A silicon–aluminum heterocycle $\text{LAl[SiH}_2\text{SiH}_2\text{]}_2\text{AlL}$ ($\text{L} = \text{PhC(NtBu)}_2$) (1) was prepared. Compound 1 exhibits a unique $(\text{N}_2\text{Al})_2$($\text{SiH}_2$)$_4$ centrosymmetric six-membered ring structure with a chair conformation, which is comparable with that of cyclohexane. Furthermore, two intermediate analogues, silylene–alane adduct $\text{LSi(AlMe}_3\text{)}_2\text{Si(AlMe}_3\text{)}_2\text{L}$ (2) and silylene–alane oxidative product $[\text{LAlHSiH}_2\text{Mes}]_2$ (3) were obtained. Compound 3 has an interesting arrangement of an Al–H and an SiH$_2$ 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. Due to their convenient availability and broad use in industry, 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 ($\text{L} = \text{PhC(NtBu)}_2$), $\text{LsiSili}$ (L = PhC(NtBu)$_2$), N-heterocyclic silylenes (NHSi)$_5$ and [Cp*Al]$_4$, 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. For example, three-silicon membered cyclic compounds R$_4$Si$_3$ ($\text{R} = \text{SiBu}_2\text{Me}$ or 2, 4, 6-iPr$_3$C$_6$H$_2$) were reported by Sekiguchi and Scheschkewitz. Tamao and Dries reported a neutral tetrasilacyclobutadiene (EMind)$_2$Si$_4$ and a tetrasilacyclobutadiene dication $[\text{L}_2\text{Si}_4\text{Si}_4(\text{SiCl}_4)]^{2+}$ ($\text{L} = \text{PhC(NtBu)}_2$) both containing a central Si$_4$ ring. The most extensively studied cyclic silicon compounds are cyclohexasilanes, Si$_6$X$_{12}$ ($X = \text{H, Me, Ph}$, halides$)$, 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 R$_6$Si$_6$ ($\text{R} = 2,4,6$-iPr$_3$C$_6$H$_3$), which is aromatic. Subsequently, a large amount of research has been dedicated to studying hexasilbenzenes and their isomers. Compared to silicon, however, cyclic aluminum compounds are more likely to form aluminum clusters. Nevertheless, Power reported compounds with a central three-membered Al$_3$ ring of [Ar*$_3$Al$_3$]$^{2+}$ (Ar* = 2,6-Tip$_2$C$_6$H$_3$, Tip = 2,4,6-iPr$_3$C$_6$H$_3$) 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. 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. Furthermore, compounds containing the Al–SiH$_2$R unit are rarely reported, probably due to the limited utility of the RH$_2$Si$^-$ anion. So far only Nikonor et al. reported on the oxidative addition of the Si–H bond of PhSiH$_3$ to the Al(0) center of NacacAl(0), resulting in the formation of NacacAlH$_2$SiH$_2$Ph. However, this compound does not show any hydrogen bridging character. Inspired by the high reactivity of low-valent silicon explored by our group, 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 Al$_2$(SiH$_3$)$_4$ six-membered rings, where two silicon atoms of cyclohexasilane are replaced by two aluminum atoms to yield LAli(SiH$_3$)$_2$AlL (1) and silylene–alane oxidative product [LAiHSiH$_2$Mes]$_2$ (3). The latter and the silylene–alane adduct LSi(AlMe)$_3$–Si(AlMe)$_3$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.
We initially attempted the reaction of disilylene LSi-SiL (L = PhC(NiBu)₂) with AlH₃-NEtMe₂ 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 L₂AlH, 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 L₂AlH, we unexpectedly obtained LAl(SiH₂SiH₂)₂AlL (1) as a crystalline solid in low yield (18%) (Scheme 1). Similar to reported results of the reaction between silylene and borane, we propose that on the basis of the ratio of the precursors and the final results, the disilylacetylene intermediate LAlHSiH₂SiH₂AlHL is unstable. It presumably reacts further with another equivalent of disilylene LSi-SiL in the presence of an equivalent amount of alane Al₂H₂NETMe₂. Unfortunately, the attempt to characterize the intermediates was unsuccessful. However, for comparison we treated LSi-SiL with AlMe₃ 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, AlMe₃ undergoes oxidative addition at the Si(n) atom of N-heterocyclic silylene LSi (L = [ArN(C(CH₂)₂CHC(Me)-NAr), Ar = 2,6-iPr₂C₆H₃]. The formation of compound 2 suggests that compound 1 also proceeds under adduct formation of LSi-SiL with two AlH₃ followed by the insertion of the Si atom indicating remaining silylene character. The Si–H hydrides of CHC(Me)(NAr), Ar = 2,6-iPr₂C₆H₃. The formation of compound 2 and a similar color change of the solution from red to colorless was observed. After separation of L₂AlH, we unexpectedly obtained LAl(SiH₂SiH₂)₂AlL (1) as a crystalline solid in low yield (18%) (Scheme 1). Similar to reported results of the reaction between silylene and borane, we propose that on the basis of the ratio of the precursors and the final results, the disilylacetylene intermediate LAlHSiH₂SiH₂AlHL is unstable. It presumably reacts further with another equivalent of disilylene LSi-SiL in the presence of an equivalent amount of alane Al₂H₂NETMe₂. Unfortunately, the attempt to characterize the intermediates was unsuccessful. However, for comparison we treated LSi-SiL with AlMe₃ 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, AlMe₃ undergoes oxidative addition at the Si(n) atom of N-heterocyclic silylene LSi (L = [ArN(C(CH₂)₂CHC(Me)-NAr), Ar = 2,6-iPr₂C₆H₃]. The formation of compound 2 suggests that compound 1 also proceeds under adduct formation of LSi-SiL with two AlH₃ followed by the insertion of the Si atom into the Al–H bonds.

Compounds 1 and 2 are air and moisture sensitive. Under N₂ 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 ²⁹Si 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). However, in the ²⁹Si 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 NacnacAlHSiH₂Ph (3.87 ppm). 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 tBu groups on the aminate ligands and methyl groups on aluminum were observed at 1.21 ppm and −0.02 ppm, respectively.
mesitylsilylene LSiMes \(^{29}\) \((\text{Mes} = 2,4,6-\text{Me}_3\text{C}_6\text{H}_2)\) with alane \(\text{AlH}_3\) and \(\text{Me}_2\text{NMe}_2\) 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 \(\text{[LAlHSiH}_2\text{Mes}]_2\) \((3)\) was collected by filtration in \(76\%\) yield. Compound 3 was characterized by \(^1\text{H}, \)\(^{13}\text{C},\) and \(^{29}\text{Si}\) NMR spectroscopy and single crystal X-ray structure analysis. The \(^{29}\text{Si}\) NMR spectrum of 3 shows a broad resonance at \(-91.7\) ppm that is shifted upfield with respect to that of \(\text{LSiMes} \) \((24.0\) 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 \(^1\text{H}\) NMR spectrum, the broad resonance at 5.26 ppm for two hydrogens is attributed to the aluminum hydride \(\text{Al-H}\), and the singlet at 4.54 ppm for four hydrogens is attributed to silane hydrides \(\text{SiH}_2\). 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 \(\text{Bu}\) 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 \(L\) \((L = \text{PhC(NBu)}_3)\) coordinates to the \(\text{Al}\) atom together with the \(\text{SiH}_2\text{Mes}\) group. The five-coordinated \(\text{Al}\) atom adopts a distorted square-based pyramidal rather than a trigonal pyramidal geometry. The \(\text{Si1-Al1}\) 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 \(\text{Al-H}\) 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 \(\text{[LAlH}_2\text{]}_2 \) \((L = \text{RC(NAr)}_2, \ R = \text{Ni} \text{Pr}_3, \text{Ar} = 2,6-\text{iPr}_2\text{C}_6\text{H}_3)\) \((1.60(2)\) 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 3 a strong tendency of forming an equal \(\text{Al-H}\) 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 (1 + \(\text{AlH}_3\) \(\rightarrow\) 1) is highly exergonic \((\Delta G_1^9 = -188.5\) kcal mol\(^{-1}\)) indicating a facile, thermodynamically favorable product formation (Scheme 3). The reaction begins with two successive oxidative additions of \(\text{AlH}_3\) at two different \(\text{Si}\) centers leading to the formation of intermediate \(1\). Thereafter, subsequent migrations of the hydride from \(\text{Al}\) to \(\text{Si}\) centers allow the formation of intermediate \(C\) (Fig. S3.1 and S3.2, ESI†). Finally, the addition of \(\text{AlH}_3\) and 1 with intermediate \(C\) furnished 1 by releasing one molecule of \(\text{L}_2\text{AlH}\). This step is highly exergonic \((\Delta G_1^9 = -91.7\) kcal mol\(^{-1}\)) with respect to intermediate \(C\). The first hydride transfer step \((L_2 \rightarrow 1; \ \Delta G_2^9 = 32.6\) 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 \(\text{Al-}\text{H}\) bond of an alane, which is followed by a rearrangement of the amidinate ligand from \(\text{Si}\) to \(\text{Al}\) and subsequent migration of hydride from aluminum to silicon. \(\text{[LAlSiH}_2\text{SiH}_3\text{]}_2\text{Al}\) (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, \(\text{LSi(AlMe}_3\text{)}_2\text{-Si(AlMe}_3\text{)}_2\text{L}\) (2) and \([\text{LAlHSiH}_2\text{Mes}]_2\) (3) were...
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 Schmidbauer.

Conflicts of interest

There are no conflicts to declare.

Notes and references

Crystal data for 1 at 100(2) K: C_{21}H_{34}Al_{5}N_{4}Si, M_{r} = 637.03 g mol^{-1}, 0.210 x 0.150 x 0.150 mm, monoclinic, P2_{1}/c, a = 13.599(2) Å, b = 8.253(2) Å, c = 17.689(3) Å, β = 103.311(7), V = 1926.2(7) Å³, Z = 2, ρ(Mo Kα) = 0.224 mm^{-1}, 32188 reflections measured, 3950 independent (R_{int} = 0.0532), R_{1} = 0.0410 ([I > 2σ(I)], wR_{2} = 0.1143 (all data), res. density peaks: 0.252–0.266 e Å^{-3}, CCDC: 1875009. Crystal data for 2 at 100(2) K: C_{21}H_{34}Al_{5}N_{4}Si, M_{r} = 709.11 g mol^{-1}, 0.260 x 0.170 x 0.100 mm, monoclinic, P2_{1}/c, a = 18.949(2) Å, b = 11.775(2) Å, c = 20.216(3) Å, β = 102.27(2), V = 4407.6(11) Å³, Z = 4, ρ(Mo Kα) = 0.150 mm^{-1}, ρ_{min} = 86.5, 86568 reflections measured, 9064 independent (R_{int} = 0.0665), R_{1} = 0.0306 ([I > 2σ(I)], wR_{2} = 0.0921 (all data), res. density peaks 0.276–0.211 e Å^{-3}, CCDC: 1875010. Crystal data for 3 at 100(2) K: C_{21}H_{34}Al_{5}N_{4}Si, M_{r} = 817.25 g mol^{-1}, 0.195 x 0.150 x 0.144 mm, triclinic, P1, a = 10.032(2) Å, b = 10.144(2) Å, c = 13.833(3) Å, α = 103.40(2), β = 97.39(2), γ = 114.85(3), V = 1202.2(5) Å³, Z = 1, ρ(Mo Kα) = 0.083 mm^{-1}, ρ_{min} = 20.5, 46654 reflections measured, 4929 independent (R_{int} = 0.0469), R_{1} = 0.0370 ([I > 2σ(I)], wR_{2} = 0.0955 (all data), res. density peaks 0.313–0.335 e Å^{-3}, CCDC: 1875008. The data were integrated with SAINT. A multi-scan absorption correction was applied using SA补充。The structures were solved by SHELXTL® and refined on F^{2} using SHELXL® in the graphical user interface SHELXLE®.