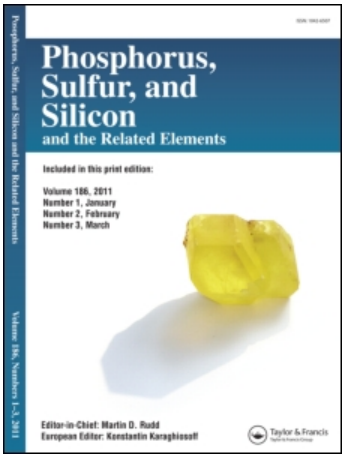

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CHEMICAL REACTIVITY OF ALUMAZENE

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Alumazene is a reactive trimeric iminoalane that undergoes dealkylsilylation reactions with a variety of trimethylsilyl esters.

Keywords: Aluminum; dealkylsilylation; iminoalanes; nitriles; phosphonates; sulfonates

Iminoalanes $[RNAlR']_n$ constitute a large family of homologous compounds possessing a multitude of different molecular structures. A large number of oligomers with $n \geq 4$ form polyhedral cage structures that obey Smith's rule, i.e., they are composed of six squares and n-4 hexagons. On the other hand, smaller iminoalane oligomers ($n = 1$ to 3) are much rarer. Monomeric[1] and dimeric[2] derivatives were synthesized and structurally characterized only recently. They were prepared from precursors, such as low-valent aluminum compounds, bulky arylaluminum hydrides, dichloroalanes and Cp_3Al, and kinetically stabilized by sterically demanding organic substituents. Alumazene $[2,6\text{-}i\text{-}Pr_2C_6H_3NAlMe]_3$ (**1**) represents the only example of a trimeric iminoalane.[3] It features a central planar six-membered Al_3N_3 ring with equal Al—N bonds (1.782(4) Å). A high polarity of the Al—N bonds and a small delocalization of the π electrons in the ring imparts a considerable reactivity to **1**.[4] However, its chemical behavior started to be uncovered only recently.[5] A stepwise fluorination of **1** was accomplished by a Me/F exchange with Me_3SnF and $BF_3{\cdot}OEt_2$.[6] Reactions with a formal three-fold addition of the O—H and N—H groups on the Al—N bonds were reported for silanetriols and triaminosilanes,[7] respectively,

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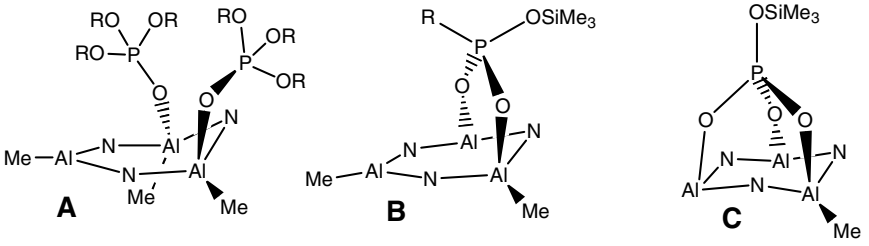
and furnish isostructural adamantane-like molecules. Piano-stool Cp metal trifluorides[8] provided also products with heteroadamantane cores where the fluorine atoms coordinate to the aluminium centers and subsequent fluorine-nitrogen exchange leads to bimetallic amidofluorides.

RESULTS AND DISCUSSION

We carried out studies on the reactivity of alumazene with a variety of phosphorus, sulfur, and nitrogen reagents with the aim of obtaining new polycyclic and polyhedral molecules. Previously we found that trialkylesters of phosphoric acid and dialkylesters of phosphonic acids in the reaction with **1** at room temperature form adducts of the type **A** (Scheme 1, 2,6-diisopropylphenyl substituents on nitrogens were omitted for clarity) and on heating afford intractable mixtures of products.[9] On the other hand a dealkylsilylation reaction[10] of trimethylsilyl ester of phosphoric acid, $OP(OSiMe_3)_3$, provided a heteroadamantane compound $(MeAl)[2,6\text{-}(i\text{-}Pr)_2C_6H_3N]_3\{Al[OP(OSiMe_3)_3]\}_2(O_3POSiMe_3)$ (type **C**, Scheme 1) with two additional $OP(OSiMe_3)_3$ molecules coordinated to the two aluminum centers devoid of the methyl groups.[11]



SCHEME 1

As an extension of these results, we studied the dealkylsilylation reactions of **1** with the bis(trimethylsilyl) esters of phosphonic acids, $RP(O)(OSiMe_3)_2$, R = H, Me, *t*-Bu, CCl_3, Bz, Ph. The reactions proceed under the $SiMe_4$ elimination. We obtained bicyclic products of the type **B** that were characterized by the ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy, mass spectrometry, and elemental analysis. They can be thought of as model compounds for an intermediate in the reaction of **1** with $OP(OSiMe_3)_3$ leading to the heteroadamantane

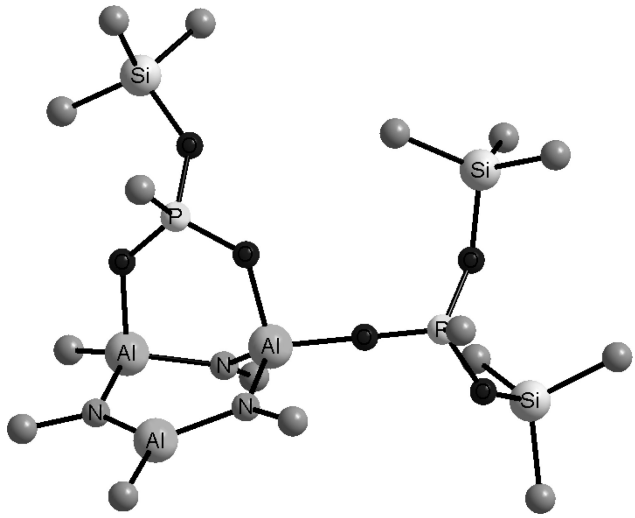
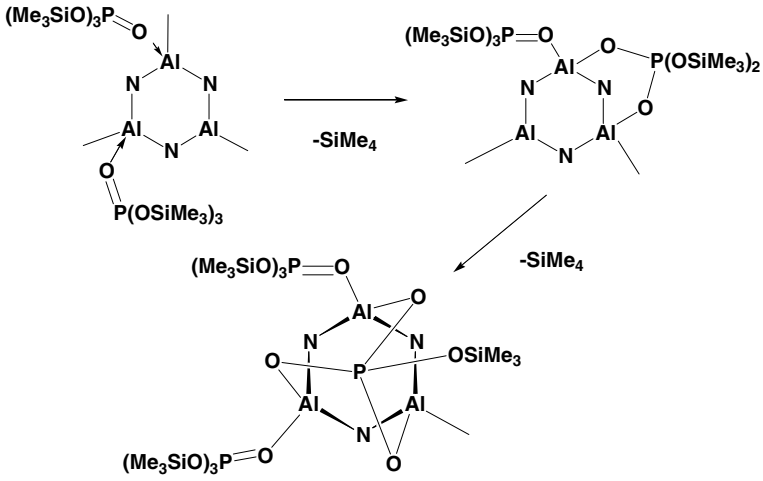


FIGURE 1 Molecular structure of **2** (2,6-diisopropylphenyls on nitrogens are represented by their ipso carbons).

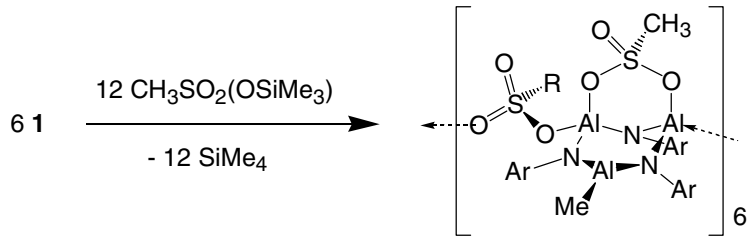
product **C**. The molecular structure of a bicyclic compound $(MeAl)_2$[2,6-$(i\text{-}Pr)_2C_6H_3N]_3$[$OP(Me)(OSiMe_3)_2$] [$O_2P(Me)(OSiMe_3)$] (**2**) was established by the x-ray diffraction experiment (Figure 1). In an agreement with the solution NMR data only one isomer of **2** is formed, whose bridging phosphonate methyl group points above the alumazene ring. This configuration is apparently forced by the steric demand of the $SiMe_3$ group and no conversion to the other isomer or to a heteroadamantane was observed even upon heating **2** in toluene to 120°C for several hours. The ^1H and ^{29}Si NMR spectra revealed diastereotopicity of the geminal $OSiMe_3$ groups in the coordinated ester molecule and thus confirm the kinetic inertness of this coordination bond in the solution. The magnetic anisotropy of the N—Al—N moiety in **2** was manifested in shielding of the apical P—CH_3 protons and the resulting upfield shift of this resonance in the ^1H NMR spectrum.

The suggested reaction course (Scheme 2) was deduced from the time evolution of the ^1H, ^{29}Si, and ^{31}P NMR spectra of the reaction mixtures. The primary reaction step most probably involves an adduct formation of **1** with $OP(OSiMe_3)_3$, similar to the one observed crystallographically by us in the bis-adduct **A**.[9] As the subsequent reaction event we envision the formation of a bridging $O_2P(OSiMe_3)_2$ group in the bicyclic intermediate similar to **2** through the dealkylsilylation. The formation of the adamantane core **C** is finally completed by a second dealkylsilylation.



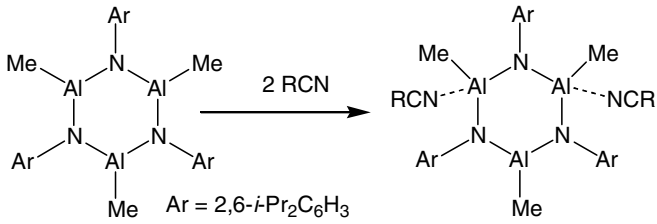
SCHEME 2

A dealkylsilylation reaction was observed also with trimethylsilyl ester of sulfonic acid, $CH_3SO_2(OSiMe_3)$, and provided bicyclic moieties similar to **2** (Scheme 3). These units further assemble into hexameric supramolecular rings in the solid state through the coordination of the sulfonate oxygen to a neighboring Al center.



SCHEME 3

The reactions of nitriles (RCN, R = Me, Me_3Si, *i*-Pr, 4-$MeOC_6H_4$, 4-MeC_6H_4, 2,6-$F_2C_6H_3$) with **1** were studied in analogy to their reactions with $AlMe_3$ (Scheme 4). The adduct formation in solution was demonstrated by an upfield shift of the Al–CH_3 resonance in the ^1H NMR spectra and in the case of CH_3CN also by a downfield shift of its methyl resonance. The tris-adduct was observed mass spectrometrically only in the case of *i*-PrCN. The *cis* and *trans* isomers were crystallographically characterized in the solid state for the bis-adducts of **1**



SCHEME 4

with 2,6-$F_2C_6H_3CN$ and MeC_6H_4CN respectively. The reason for the formation of the *cis* configuration in **1**(2,6-$F_2C_6H_3CN)_2$ can be traced to an attractive F-pi interaction.

REFERENCES

[1] a) N. J. Hardman, C. Cui, H. W. Roesky, W. H. Fink, and P. P. Power, *Angew. Chem.*, **113,** 2230 (2001); b) *Angew. Chem., Int. Ed.*, **40,** 2172 (2001).

[2] a) S. Schulz, L. Häming, R. Herbst-Irmer, H. W. Roesky, and G. M. Sheldrick, *Angew. Chem.*, **106,** 1052 (1994) and *Angew. Chem., Int. Ed.*, **33,** 969 (1994); b) J. D. Fisher, P. J. Shapiro, G. P. A. Yap, and A. L. Rheingold, *Inorg. Chem.*, **35,** 271 (1996); c) R. J. Wehmschulte and P. P. Power, *J. Am. Chem. Soc.*, **118,** 791 (1996); d) S. Schulz, A. Voigt, H. W. Roesky, L. Häming, and R. Herbst-Irmer, *Organometallics*, **15,** 5252 (1996); e) R. J. Wehmschulte and P. P. Power, *Inorg. Chem.*, **37,** 6906 (1998); f) W. Uhl, J. Molter, and R. Koch, *Eur. J. Inorg. Chem.*, 2021 (1999).

[3] a) K. M. Wagonner, H. Hope, and P. P. Power, *Angew. Chem.*, **100,** 1765 (1988); *Angew. Chem., Int. Ed. Engl.*, **27,** 1699 (1988); b) K. M. Wagonner and P. P. Power, *J. Am. Chem. Soc.*, **113,** 3385 (1991).

[4] J. Pinkas, in *Inorganic Experiments*, edited by J. D. Woollins (VCH, Weinheim, 2nd ed., 2003).

[5] J. Pinkas and H. W. Roesky, *J. Fluorine Chem*., **122,** 125 (2003).

[6] H. Hohmeister, H. Wessel, P. Lobinger, H. W. Roesky, P. Müller, I. Usón, H.-G. Schmidt, M. Noltemeyer, and J. Magull, *J. Fluorine Chem.*, **120,** 59 (2003).

[7] H. Wessel, C. Rennekamp, S.-D. Waezsada, H. W. Roesky, M. L. Montero, and I. Usón, *Organometallics*, **16,** 3243 (1997).

[8] a) H. Wessel, C. Rennekamp, H. W. Roesky, M. L. Montero, P. Müller, and I. Usón, *Organometallics*, **17,** 1919 (1998); b) H. Wessel, M. L. Montero, C. Rennekamp, et al., *Angew. Chem.*, **110,** 862 (1998); *Angew. Chem., Int. Ed.*, **37,** 843 (1998).

[9] J. Pinkas, H. Wessel, Y. Yang, et al., *Inorg. Chem.*, **37,** 2450 (1998).

[10] J. Pinkas, D. Chakraborty, Y. Yang, et al., *Organometallics*, **18,** 523 (1999).

[11] J. Pinkas, J. Löbl, D. Dastych, M. Necas, and H. W. Roesky, *Inorg. Chem.*, **41,** 6914 (2002).