A silicon–aluminum heterocycle LAl(SiH₂SiH₂)₂Al (L = PhC(NBu₂)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(AlMe₂)₂Si(AlMe₂)₃L (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(NBu₂)₂),3 Lsi-Si-L (L = PhC(NBu₂)₂),4 N-heterocyclic silylenes (NHSi)₅ and [Cp*Al]₄,6,8 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 R₂Si₃ (R = SiBu₂Me or 2, 4, 6-iPr₃C₆H₃) were reported by Sekiguchi7 and Scheschkewitz.9 Tamao10 and Dries11 reported a neutral tetrasilacyclobutadiene (EMind)₂Si₄ and a tetrasilacyclobutadiene dication [L₂Si₄Si₄[(Si(CF₃))₄]²⁺ (L = PhC(NBu₂)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-iPr₃C₆H₃), which is aromatic.16 Subsequently, a large amount of research has been dedicated to studying hexasilabenzenes 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-iPr₃C₆H₃) 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⁻ center of NaacnacAl⁻, resulting in the formation of NaacnacAlSiH₃Ph.22 However, this compound does not show any hydrogen bridging character. Inspired by the high reactivity of low-valent silicon explored by our group,5,4 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 Al₃(SiH₂)₄ six-membered rings, where two silicon atoms of cyclohexasilane are replaced by two aluminum atoms to yield LAl(SiH₂SiH₂)₂Al (1) and silylene–alane oxidative product [LAlHSiH₂Mes]₂ (3). The latter and the silylene–alane adduct LSi(AlMe₂)₂Si(AlMe₂)₃L (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(NtBu)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,21 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 LAI(SiH2SiH2)2Al (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 disilylaluminum intermediate LAIHSiH2SiH2AlH is unstable. It presumably reacts further with another equivalent of disilylene LSi–SiL in the presence of an equivalent amount of alane AlH2·NEtMe2. 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)−CHC(Me)−(NAr), Ar = 2,6-iPr2C6H3).25 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.

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 [°]: A1−Si1 2.4473(9), A1−Si2A 2.4545(9), A1−N1 1.9100(16), A1−N2 1.9236(17), N1−A1−N2 69.47(7), Si1−A1−Si2A 114.94(3).

Scheme 1 Preparation of compounds 1 and 2.

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 −SiH2−SiH3– units (Fig. 1). The Al3Si4 heterocycle adopts a chair conformation, typical of cyclohexane congeners where the six methylene groups are replaced by two N3Al units and four SiH2 moieties. These four silicon atoms are in the same plane while one Al atom is located above and one below that Si4 plane. The dihedral angle between the planes defined by Si4 and Al1Si1Si2A is 50.03(10)°. The bond lengths of Al–Si (2.4473(9) and 2.4545(9) Å) in 1 are comparable with those in NacacAlHSiH2Ph (2.4522(8) Å).22 NacacAlHSiHMePh (2.4548(7) Å)22 and LSiHAlH2(NMe3) (L = (ArN)C(CH2)CHC(Me)(NAr), Ar = 2,6-iPr2C6H3) (2.487(1) Å).25 The two SiH2−SiH3 bond lengths (2.3413(9) Å) are crystallographically equivalent and comparable with the corresponding distances in the [(BuN)2SiH2]2Al 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 (Al2Si4) and four-membered (CN2Al) rings. The ligand bite angle N1−Al1−N2 (69.47(7)°) is rather sharp, whereas the Si1–Al1–Si2A angle (114.84(3)°) is rather wide. However, the Si-centered bond angle in Al3Si4 (Al1−Si1−Si2 (107.57(3)°)) 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−Si1−Si2−Al is −68.57(4)°. To the best of our knowledge, compound 2 represents a rare example of silylene–alane adducts, and the only other two examples are [PhC(NiPr)2]2Si → AlPh3 and [C(NiPr)2]2Si → AlPr3.27 The Si → 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 [PhC(NiPr)2]2Si → AlPh3 (2.5293(14) Å) and [C(NiPr)2]2Si → AlPr3 (2.5544(17) Å). The Si1−Si2 bond (2.3937(7) Å) is comparable with those in LSi–SiL (2.413(2) Å) and LSi→M–Si→M)L adducts (2.376(5) Å for M = Ir and 2.388(2) Å for M = Rh).18

In order to get the analogues of intermediate C (Scheme 3) in the formation of compound 1, we turned to the reaction of amidinate...
mesitylsilylene LSiMes\(^{29}\) (Mes = 2,4,6-Me\(_3\)C\(_6\)H\(_3\)) with alane AlH\(_3\)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 [LAlHSiH\(_2\)Mes]\(_2\) (1) was collected by filtration in 76% yield. Compound 3 was characterized by \(^1\)H, \(^{13}\)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 NacnaAlHSiH\(_2\)Ph (74.3 ppm),\(^{22}\) but downfield compared with that of compound 1 (\(-128.9\) ppm). In the \(^1\)H NMR spectrum, the broad resonance at 5.26 ppm for two hydrogens is attributed to the alane hydride Al–H, and the singlet at 4.54 ppm for four hydrogen atoms is attributed to silane hydrides SiH\(_4\). 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 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 = PhC(NBu\(_t\))\(_2\)) coordinates to the Al atom together with the SiH\(_2\)Mes 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 [LAlH\(_2\)]\(_2\) (L = RC(NAr)\(_2\), R = N(iPr)\(_2\), Ar = 2,6'iPr\(_2\)C\(_6\)H\(_3\)) (1.60(2) Å and 1.81(2) Å)\(^{30}\) and 2-aminophenylaluminum dihydride [[2-tmp-C\(_6\)H\(_4\)]AlH\(_2\)] (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\(^\dagger\)) are performed to support the mechanism for the generation of silicon–aluminum heterocycle 1. The reaction energy (I + AlH\(_3\) \rightarrow 1) is highly exergonic (\(\Delta G_{CI}^{\circ} = -188.5\) 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 IC. Thereafter, subsequent migrations of the hydride from Al to Si centers allow the formation of intermediate IC. Finally, the addition of AlH\(_3\) and I with intermediate IC furnished 1 by releasing one molecule of L\(_2\)AlH. This step is highly exergonic (\(\Delta G_{CI}^{\circ} = -91.7\) kcal mol\(^{-1}\)) with respect to intermediate IC. The first hydride transfer step (I \(_{CI} \rightarrow 1_{CI} ; \Delta G_{CI}^{\circ} = 32.6\) kcal mol\(^{-1}\); Fig. S3.1, ESI\(^\dagger\))\(^{24,32}\) 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. LAl(SiH\(_2\)SiH\(_3\))\(_2\)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, LSi(AlMe\(_3\))\(_2\)-Si(AlMe\(_3\))L (2) and [LAlHSiH\(_2\)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 Schmidbaur.

Conflicts of interest

There are no conflicts to declare.

Notes and references

Crystal data for 1 at 100(2) K: C_{64}H_{107}Al_{2}N_{2}Si_{4}·C_{2}H_{5}OMe. M_{r} = 637.69 g mol^{-1}, 0.210 × 0.150 × 0.150 mm, monoclinic, P2_{1}/c, a = 13.599(2) Å, b = 8.253(2) Å, c = 17.672(3) Å, β = 103.631(2), V = 1926.37 Å^3, Z = 2, \rho(Mo K\alpha) = 0.224 mm\(^{-1}\), 32188 reflections measured, 3989 independent (R_{int} = 0.0532), R_{I} = 0.0410 [I > 2\sigma(I)], wR_{2} = 0.1143 (all data), res. density peaks: 0.313 Å\(^{-3}\), U_{G} = 0.150 mm, \theta_{max} = 26.4. Crystal data for 2 at 100(2) K: C_{64}H_{107}Al_{2}N_{2}Si_{4}·C_{2}H_{5}OMe. M_{r} = 709.11 g mol^{-1}, 0.260 × 0.170 × 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 = 4007.61 Å^3, Z = 4, \rho(Mo K\alpha) = 0.150 mm\(^{-1}\), \theta_{max} = 38.5. 86586 reflections measured, 9064 independent (R_{int} = 0.0665), R_{I} = 0.0361 [I > 2\sigma(I)], wR_{2} = 0.0921 (all data), res. density peaks 0.276−0.211 Å\(^{-3}\), U_{G} = 0.150 mm, \theta_{max} = 26.4. Crystal data for 3 at 100(2) K: C_{64}H_{107}Al_{2}N_{2}Si_{4}·C_{2}H_{5}OMe. M_{r} = 817.25 g mol^{-1}, 0.195 × 0.150 × 0.144 mm, triclinic, P1, a = 10.144(2) Å, b = 10.144(2) Å, c = 13.833(3) Å, α = 103.40(2), β = 97.39(2), γ = 114.83(3), V = 1202.2(5) Å^3, Z = 1, \rho(Mo K\alpha) = 0.083 mm\(^{-1}\), \theta_{max} = 20.5, 46646 reflections measured, 4929 independent (R_{int} = 0.0469), R_{I} = 0.0370 [I > 2\sigma(I)], wR_{2} = 0.0955 (all data), res. density peaks 0.276−0.211 Å\(^{-3}\), U_{G} = 0.150 mm, \theta_{max} = 26.4. The data were integrated with SADABS. A multi-scan absorption correction was applied using SADABS. The structures were solved by SHELXTL\(^{35}\) and refined on F\(^{2}\) using SHELXL\(^{36}\) in the graphical user interface ShelXle.\(^{37}\)