



(PhC(NtBu)₂Al)₂(SiH₂)₄ six-membered heterocycle: comparable in structure to cyclohexane†

 Cite this: *Chem. Commun.*, 2019, 55, 2360

 Received 21st December 2018,
 Accepted 24th January 2019

DOI: 10.1039/c8cc10124h

rsc.li/chemcomm

 Jiancheng Li,^{ab} Mingdong Zhong,^b Helena Keil,^b Hongping Zhu,^{id} *^a
 Regine Herbst-Irmer,^{id} ^b Dietmar Stalke,^{id} *^b Sriman De,^{id} ^c Debasis Koley^{id} *^c
 and Herbert W. Roesky^{id} *^b

A silicon–aluminum heterocycle LAl(SiH₂SiH₂)₂AlL (L = PhC(NtBu)₂) (**1**) was prepared. Compound **1** exhibits a unique (N₂Al)₂(SiH₂)₄ centrosymmetric six-membered ring structure with a chair conformation, which is comparable with that of cyclohexane. Furthermore, two intermediate analogues, silylene–alane adduct LSi(AlMe₃)–Si(AlMe₃)L (**2**) and silylene–alane oxidative product [LAlHSiH₂Mes]₂ (**3**) were obtained. Compound **3** has an interesting arrangement of an Al–H and an SiH₂ unit, which are in close vicinity to each other. **3** might be important to function as a catalyst, due to the already activated bridging Al–H bonds.

Aluminum is the most abundant metal and silicon is the second most abundant element in the earth's crust.¹ Due to their convenient availability and broad use in industry,² the research of aluminum and silicon chemistry is very important. In recent decades, our group and others have focused on low-valent silicon and aluminum chemistry and many representative compounds, such as LSiR (L = PhC(NtBu)₂),³ LSi–SiL (L = PhC(NtBu)₂),⁴ N-heterocyclic silylenes (NHSi)⁵ and [Cp*Al]₄,⁶ have been prepared using alkaline metals or non-metals as reducing agents. Recently, cyclic silicon and cyclic aluminum compounds have attracted much attention because of their unique bonding nature and reactivities.⁷ For example, three-silicon membered cyclic compounds R₄Si₃ (R = Si^tBu₂Me or 2, 4, 6-iPr₃C₆H₂) were reported by Sekiguchi⁸ and Scheschkewitz.⁹ Tamao¹⁰ and Driess¹¹ reported a neutral tetrasilacyclobutadiene (EMind)₄Si₄ and a tetrasilacyclobutadiene

dication [L₂Si₂Si₂(:Si(Cl)L)]²⁺ (L = PhC(NtBu)₂) both containing a central Si₄ ring. The most extensively studied cyclic silicon compounds are cyclohexasilanes, Si₆X₁₂ (X = H,¹² Me,¹³ Ph,¹⁴ halides¹⁵), which were prepared by the reduction of silicon halides or by using a silicon anion. It is worth mentioning that Scheschkewitz *et al.* reported a silicon analogue of benzene R₆Si₆ (R = 2,4,6-iPr₃C₆H₂), which is aromatic.¹⁶ Subsequently, a large amount of research has been dedicated to studying hexasilanes and their isomers.¹⁷ Compared to silicon, however, cyclic aluminum compounds are more likely to form aluminum clusters.^{6,18} Nevertheless, Power¹⁹ reported compounds with a central three-membered Al₃-ring of [Ar*₃Al₃]²⁺ (Ar* = 2,6-Tip₂C₆H₃, Tip = 2,4,6-iPr₃C₆H₂) by using bulky substituents.

Despite the numerous reports on cyclic silicon and aluminum compounds, to the best of our knowledge, molecular cyclic compounds containing silicon and aluminum are not known. However, aluminum-doped silicon clusters contain these combinations, and their structures were only studied by theoretical calculations.²⁰ The difficulty in preparing silicon–aluminum heterocycles is probably due to the metathesis of the silicon anion with aluminum halides. Generally, this could realize the formation of a compound with acyclic Si–Al bonds.²¹ Furthermore, compounds containing the Al–SiH₂R unit are rarely reported, probably due to the limited utility of the RH₂Si[−] anion. So far only Nikonov *et al.* reported on the oxidative addition of the Si–H bond of PhSiH₃ to the Al(i) center of NacnacAl(·), resulting in the formation of NacnacAlHSiH₂Ph.²² However, this compound does not show any hydrogen bridging character. Inspired by the high reactivity of low-valent silicon explored by our group,^{3,4} we recently were interested in the reactions of amidinate supported low-valent silicon with aluminum compounds.‡ Herein, we report two unexpected results of the synthesis of Al₂(SiH₂)₄ six-membered rings, where two silicon atoms of cyclohexasilane are replaced by two aluminum atoms to yield LAl(SiH₂SiH₂)₂AlL (**1**) and silylene–alane oxidative product [LAlHSiH₂Mes]₂ (**3**). The latter and the silylene–alane adduct LSi(AlMe₃)–Si(AlMe₃)L (**2**) were prepared to get a better insight into the formation of compound **1**. Compounds **2** and **3** are important species to explain the formation of **1**.

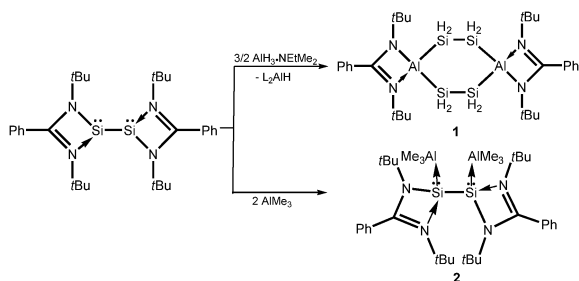
^a State Key Laboratory of Physical Chemistry of Solid Surface, National Engineering Laboratory for Green Chemical Productions of Alcohols-Ethers-Esters College of Chemistry and Chemical Engineering Xiamen University, Xiamen 361005, China. E-mail: hpzhu@xmu.edu.cn

^b Institut für Anorganische Chemie, Universität Göttingen, Tammannstraße 4, 37077 Göttingen, Germany. E-mail: hroesky@gwdg.de, dstalke@chemie.uni-goettingen.de

^c Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur-741 246, India. E-mail: koley@iiserkol.ac.in

† Electronic supplementary information (ESI) available: Experimental details, analytical data, X-ray structure determination, and computational details. CCDC 1875009 (**1**), 1875010 (**2**) and 1875008 (**3**) contain the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc10124h





Scheme 1 Preparation of compounds **1** and **2**.

We initially attempted the reaction of disilylene LSi-SiL ($L = \text{PhC}(\text{N}t\text{Bu})_2$) with $\text{AlH}_3 \cdot \text{NETMe}_2$ in a ratio of 1 : 2 in toluene in the temperature range from -78°C to room temperature (Scheme 1). Colorless crystals were obtained of composition L_2AlH ,²³ which was confirmed by NMR and mass spectrometry. However, attempts to separate a second silicon compound failed. We then changed the ratio of the precursors to 2 : 3 and a similar color change of the solution from red to colorless was observed. After separation of L_2AlH , we unexpectedly obtained $\text{LAl}(\text{SiH}_2\text{SiH}_2)_2\text{AlL}$ (**1**) as a crystalline solid in low yield (18%) (Scheme 1). Similar to reported results of the reaction between silylene and borane,²⁴ we propose that on the basis of the ratio of the precursors and the final results, the disilylanylaluminum intermediate $\text{LAlHSiH}_2\text{SiH}_2\text{AlHL}$ is unstable. It presumably reacts further with another equivalent of disilylene LSi-SiL in the presence of an equivalent amount of alane $\text{AlH}_3 \cdot \text{NETMe}_2$. Unfortunately, the attempt to characterize the intermediates was unsuccessful. However, for comparison we treated LSi-SiL with AlMe_3 and isolated only product **2** as a colorless crystalline solid (Scheme 1). Compound **2** is a Lewis acid-base adduct, with the Si atom acting as a two electron donor. Note, AlMe_3 undergoes oxidative addition at the Si(II) atom of N-heterocyclic silylene LSi: ($L = (\text{ArN})\text{C}(\text{CH}_2)\text{CHC}(\text{Me})(\text{NAr})$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$).²⁵ The formation of compound **2** suggests that compound **1** also proceeds under adduct formation of LSi-SiL with two AlH_3 followed by the insertion of the Si atom into the Al-H bonds.

Compounds **1** and **2** are air and moisture sensitive. Under N_2 atmosphere, they are both stable for more than one month in the solid state. However, compound **1** in solution decomposed into an unidentified mixture within a few days at room temperature. For compound **1**, the ^{29}Si INEPT spectrum displays a broad resonance at -128.9 ppm, which is highly upfield shifted when compared with that of compound LSi-SiL (76.3 ppm).⁴ However, in the ^{29}Si NMR spectrum of compound **2**, the Si resonance is at $+56.9$ ppm, indicating remaining silylene character. The Si-H hydrides of compound **2** give rise to the ^1H NMR resonance at 3.36 ppm, which is upfield-shifted when compared with that of compound **3** (4.54 ppm, see below) and $\text{NacnacAlHSiH}_2\text{Ph}$ (3.87 ppm).²² The IR spectrum of compound **2** displays a broad band at 2074 cm^{-1} , attributed to Si-H bond stretching. No resonance for the Al-H bond is observed. In the ^1H NMR spectrum of compound **2**, the resonances for $t\text{Bu}$ groups on the amidinate ligands and methyl groups on aluminum were observed at 1.21 ppm and -0.02 ppm, respectively.

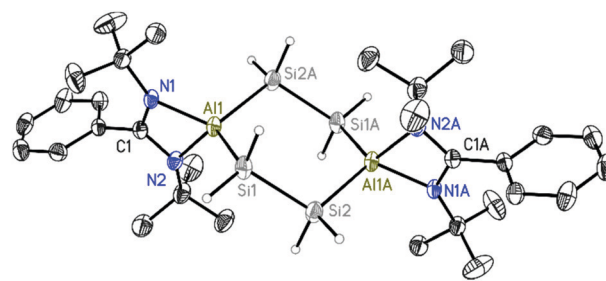


Fig. 1 Molecular structure of **1** with anisotropic displacement parameters at 50% probability level. The hydrogen atoms except silicon hydride atoms are omitted for clarity. Their positions are taken from the difference map and refined freely. Selected bond distances [Å] and angles [$^\circ$]: Al1-Si1 2.4473(9), Al1-Si2A 2.4545(9), Al1-N1 1.9100(16), Al1-N2 1.9236(17), N1-Al1-N2 69.47(7), Si1-Al1-Si2A 114.84(3).

Single-crystal X-ray structural analysis of compound **1** clearly revealed a centrosymmetric six-membered heterocycle with two Al atoms at the 1,4-positions which are linked by two $-\text{SiH}_2-\text{SiH}_2-$ units (Fig. 1). The Al_2Si_4 heterocycle adopts a chair conformation, typical of cyclohexane congeners where the six methylene groups are replaced by two N_2Al units and four SiH_2 moieties. These four silicon atoms are in the same plane while one Al atom is located above and one below that Si_4 plane. The dihedral angle between the planes defined by Si_4 and Al1Si1Si2A is $50.03(4)^\circ$, while the distance between the Al atom and the Si_4 plane is $1.0113(10)$ Å. The bond lengths of Al-Si (2.4473(9) and 2.4545(9) Å) in **1** are comparable with those in $\text{NacnacAlHSiH}_2\text{Ph}$ (2.4522(8) Å),²² NacnacAlHSiHMePh (2.4548(7) Å)²² and $\text{LSiHAlH}_2(\text{NMe}_3)$ ($L = (\text{ArN})\text{C}(\text{CH}_2)\text{CHC}(\text{Me})(\text{NAr})$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) (2.487(1) Å).²⁵ The two $\text{SiH}_2-\text{SiH}_2$ bond lengths (2.3413(9) Å) are crystallographically equivalent and comparable with the corresponding distances in the $(t\text{BuN})_2(\text{SiH}_2)_4$ heterocycle (2.337(1) and 2.334(1) Å).²⁶ The Si-H distances (1.440(17) to 1.448(18) Å) fall in the common range of Si-H bonds. Both Al atoms in compound **1** show distorted tetrahedral coordination environments, with both Al atoms at the spiro centers of six-membered (Al_2Si_4) and four-membered (CN_2Al) rings. The ligand bite angle N1-Al1-N2 ($69.47(7)^\circ$) is rather sharp, whereas the Si1-Al1-Si2A angle ($114.84(3)^\circ$) is rather wide. However, the Si-centered bond angle in Al_2Si_4 (Al1-Si1-Si2 ($107.57(3)^\circ$)) is close to the ideal tetrahedral angle of 109.47° . Compound **2** was also characterized by X-ray crystallography (see ESI†). The molecular structure of **2** shows that each silicon atom coordinates to one aluminum atom. The torsion angle Al-Si-Si-Al is $-68.57(4)^\circ$. To the best of our knowledge, compound **2** represents a rare example of silylene-alane adducts, and the only other two examples are $[\text{PhC}(\text{NiPr})_2]_2\text{Si} \rightarrow \text{AlPh}_3$ and $[\text{C}(\text{NiPr})_3]_2\text{Si} \rightarrow \text{AlPh}_3$.²⁷ The Si \rightarrow Al dative bond lengths (2.5921(7) and 2.5799(8) Å) in compound **2** are much longer than the Si-Al σ bonds in compound **1** (2.4473(9) and 2.4545(9) Å). However, they are comparable with those in $[\text{PhC}(\text{NiPr})_2]_2\text{Si} \rightarrow \text{AlPh}_3$ (2.5293(14) Å) and $[\text{C}(\text{NiPr})_3]_2\text{Si} \rightarrow \text{AlPh}_3$ (2.5544(17) Å). The Si1-Si2 bond (2.3937(7) Å) is comparable with those in LSi-SiL (2.413(2) Å) and $\text{LSi}(\rightarrow\text{M})\text{-Si}(\rightarrow\text{M})\text{L}$ adducts (2.376(5) Å for $\text{M} = \text{Ir}$ and 2.388(2) Å for $\text{M} = \text{Rh}$).²⁸

In order to get the analogues of intermediate C (Scheme 3) in the formation of compound **1**, we turned to the reaction of amidinate



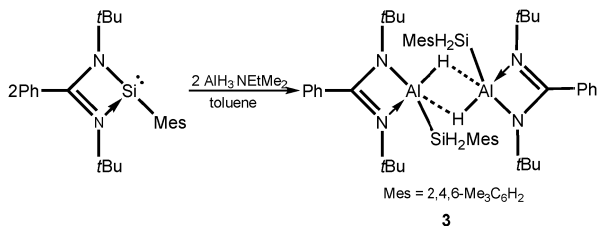
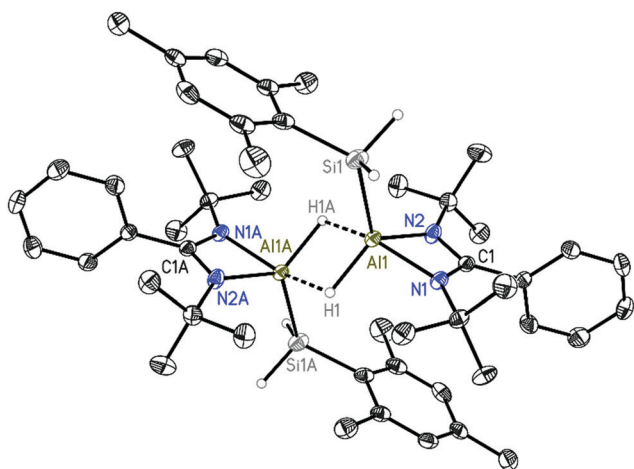
Scheme 2 Preparation of compound **3**.

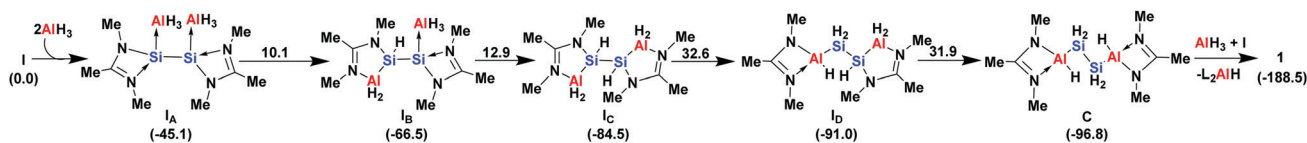
Fig. 2 Molecular structure of **3** with anisotropic displacement parameters at the 50% probability level. The hydrogen atoms except for aluminum hydride and silicon hydride atoms are omitted for clarity. Their positions were taken from the difference map and refined freely. Selected bond distances [Å] and angles [°]: Al1–Si1 2.4602(8), Al1–H1 1.653(16), Al1–H1A 1.796(17), Al1–N1 1.9543(16), Al1–N2 1.9220(14), N1–Al1–N2 68.60(6), H1–Al1–H1A 77.0(9).

mesitylsilylene LSiMes^{29} (Mes = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$) with alane $\text{AlH}_3 \cdot \text{NEtMe}_2$ in the ratio of 1:1, which was accomplished in toluene in the temperature range from -78°C to room temperature (Scheme 2). After the removal of all volatiles and treating the residue with *n*-hexane, a white solid of $[\text{LAHSiH}_2\text{Mes}]_2$ (**3**) was collected by filtration in 76% yield. Compound **3** was characterized by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy and single crystal X-ray structure analysis. The ^{29}Si NMR spectrum of **3** shows a broad resonance at -91.7 ppm that is shifted upfield with respect to that of LSiMes (24.0 ppm)²⁹ and $\text{NacnacAlHSiH}_2\text{Ph}$ (-74.3 ppm),²² but downfield compared with that of compound **1** (-128.9 ppm). In the ^1H NMR spectrum, the broad resonance at 5.26 ppm for two hydrogens is attributed to the aluminum hydride Al–H, and the singlet at 4.54 ppm for four hydrogen atoms is attributed to silane hydrides

SiH_2 . The existence of aluminum hydrides and silicon hydrides is also proved by the observation of broad bands at 1645 cm^{-1} and 2095 cm^{-1} in the IR spectra, respectively. The resonance for the *t*Bu group of the amidinate ligand appears at 0.93 ppm and the characteristic resonances for the mesityl group were observed at 2.18, 2.70, and 6.88 ppm, respectively. The structure of **3** was further confirmed in a single crystal X-ray diffraction study (Fig. 2). It unambiguously displays that it dimerizes by two bridging hydrogen atoms from each aluminum, and the bidentate ligand L (L = $\text{PhC}(\text{N}t\text{Bu})_2$) coordinates to the Al atom together with the SiH_2Mes group. The five-coordinated Al atom adopts a distorted square-based pyramidal rather than a trigonal bipyramidal geometry. The Si1–Al1 bond length of 2.4602(8) Å is slightly longer than that in compound **1** (2.4473(9) and 2.4545(9) Å). The two Al–H bond distances are 1.653(16) Å and 1.796(17) Å, with one slightly longer and the other one slightly shorter than those of corresponding bonds in similar aluminum hydride dimers $(\text{LAH}_2)_2$ (L = $\text{RC}(\text{NAr})_2$, R = $\text{N}(\text{iPr})_2$, Ar = 2,6- $\text{iPr}_2\text{C}_6\text{H}_3$) (1.60(2) Å and 1.81(2) Å)³⁰ and 2-aminophenylaluminum dihydride $[(2\text{-tmp-C}_6\text{H}_4)\text{AlH}_2]_2$ (1.585(16) Å and 1.896(16) Å),³¹ indicating in **3** a strong tendency of forming an equal Al–H bond length within a stable dimer.

Finally, DFT calculations (see computational details, ESI†) are performed to support the mechanism for the generation of silicon–aluminum heterocycle **1**. The reaction energy ($\text{I} + \text{AlH}_3 \rightarrow \text{1}$) is highly exergonic ($\Delta G_{\text{T}}^{\ddagger} = -188.5\text{ kcal mol}^{-1}$) indicating a facile, thermodynamically favorable product formation (Scheme 3). The reaction begins with two successive oxidative additions of AlH_3 at two different Si centers leading to the formation of intermediate I_C . Thereafter, subsequent migrations of the hydride from Al to Si centers allow the formation of intermediate C (Fig. S3.1 and S3.2, ESI†). Finally, the addition of AlH_3 and **1** with intermediate C furnished **1** by releasing one molecule of L_2AlH . This step is highly exergonic ($\Delta G_{\text{T}}^{\ddagger} = -91.7\text{ kcal mol}^{-1}$) with respect to intermediate C. The first hydride transfer step ($\text{I}_\text{C} \rightarrow \text{I}_\text{B}$; $\Delta^{\ddagger}G_{\text{T}}^{\ddagger} = 32.6\text{ kcal mol}^{-1}$; Fig. S3.1, ESI†)^{24,32} was calculated to be the rate determining step for the overall transformation, which justifies the formation of **1** with a very low yield.

In conclusion, we report a new method for preparing a silicon–aluminum heterocycle by insertion reaction of a low valent silicon atom supported by an amidinate ligand into the Al–H bond of an alane, which is followed by a rearrangement of the amidinate ligand from Si to Al and subsequent migration of hydride from aluminum to silicon. $\text{LAl}(\text{SiH}_2\text{SiH}_2)_2\text{AL}$ (**1**) exhibits a unique centrosymmetric six-membered ring with chair conformation, which is reminiscent of cyclohexane. **1** contains 4 silicon and two aluminum atoms, and exhibits a new six-membered ring system. In addition, $\text{LSi}(\text{AlMe}_3)\text{--Si}(\text{AlMe}_3)\text{L}$ (**2**) and $[\text{LAHSiH}_2\text{Mes}]_2$ (**3**) were



Scheme 3 Relative Gibbs free energy (in kcal mol^{-1}) for the intermediates involved in the formation of **1**. Values in parentheses are energy values ($\Delta G_{\text{T}}^{\ddagger}$; in kcal mol^{-1}) relative to the starting material ($\text{I} + \text{AlH}_3$). Values above the arrows are the activation barriers between the two corresponding intermediates. For further details see the ESI.†



prepared, which could be viewed as two intermediate analogues, indicating that the formation of compound **2** involves a silylene–alane adduct, a silylene–alane oxidative addition and finally rearrangement of the ligand along with migration of a hydride. The formation of **1** was also explored employing DFT calculations. Compound **3** is prone to generating aluminum cations that could function as catalysts.

H. W. R. thanks the Deutsche Forschungsgemeinschaft for financial support RO224/68-1. J. Li thanks the China Scholarship Council (CSC) for the fellowship (201706310031). D. S. thanks the Danish National Research Foundation (DNRF93) funded Centre for Materials Crystallography (CMC) for partial support. S. D. thanks UGC for an SRF fellowship, and D. K. acknowledges IISER Kolkata for the financial support. This study is dedicated to Professor Hubert Schmidbaur.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Crystal data for **1** at 100(2) K: $C_{30}H_{54}Al_2N_4Si_4$, $M_r = 637.09 \text{ g mol}^{-1}$, $0.210 \times 0.150 \times 0.150 \text{ mm}$, monoclinic, $P2_1/c$, $a = 13.559(2) \text{ \AA}$, $b = 8.253(2) \text{ \AA}$, $c = 17.689(3) \text{ \AA}$, $\beta = 103.31(2)^\circ$, $V = 1926.3(7) \text{ \AA}^3$, $Z = 2$, $\mu(\text{Mo K}\alpha) = 0.224 \text{ mm}^{-1}$, $\theta_{\text{max}} = 26.4^\circ$, 32 188 reflections measured, 3950 independent ($R_{\text{int}} = 0.0532$), $R_1 = 0.0410$ [$I > 2\sigma(I)$], $wR_2 = 0.1143$ (all data), res. density peaks: $0.425/-0.266 \text{ e \AA}^{-3}$, CCDC: 1875009. Crystal data for **2** at 100(2) K: $C_{36}H_{64}Al_2N_4Si_2 \cdot 0.5 (C_7H_8)$, $M_r = 709.11 \text{ g mol}^{-1}$, $0.260 \times 0.170 \times 0.100 \text{ mm}$, monoclinic, $P2_1/c$, $a = 18.949(2) \text{ \AA}$, $b = 11.775(2) \text{ \AA}$, $c = 20.216(3) \text{ \AA}$, $\beta = 102.27(2)^\circ$, $V = 4407.6(11) \text{ \AA}^3$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 0.150 \text{ mm}^{-1}$, $\theta_{\text{max}} = 26.5^\circ$, 86 568 reflections measured, 9064 independent ($R_{\text{int}} = 0.0665$), $R_1 = 0.0368$ [$I > 2\sigma(I)$], $wR_2 = 0.0921$ (all data), res. density peaks $0.276/-0.211 \text{ e \AA}^{-3}$, CCDC: 1875010. Crystal data for **3** at 100(2) K: $C_{48}H_{74}Al_2N_4Si_2$, $M_r = 817.25 \text{ g mol}^{-1}$, $0.195 \times 0.150 \times 0.144 \text{ mm}$, triclinic, $P\bar{1}$, $a = 10.039(2) \text{ \AA}$, $b = 10.144(2) \text{ \AA}$, $c = 13.835(3) \text{ \AA}$, $\alpha = 103.40(2)^\circ$, $\beta = 97.39(2)^\circ$, $\gamma = 114.85(3)^\circ$, $V = 1202.2(5) \text{ \AA}^3$, $Z = 1$, $\mu(\text{Ag K}\alpha) = 0.083 \text{ mm}^{-1}$, $\theta_{\text{max}} = 20.5^\circ$, 46 064 reflections measured, 4929 independent ($R_{\text{int}} = 0.0469$), $R_1 = 0.0370$ [$I > 2\sigma(I)$], $wR_2 = 0.0955$ (all data), res. density peaks: $0.313/-0.335 \text{ e \AA}^{-3}$, CCDC: 1875008. The data were integrated with SAINT.³³ A multi-scan absorption correction was applied using SADABS.³⁴ The structures were solved by SHELXT³⁵ and refined on F^2 using SHELXL³⁶ in the graphical user interface ShelXle.³⁷

1 S. R. Taylor, *Geochim. Cosmochim. Acta*, 1964, **28**, 1273–1285.

2 (a) G. E. Totten and D. S. Mackenzie, *Handbook of Aluminum*, CRC Press, New York, 2003; (b) J. Boor, *Ziegler-Natta catalysts and polymerization*, Academic Press, New York, 1979; (c) G. A. Olah, *Friedel-Crafts and related reactions*, Wiley, New York, 1963; (d) F. Peng, Y. Su, Y. Zhong, C. Fan, S.-T. Lee and Y. He, *Acc. Chem. Res.*, 2014, **47**, 612–623.

3 (a) S. S. Sen, H. W. Roesky, D. Stern, J. Henn and D. Stalke, *J. Am. Chem. Soc.*, 2010, **132**, 1123–1126; (b) R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf and D. Stalke, *Organometallics*, 2012, **31**, 4588–4592; (c) R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf and D. Stalke, *Chem. Commun.*, 2012, **48**, 4561–4563.

4 (a) S. S. Sen, A. Jana, H. W. Roesky and C. Schulzke, *Angew. Chem., Int. Ed.*, 2009, **48**, 8536–8538; (b) S. S. Sen, S. Khan, S. Nagendran and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 578–587.

5 (a) M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691–2692; (b) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354–396.

6 (a) C. Dohmeier, C. Robl, M. Tacke and H. Schnöckel, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 564–565; (b) S. Schulz, H. W. Roesky, H. J. Koch, G. M. Sheldrick, D. Stalke and A. Kuhn, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1729–1731.

7 (a) A. Rammo and D. Scheschke, *Chem. – Eur. J.*, 2018, **24**, 6866–6885; (b) P. Bag, C. Weetman and S. Inoue, *Angew. Chem., Int. Ed.*, 2018, **57**, 14394–14413.

8 M. Ichinohe, T. Matsuno and A. Sekiguchi, *Angew. Chem., Int. Ed.*, 1999, **38**, 2194–2196.

9 K. Leszczyńska, K. Abersfelder, A. Mix, B. Neumann, H.-G. Stammer, M. J. Cowley, P. Jutzi and D. Scheschke, *Angew. Chem., Int. Ed.*, 2012, **51**, 6785–6788.

10 K. Suzuki, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka and K. Tamao, *Science*, 2011, **331**, 1306–1309.

11 S. Inoue, J. D. Epping, E. Irran and M. Driess, *J. Am. Chem. Soc.*, 2011, **133**, 8514–8517.

12 E. Hengge and D. Kovar, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 403.

13 (a) C. A. Burkhard, *J. Am. Chem. Soc.*, 1949, **71**, 963–964; (b) H. Gilman and R. A. Tomasi, *J. Org. Chem.*, 1963, **28**, 1651–1653.

14 (a) H. J. S. Winkler, A. W. P. Jarvie, D. J. Peterson and H. Gilman, *J. Am. Chem. Soc.*, 1961, **83**, 4089–4093; (b) H. Gilman, D. J. Peterson, A. W. P. Jarvie and H. J. S. Winkler, *Tetrahedron Lett.*, 1960, **23**, 5–7.

15 X. Dai, J. D. Schulz, C. W. Braun, A. Ugrinov and P. Boudjouk, *Organometallics*, 2010, **29**, 2203–2205.

16 (a) K. Abersfelder, A. J. P. White, H. S. Rzepa and D. Scheschke, *Science*, 2010, **327**, 564–566; (b) K. Abersfelder, A. J. P. White, R. J. F. Berger, H. S. Rzepa and D. Scheschke, *Angew. Chem., Int. Ed.*, 2011, **50**, 7936–7939; (c) D. Kratzert, D. Leusser, J. J. Holstein, B. Dittrich, K. Abersfelder, D. Scheschke and D. Stalke, *Angew. Chem., Int. Ed.*, 2013, **52**, 4478–4482.

17 (a) K. Abersfelder, A. Russell, H. S. Rzepa, A. J. P. White, P. R. Haycock and D. Scheschke, *J. Am. Chem. Soc.*, 2012, **134**, 16008–16016; (b) A. Tsurusaki, C. Iizuka, K. Otsuka and S. Kyushin, *J. Am. Chem. Soc.*, 2013, **135**, 16340–16343; (c) T. Szilvási and T. Veszprémi, *Organometallics*, 2012, **31**, 3207–3212; (d) Z. Benedek, T. Szilvási and T. Veszprémi, *Dalton Trans.*, 2014, **43**, 1184–1190.

18 (a) V. W. Hiller, K.-W. Klinkhammer, W. Uhl and J. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 179–180; (b) V. U. Schneider, R. Ahlrichs, H. Horn and A. Schäfer, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 353–355.

19 R. J. Wright, M. Brynda and P. P. Power, *Angew. Chem., Int. Ed.*, 2006, **45**, 5953–5956.

20 (a) M. Akutsu, K. Koyasu, J. Atobe, K. Miyajima, M. Mitsui, H. Tsunoyama and A. Nakajima, *Phys. Chem. Chem. Phys.*, 2017, **19**, 20401–20411; (b) O. P. Charkin and N. M. Klimenko, *Russ. J. Inorg. Chem.*, 2016, **61**, 594–603; (c) N. M. Tam, T. B. Tai, V. T. Ngan and M. T. Nguyen, *J. Phys. Chem. A*, 2013, **117**, 6867–6882; (d) M. Su, N. Du and H. Chen, *J. Cluster Sci.*, 2018, **29**, 141–150.

21 (a) P. Bag, A. Porzelt, P. J. Altmann and S. Inoue, *J. Am. Chem. Soc.*, 2017, **139**, 14384–14387; (b) M. Nakamoto, T. Yamasaki and A. Sekiguchi, *J. Am. Chem. Soc.*, 2005, **127**, 6954–6955; (c) N. Wiberg, T. Blank, K. Amelunxen, H. Nöth, H. Schnöckel, E. Baum, A. Purath and D. Fenske, *Eur. J. Inorg. Chem.*, 2002, 341–350; (d) N. Wiberg, T. Blank, H. Lemer, H. Nöth, T. Haberer and D. Fenske, *Z. Naturforsch.*, 2001, **56b**, 652–658.

22 T. Chu, I. Korobkov and G. I. Nikonov, *J. Am. Chem. Soc.*, 2014, **136**, 9195–9202.

23 Unpublished compound from our group which is prepared from LLI (L = PhC(NtBu)₂) and AlHCl₂.

24 S. Khoo, Y.-L. Shan, M.-C. Yang, Y. Li, M.-D. Su and C.-W. So, *Inorg. Chem.*, 2018, **57**, 5879–5887.

25 Y. Xiong, S. Yao and M. Driess, *Chem. – Eur. J.*, 2012, **18**, 3316–3320.

26 M. Söldner, A. Schier and H. Schmidbaur, *Inorg. Chem.*, 1997, **36**, 1758–1763.

27 F. M. Mück, J. A. Baus, R. Bertermann, C. Burschka and R. Tacke, *Organometallics*, 2016, **35**, 2583–2588.

28 S. Khoo, H.-Y. Yeong, Y. Li, R. Ganguly and C.-W. So, *Inorg. Chem.*, 2015, **54**, 9968–9975.

29 J. A. Cabeza, P. García-Álvarez and L. González-Álvarez, *Chem. Commun.*, 2017, **53**, 10275–10278.

30 S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones and A. Stasch, *Nat. Chem.*, 2010, **2**, 865–869.

31 S. Chen, B. Li, X. Wang, Y. Huang, J. Li, H. Zhu, L. Zhao, G. Frenking and H. W. Roesky, *Chem. – Eur. J.*, 2017, **23**, 13633–13637.

32 Z. Yang, Y. Yi, M. Zhong, S. De, T. Mondal, D. Koley, X. Ma, D. Zhang and H. W. Roesky, *Chem. – Eur. J.*, 2016, **22**, 6932–6938.

33 Bruker Apex CCD, SAINTv8.30C, ed. Bruker AXS Inst. Inc., Bruker AXS Inc., WI, USA, Madison, 2013.

34 L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3–10.

35 G. M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3–8.

36 G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3–8.

37 C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281–1284.

