-like Aluminum Amide-Phosphate from Alumazene

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A dealkylsilylation reaction between alumazene [2,6-(*i*-Pr)$_2$C$_6$H$_3$NAlMe]$_3$ (**1**) and tris(trimethylsilyl) ester of phosphoric acid (**2**) in a 1:3 molar ratio provides the heteroadamantane molecule (MeAl)[2,6-(*i*-Pr)$_2$C$_6$H$_3$N]$_3${Al[OP(OSiMe$_3$)$_3$]}$_2$(O$_3$POSiMe$_3$) (**3**). Compound **3** was characterized by analytical and spectroscopic methods, and its molecular structure was established by a single-crystal X-ray diffraction experiment. Moreover, trialkyl and triaryl phosphates and dialkyl phosphonates react with **1** at elevated temperature to afford an intractable mixture of products. The reaction of phosphonic acids with **1** proceeds under decomposition to yield 2,6-diisopropylaniline and aluminophosphonates.

Introduction

Alumazene [2,6-(*i*-Pr)$_2$C$_6$H$_3$NAlMe]$_3$ (**1**) still remains, after more than a dozen years from its first synthesis,[1] the sole example of a trimeric iminoalane ring isoelectronic with benzene, borazine, and the B−P, Al−P, Ga−P, and Al−As[2] analogues. This exclusivity can be ascribed to the extreme reactivity of **1**, which stems from a high polarity of the Al−N bonds and from a small delocalization of the π electrons in the ring. The fortunate choice of substituents stabilizes a very reactive electronically and coordinately unsaturated system. Other combinations of organic groups on Al and N led to the formation of higher iminoalane oligomers or to the activation of ligand C−H bonds.[3] Alumazene is also important as the first example of iminoalanes with coordination numbers of three at both aluminum and nitrogen. More recent examples of such compounds include monomeric[4] and dimeric[5] iminoalanes. In contrast to the extensive and well-understood chemistry of borazine, the reactions of its heavier counterparts are much less developed. The chemical reactivity of **1** was examined on several occasions. Interestingly, the reactions with silanetriols, triaminosilanes, and piano-stool metal trifluorides provided products with related adamantane-like cores. Silanetriols and triaminosilanes react with **1** by a formal 3-fold addition of their O−H and N−H groups on the Al−N bonds, respectively.[6] A different reactivity mode was observed in the case of metal trifluorides. The fluorine atoms coordinate to the aluminum centers, and a subsequent fluorine−nitrogen exchange leads to new bimetallic amidofluorides.[7] Finally, an incremental fluorination of **1**, with a stepwise substitution of the three methyl groups by fluorides, was accomplished by Me$_3$SnF.[8]

We are also interested in developing new routes to aluminophosphate microporous materials by nonaqueous and building-block synthetic methods. To this end, we developed reactions of phosphoric acid triesters with aluminum amides[9] and alkyls.[10] In these reaction mixtures we have evidenced

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or surmised the presence of cyclic and polyhedral species that are analogous to the secondary building units of zeolites.[11] In a parallel effort, we also prepared and structurally characterized a series of molecular organic-soluble aluminophosphonates that can serve as models mimicking some of the structural motifs of microporous aluminophosphates, such as a single four-ring (4R),[12] a single six-ring (6R),[13] a double four-ring (D4R),[14] a double six-ring (D6R),[15] and an incomplete cubic unit 6 ≡ 1.[16] In our previous attempts to employ **1** as a source of aluminum, the reaction of $OP(OMe)_3$ with **1** yielded a bis-adduct **1**$(OP(OMe)_3)_2$.[9] Here we report further investigation on the reactivity of alumazene **1**. The tris(trimethylsilyl) ester of phosphoric acid (**2**) reacts with **1** with a dealkylsilylation and provides an aluminum amide-phosphate cage compound with the central heteroadamantane core, $(MeAl)[2,6\text{-}(i\text{-}Pr)_2C_6H_3N]_3\{Al[OP(OSiMe_3)_3]\}_2(O_3POSiMe_3)$ (**3**). This compound could serve as a precursor for developing other structural units as it still contains reactive groups.

Experimental Section

General Procedures. All manipulations were performed under a dry nitrogen atmosphere by Schlenk techniques or in a M. Braun Unilab drybox. Solvents were dried over and distilled from Na/benzophenone under nitrogen. Deuterated solvents were dried over and distilled from Na/K alloy and degassed prior to use. Compound **1** was prepared according to the previously published procedure.[1] NMR spectra (^1H, ^{13}C, ^{29}Si, and ^{31}P) were acquired on Avance DRX 500 and 300 MHz spectrometers in C_6D_6 or toluene-d_8. Chemical shifts were referenced to the residual resonances of solvents (7.15 and 128.5 ppm for ^1H and ^{13}C in C_6D_6, respectively) or externally to $SiMe_4$ and H_3PO_4 (^{29}Si and ^{31}P). Diffraction data were collected on a KUMA KM-4 κ-axis diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and a CCD camera at 120 K. The intensity data were corrected for Lorentz and polarization effects. Details of the data collection and refinement are summarized in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares methods using the SHELXTL program package.[17] The H atoms were positioned geometrically and refined as riding. Mass spectra were measured on Finnigan MAT 8230 and MAT 95 (Fisons Instruments) systems. IR spectra (4000−400 cm^{-1}) were collected on an EQUINOX 55/S/NIR FTIR spectrometer. Samples were prepared as KBr pellets. The FT Raman spectral measurements with FT-RA module FRA 106/S were performed with a resolution of 1.5 cm^{-1}. An air-cooled Nd:YAG laser (1064 μm, max output 500 mW) was used for spectra excitation. Elemental analyses were carried out by the Analytisches Labor des Anorganischen Instituts, Göttingen. Melting points were measured in sealed capillaries and are uncorrected.

Table 1. Crystal Data and Structure Refinement Details for $\mathbf{3}\cdot C_7H_8$[a]

empirical formula	$C_{65}H_{125}Al_3N_3O_{12}P_3Si_7$
fw	1511.16
T, K	120(2)
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	14.377(3)
b, Å	21.051(4)
c, Å	28.948(6)
α, deg	96.93(3)
β, deg	96.52(3)
γ, deg	90.28(3)
V, Å^3	8639(3)
Z	4
calcd density, g cm^{-3}	1.162
μ, mm^{-1}	0.248
cryst size, mm	0.20 × 0.10 × 0.10
θ range, deg	3.07−25.00
no. of reflns colld	56012
no. of unique reflns	29447
no. of params	1639
GOF on F^2	1.100
R1 [$I > 2\sigma(I)$]	0.1219
wR2 (all data)	0.1371
largest diff. peak and hole, e A^{-3}	0.377, −0.378

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

Synthesis of $(MeAl)[2,6\text{-}(i\text{-}Pr)_2C_6H_3N]_3\{Al[OP(OSiMe_3)_3]\}_2(O_3POSiMe_3)$ (3). Neat $OP(OSiMe_3)_3$ (0.740 g, 2.35 mmol) was added dropwise by a syringe to alumazene **1** (0.502 g, 0.770 mmol) in dry deoxygenated toluene (20 mL). The reaction mixture was refluxed for 24 h under a flow of dry nitrogen. After being cooled to room temperature, colorless crystals of **1** (0.39 g, 36%) precipitated from the solution. mp: 268 °C dec. ^1H NMR (500 MHz, toluene-d_8): δ −0.904 (s, ^{13}C satellites, $^1J_{CH} = 113$ Hz, $AlCH_3$, 3 H), 0.114 (s,^{29}Si satellites, $^2J_{SiH} = 6.7$ Hz, ^{13}C satellites, $^1J_{CH} = 120$ Hz, $SiMe_3$ coordinated, 54 H), 0.632 (s,^{13}C satellites, $^1J_{CH} = 119$ Hz, ^{29}Si satellites, $^2J_{SiH} = 7.1$ Hz, $SiMe_3$ apical, 9 H), 1.462, 1.470, 1.557, 1.615, 1.664, 1.674 (all d, $^3J_{HH} = 6.8$ Hz, $(CH_3)_2CH$, 3 H, for the assignment see Supporting Information), 4.863 (sept, $^3J_{HH} = 6.8$ Hz, $(CH_3)_2CH$-on, 2 H), 4.962 (sept, $^3J_{HH} = 6.8$ Hz, $(CH_3)_2CH$-off, 4 H), 6.94 (t, p-C_6H_3, 3 H), 7.25 (m, m-C_6H_3, 6 H). $^{13}C\{^1H\}$ NMR (125.76 MHz, benzene-d_6): δ −13 (broad s, $AlCH_3$), 1.40 (d, $^3J_{PC} = 1.5$ Hz, ^{29}Si satellites, $^1J_{SiC} = 60.3$ Hz, $SiMe_3$ coordinated), 2.19 (d, $^3J_{PC} = 1.5$ Hz, $SiMe_3$ apical), 26.02, 27.15, 27.52, 28.07 $(CH_3)_2CH$-off, 27.78 $(CH_3)_2CH$-off, 27.21, 27.44 $(CH_3)_2CH$-on, 28.11 $(CH_3)_2CH$-on, 117.96, 118.00, 123.29, 123.51, 123.81, 123.90, 144.95, 145.57, 146.47, 147.42, 154.94, 155.83 (C_6H_3, for the assignment see Supporting Information). $^{31}P\{^1H\}$ NMR (202.40 MHz, benzene-d_6): δ −8.7 (s, apical, 1 P), −38.5 (s, coordinated, 2 P). $^{29}Si\{^1H\}$ NMR (99.36 MHz, benzene-d_6): δ 17.05 (d, $^2J_{POSi} = 2.7$ Hz, apical), 26.47 (d, $^2J_{POSi} = 6.9$ Hz, coordinated). IR (KBr pellet, cm^{-1}): 3043 vw, 2960 s, 2905 w, 2866 w, 1582 vw, 1461 w, 1420 m, 1377 vw, 1357 vw, 1317 w, 1260 s, 1238 s, 1204 s, 1085 vs, 1062 vs, 899 m, 850 vs, 766 s, 724 w, 702 w, 618 w, 550 w, 492 w, 454 w. RA (cm^{-1}): 3056 m, 3037 m, 2961 s, 2904 vs, 2866 s, 1585 s, 1462 m, 1442 m, 1417 m, 1260 s, 1237 w, 1207 w, 1155 w, 1104 w, 1042 m, 1003 m, 898 w, 784 w, 709 w, 642 m, 626 m, 283 m, 174 w, 148 w. Anal. Calcd for $C_{58}H_{117}Al_3N_3O_{12}P_3Si_7$: C, 49.10; H, 8.32; Al, 5.71; N, 2.96; P, 6.55; Si, 13.82. Found: C, 50.78; H, 8.16; Al, 5.48; N, 2.79; P, 6.19; Si, 13.63.

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Results and Discussion

Synthesis and Spectroscopy. The reaction of alumazene $[2,6\text{-}(i\text{-Pr})_2C_6H_3NAlMe]_3$ (**1**) with tris(trimethylsilyl) phosphate (**2**) in a 1:3 molar ratio in boiling toluene resulted in the formation of $(MeAl)[2,6\text{-}(i\text{-Pr})_2C_6H_3N]_3\{Al[OP(OSiMe_3)_3]\}_2(O_3POSiMe_3)$ (**3**). Compound **3** was isolated in a moderate yield and characterized by analytical and spectroscopic methods. Its molecular structure was established by a single-crystal X-ray diffraction experiment, which revealed an $Al_3N_3O_3P$ heteroadamantane core (vide infra).

The solution NMR spectra of **3** were consistent with the C_s symmetry of the molecule. The high-field resonances in both ^1H (−0.904 ppm) and $^{13}C\{^1H\}$ NMR (−13 ppm) spectra pointed to the presence of a remaining Al-CH_3 group in the molecule. Two proton singlets with a 1:6 intensity ratio possessing ^{29}Si satellites were assigned to the $OSiMe_3$ moieties. A set of six doublets in the ^1H NMR spectrum attested to the diastereotopicity of some *i*-Pr groups. The corresponding methine septets display a 2:1 intensity ratio. This implies that one 2,6-diisopropylphenyl group lies on the molecular mirror plane. Its two *i*-Pr groups are chemically inequivalent when the phenyl group rotates around the N−C bond slowly on the NMR time scale. The other two aromatic substituents are equivalent and situated away from the mirror. Therefore, their methyl groups are diastereotopic and furnish four separate signals. The assignment of the *i*-Pr signals to on- and off-the-mirror-plane groups was accomplished by the combination of $^1H-^1H$ COSY45 and $^1H-^{13}C$ HMQC NMR experiments. We also recorded the ^{13}C APT NMR spectrum at room temperature, and it also revealed six resonances for the isopropyl CH_3 groups and thus confirmed our insight gleaned from the proton spectrum. Moreover, 12 aromatic carbon signals that could be grouped in two sets of six lines with an approximate 2:1 intensity ratio attest to the slow rotation of the bulky 2,6-diisopropylphenyl groups on the NMR time scale. The $^1H-^{13}C$ correlation table is given in the Supporting Information.

Two singlets with a 2:1 intensity ratio in the $^{31}P\{^1H\}$ NMR spectrum and two doublets in the $^{29}Si\{^1H\}$ NMR spectrum displaying P−O−Si couplings evidenced the presence of two types of the $POSiMe_3$ moieties. The extremely deshielded ^{31}P NMR signal at −8.7 ppm belongs to the apical phosphate group (atom P(3) in Figures 1 and 2). In comparison with other $(SiO)_nP(OAl)_{4-n}$ moieties,[10] this considerable downfield shift may be ascribed to geometrical constraints to the bond angles exerted by the adamantane framework. The decreasing mean Al−O−P angle around a phosphorus center (i.e., closing) in aluminophosphates is known to correlate with deshielding of its ^{31}P NMR signal.[18,19] The average of the Al−O−P angles around the apical phosphorus in **3** is 117.4(7)°. In contrast, the ^{31}P chemical shift of the $(AlO)_3POSiMe_3$ vertex in the cubic aluminophosphate $[t\text{-BuAl}(\mu\text{-O})_3P(OSiMe_3)]_4$ (**4**) is −28.4 ppm,[20] and the corresponding mean Al−O−P angle can be estimated from the structural data for related cubic alumino- and gallophosphonates[21] to be as large as 150°.

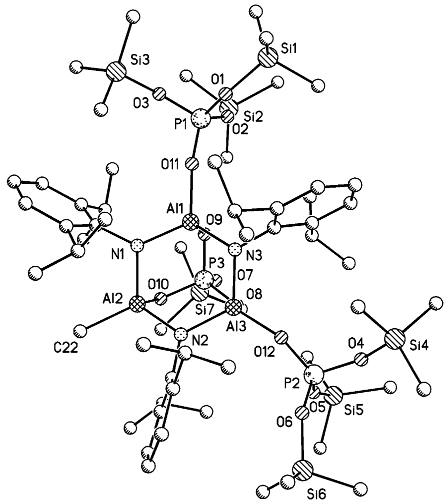


Figure 1. Molecular structure of $(MeAl)[2,6\text{-}(i\text{-Pr})_2C_6H_3N]_3\{Al[OP(OSiMe_3)_3]\}_2(O_3POSiMe_3)$ (**3**).

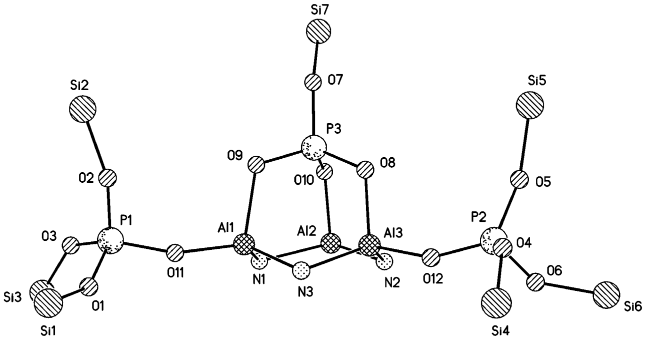
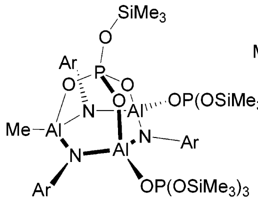


Figure 2. View of the molecular core of **3**. All carbon and hydrogen atoms were omitted for clarity.



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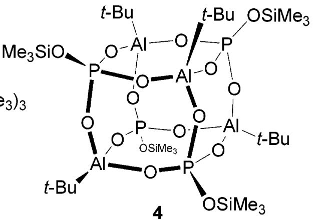

4

Ar = 2,6-di*iso*propylphenyl

The stepwise reaction course was followed by ^1H, ^{29}Si, and $^{31}P\{^1H\}$ NMR spectroscopy in toluene-d_8. We observed the presence of intermediates and a small amount of the final product **3** in the reaction mixture shortly after mixing. The intensity of phosphorus resonances with the chemical shifts of −18.3, −22.5, and −38.4 ppm and ^{29}Si chemical shifts of 27.7 and 20.6 ppm evolved with time, and the complete disappearance of the starting ester **2** and the intermediates was observed only after 48 h at room temperature. ^1H and ^{29}Si NMR spectra gave evidence to the formation of $SiMe_4$

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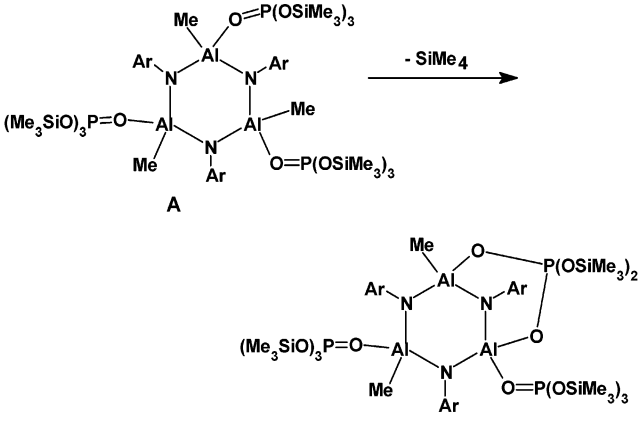
as the byproduct in a dealkylsilylation reaction. This kind of reactivity is relatively rare, and we recently observed this type of reaction between tris(trimethylsilyl) phosphate and aluminum trialkyls.[10]

Although the detailed mechanism of this reaction is still under investigation, from the changes in the NMR spectra we can draw some preliminary conclusions. The primary reaction step most probably involves an adduct formation of **1** with $OP(OSiMe_3)_3$, similar to the one observed crystallographically in the bis-adduct **1**$(OP(OMe)_3)_2$.[9] Coordination of the phosphate oxygen manifests a high acidity of the three-coordinate aluminum centers in **1**, which is caused by a low degree of delocalization within the alumazene ring.[22] This picture is further supported by the chemical shift values of a reaction intermediate (^{31}P -38.4 and ^{29}Si 27.7 ppm) that are very close to the resonances of a metal-coordinated $OP(OSiMe_3)_3$ moiety in the final product **3** (^{31}P -38.5 and ^{29}Si 26.5 ppm) and also in $R_3Al(\mu\text{-}O)P(OSiMe_3)_3$ (R = Me, Et, ^{31}P -31.7 and ^{29}Si 26.7 ppm, both derivatives) and $[Cl_3Ti(\mu\text{-}O_2P(OSiMe_3)_2)(\mu\text{-}Cl)_2TiCl_2OP(OSiMe_3)_3]$ (**5**, ^{31}P -35.2 ppm).[23]

As the subsequent reaction event we envision the formation of a bridging $O_2P(OSiMe_3)_2$ group in the bicyclic intermediate B through dealkylsilylation of A. The NMR signals of the intermediate B (^{31}P -22.5 and ^{29}Si 20.6 ppm) are comparable to the values for the bis(trimethylsilyl) phosphate bridge in **5** (^{31}P -29.8 ppm)[23] and the cyclic molecule $[Me_2Al(\mu\text{-}O)_2P(OSiMe_3)_2]_2$ (^{31}P -29.3 and ^{29}Si 23.4 ppm).[10] The formation of **3** is finally completed by a second dealkylsilylation in B.



A

B

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**

P(3)−O(7)	1.544(5)	Si(7)−O(7)	1.645(5)
P(3)−O(8)	1.523(5)	Al(1)−O(9)	1.846(5)
P(3)−O(9)	1.519(5)	Al(2)−O(10)	1.885(5)
P(3)−O(10)	1.527(4)	Al(3)−O(8)	1.817(5)
Al(1)−N(1)	1.801(6)	N(1)−Al(1)−N(3)	114.7(3)
Al(1)−N(3)	1.812(6)	N(1)−Al(2)−N(2)	110.4(3)
Al(2)−N(1)	1.853(6)	N(2)−Al(3)−N(3)	114.8(3)
Al(2)−N(2)	1.844(6)	Al(1)−N(1)−Al(2)	111.7(3)
Al(3)−N(2)	1.809(6)	Al(3)−N(2)−Al(2)	111.6(3)
Al(3)−N(3)	1.819(6)	Al(1)−N(3)−Al(3)	108.3(3)

Reactions of **1** with trialkyl and triaryl phosphates and dialkyl phosphonates in toluene at ambient and elevated temperatures gave only intractable mixtures of products. The ^{31}P{^{1}H} NMR spectra contained a number of resonances of disparate intensities and attested to a more complex reaction course. Interestingly, the spectrum of the triphenyl phosphate reaction mixture contains signals that can be attributed to compounds with P−N bonds. One can conclude that these products arise necessarily through the amide transfer from the aluminum centers in **1** to phosphorus. This is similar to our findings in the study of the $Al(NMe_2)_3$ reaction with $OP(OPh)_3$.[9] Such a ligand exchange prevents the desired formation of Al−O−P bonds in the product, and aryl esters of phosphoric acid are therefore not suitable starting compounds for the preparation of aluminophosphates.

Phosphonic acids, $RP(O)(OH)_2$ (R = *t*-Bu, Ph), caused a complete breakdown of the alumazene cycle, and we found 2,6-(*i*-Pr)$_2C_6H_3NH_2$ and poorly crystalline solid aluminophosphonate as the decomposition product.

Crystal Structure. To establish molecular geometry of **3**, we performed an X-ray diffraction experiment on single crystals grown by slow cooling of the toluene solution. Compound **3** crystallizes with one toluene molecule of solvation. The molecular structure of **3** is shown in Figure 1, and the pertinent crystallographic data are listed in Table 1. Selected bond distances and angles are gathered in Table 2.

There are two independent molecules in the unit cell. The molecule contains a central $Al_3N_3O_3P$ adamantane unit with pseudo-C_s symmetry (Figure 2). The connectivity in the six-membered alumazene cycle is preserved, but the ring lost its planarity. All aluminum atoms increased their coordination number to four by forming bonds to the apical phosphate moiety. Two of the aluminum atoms eliminated their methyl groups in the dealkylsilylation reaction, and their coordination sphere is supplemented by oxygens from the coordinated phosphate esters. The nitrogen centers remained three-coordinate, in contrast to the adamantane-like products of reactions of **1** with silantriols and triaminosilanes.[6] Further comparison with **1** (Al−N = 1.782(4) Å) reveals that the Al−N bond distances in **3** are not equal and span a range of 1.80−1.85 Å. The two involving Al(2)−CH_3 are slightly elongated. Average intra-ring angles in the Al_3N_3 moiety are wider on aluminum (110−114°) than on nitrogen (108−112°). This situation is opposite to the one in compound **1** (Al−N−Al = 124.7°, N−Al−N = 115.3°) and may be explained by the increased coordination number of aluminum and the retained planar environment of nitrogen (average sum of angles around N is 357°). The apical $P(OSi)_1(OAl)_3$ moiety represents an addition to the list of molecular models of various *T*-units in silicoaluminophosphates (SAPO).[24] Phosphate bond lengths are unremarkable. The average P_{apical}−O−Si bond angle is 143.5(4)°.

Conclusions

We have shown a new reactivity mode for alumazene **1**, namely, the dealkylsilylation reaction with tris(trimethylsilyl)

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phosphate. A new cage compound **3** possessing the heteroadamantane core was isolated and characterized by spectroscopic methods, and its structure was established by the single-crystal X-ray diffraction experiment. This compound may serve as a model for the structural moiety $P(OSi)_1(OAl)_3$ in SAPO and also as a suitable starting material for developing other structural units as it still contains reactive groups.

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Supporting Information Available: Complete X-ray data for **3** in CIF format, listing of the NMR spectra of **3**, and the signal assignment table. This material is available free of charge via the Internet at http://pubs.acs.org.

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