ChemComm

Check for updates

(PhC(NtBu)$_2$Al)$_2$(SiH$_2$)$_4$ six-membered heterocycle: comparable in structure to cyclohexane†

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(SiH$_2$SiH$_2$)$_2$AlL (L = PhC(NtBu)$_2$) (1) was prepared. Compound 1 exhibits a unique (N$_2$Al)$_2$(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 LSi(AlMe$_3$)–Si(AlMe$_3$)L (2) and silylene–alane oxidative product [LAlHSiH$_2$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.[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 R$_4$Si$_3$ (R = SitBu$_2$Me or 2, 4, 6-iPr$_3$C$_6$H$_2$) were reported by Sekiguchi[8] and Scheschkewitz.[9] Tamao[10] and Driess[11] reported a neutral tetrasilacyclobutadiene (EMind)$_4$Si$_4$ and a tetrasilacyclobutadiene

dication $[L_2Si_2Si_2(:Si(Cl)L)]^{2+}$ (L = PhC(NtBu)$_2$) both containing a central Si$_4$ ring. The most extensively studied cyclic silicon compounds are cyclohexasilanes, Si$_6$X$_{12}$ (X = H,[12] Me,[13] Ph,[14] halides[15]), 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$_6$ (R = 2,4,6-iPr$_3$C$_6$H$_2$), 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, Power[19] 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$_2$) 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–SiH$_2$R unit are rarely reported, probably due to the limited utility of the RH$_2$Si$^-$ anion. So far only Nikonov *et al.* reported on the oxidative addition of the Si–H bond of PhSiH$_3$ to the Al(ı) center of NacnacAl(:), resulting in the formation of NacnacAlHSiH$_2$Ph.[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 Al$_2$(SiH$_2$)$_4$ six-membered rings, where two silicon atoms of cyclohexasilane are replaced by two aluminum atoms to yield LAl(SiH$_2$SiH$_2$)$_2$AlL (1) and silylene–alane oxidative product [LAlHSiH$_2$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.
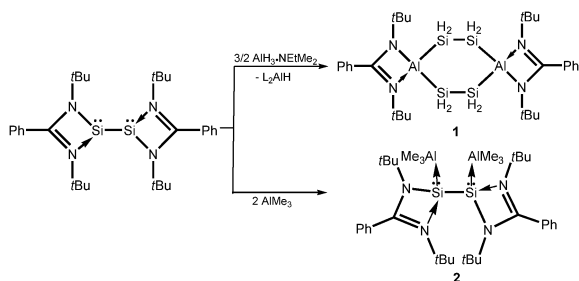
^{a} State Key Laboratory of Physical Chemistry of Solid Surface, National Engineering Laboratory for Green Chemical Productions of Alcohols-Ethers-Esters College of Chemistry and Chemical Engineering Xiamen University, Xiamen 361005, China. E-mail: hpzhu@xmu.edu.cn
^{b} Institut für Anorganische Chemie, 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

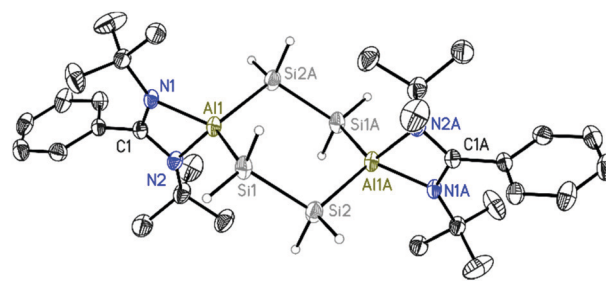**Scheme 1** Preparation of compounds **1** and **2**.

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 [°]: 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).

We initially attempted the reaction of disilylene LSi–SiL (L = PhC(NtBu)$_2$) with AlH$_3$·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$_2$AlH,[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$_2$AlH, we unexpectly obtained LAl(SiH$_2$SiH$_2$)$_2$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 disilanylaluminum intermediate LAlHSiH$_2$SiH$_2$AlHL is unstable. It presumably reacts further with another equivalent of disilylene LSi–SiL in the presence of an equivalent amount of alane AlH$_3$·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 = (ArN)C(CH$_2$)-CHC(Me)(NAr), Ar = 2,6-iPr$_2$C$_6$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 ^{1}H NMR resonance at 3.36 ppm, which is upfield-shifted when compared with that of compound **3** (4.54 ppm, see below) and NacnacAlHSiH$_2$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 ^{1}H NMR spectrum of compound **2**, the resonances for tBu groups on the amidinate ligands and methyl groups on aluminum were observed at 1.21 ppm and −0.02 ppm, respectively.

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 –SiH$_2$–SiH$_2$– units (Fig. 1). The Al$_2$Si$_4$ heterocycle adopts a chair conformation, typical of cyclohexane congeners where the six methylene groups are replaced by two N$_2$Al 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)°, 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 NacnacAlHSiH$_2$Ph (2.4522(8) Å),[22] NacnacAlHSiHMePh (2.4548(7) Å)[22] and LSiHAlH$_2$(NMe$_3$) (L = (ArN)C(CH$_2$)CHC(Me)-(NAr), Ar = 2,6-iPr$_2$C$_6$H$_3$) (2.487(1) Å).[25] The two SiH$_2$–SiH$_2$ bond lengths (2.3413(9) Å) are crystallographically equivalent and comparable with the corresponding distances in the (tBuN)$_2$(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$_2$Si$_4$) and four-membered (CN$_2$Al) 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 Al$_2$Si$_4$ (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–Si–Si–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)$_2$]$_2$Si → AlPh$_3$ and [C(NiPr)$_3$]$_2$Si → AlPh$_3$.[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)$_2$]$_2$Si → AlPh$_3$ (2.5293(14) Å) and [C(NiPr)$_3$]$_2$Si → 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 LSi(→ M)–Si(→ M)L adducts (2.376(5) Å for M = Ir and 2.388(2) Å for M = 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
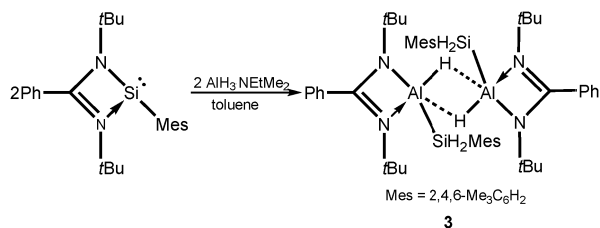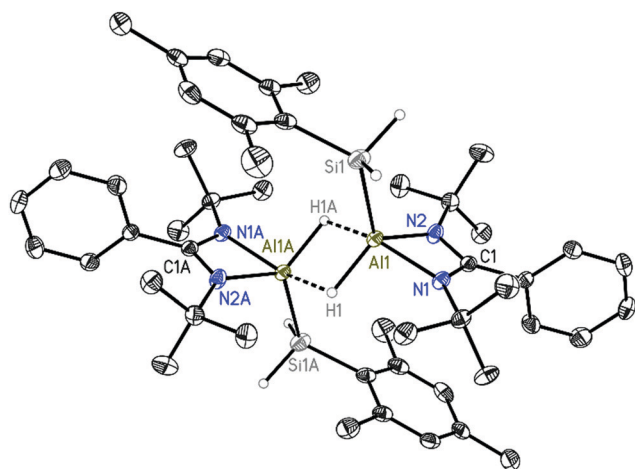
Scheme 2 Preparation of compound 3.

Fig. 2 Molecular structure of 3 with anisoptropic 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-Me$_3$C$_6$H$_2$) 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]$_2$ (3) 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 NacnacAlHSiH$_2$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 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 tBu 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(NtBu)$_2$) 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$_2$]$_2$ (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 (I + AlH$_3$ → 1) is highly exergonic (ΔG_{L}^{S} = −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 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 I with intermediate C furnished 1 by releasing one molecule of L$_2$AlH. This step is highly exergonic (ΔG_{L}^{S} = −91.7 kcal mol^{-1}) with respect to intermediate C. The first hydride transfer step (I_C → I_D; $\Delta^{\ddagger}G_{L}^{S}$ = 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 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$_2$)$_2$AlL (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$_3$)–Si(AlMe$_3$)L (2) and [LAlHSiH$_2$Mes]$_2$ (3) were
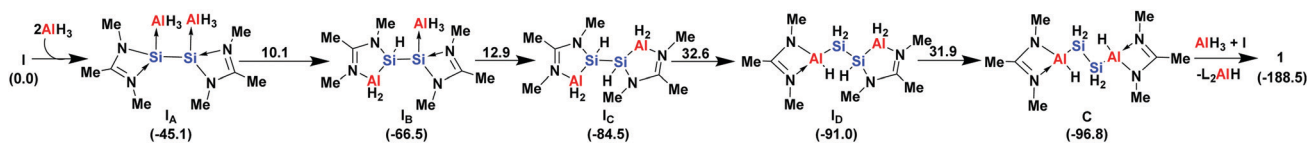
Scheme 3 Relative Gibbs free energy (in kcal mol^{-1}) for the intermediates involved in the formation of 1. Values in parentheses are energy values (ΔG_{L}^{S}; in kcal mol^{-1}) relative to the starting material (I + AlH$_3$). Values above the arrows are the activation barriers between the two corresponding 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.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Crystal data for **1** at 100(2) K: $C_{30}H_{54}Al_2N_4Si_4$, $M_r = 637.09$ g mol^{-1}, $0.210 \times 0.150 \times 0.150$ mm, monoclinic, $P2_1/c$, $a = 13.559(2)$ Å, $b = 8.253(2)$ Å, $c = 17.689(3)$ Å, $\beta = 103.31(2)$°, $V = 1926.3(7)$ Å^3, $Z = 2$, μ(Mo K$_\alpha$) = 0.224 mm^{-1}, $\theta_{max} = 26.4$°, 32188 reflections measured, 3950 independent ($R_{int} = 0.0532$), $R_1 = 0.0410$ [$I > 2\sigma(I)$], w$R_2 = 0.1143$ (all data), res. density peaks: $0.425/-0.266$ e A^{-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), $M_r = 709.11$ g mol^{-1}, $0.260 \times 0.170 \times 0.100$ mm, monoclinic, $P2_1/c$, $a = 18.949(2)$ Å, $b = 11.775(2)$ Å, $c = 20.216(3)$ Å, $\beta = 102.27(2)$, $V = 4407.6(11)$Å^3, $Z = 4$, μ(Mo K$_\alpha$) = 0.150 mm^{-1}, $\theta_{max} = 26.5$°, 86568 reflections measured, 9064 independent ($R_{int} = 0.0665$), $R_1 = 0.0368$ [$I > 2\sigma(I)$], w$R_2 = 0.0921$ (all data), res. density peaks $0.276/-0.211$ e A^{-3}, CCDC: 1875010. Crystal data for **3** at 100(2) K: $C_{48}H_{74}Al_2N_4Si_2$, $M_r = 817.25$ g mol^{-1}, $0.195 \times 0.150 \times 0.144$ mm, triclinic, $P\bar{1}$, $a = 10.039(2)$ Å, $b = 10.144(2)$ Å, $c = 13.835(3)$ Å, $\alpha = 103.40(2)$, $\beta = 97.39(2)$, $\gamma = 114.85(3)$, $V = 1202.2(5)$ Å^3, $Z = 1$, μ(Ag K$_\alpha$) = 0.083 mm^{-1}, $\theta_{max} = 20.5$°, 46064 reflections measured, 4929 independent ($R_{int} = 0.0469$), $R_1 = 0.0370$ [$I > 2\sigma(I)$], w$R_2 = 0.0955$ (all data), res. density peaks: $0.313/-0.335$ e A^{-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 SHELXT[35] and refined on F^2 using SHELXL[36] 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, *Zieglar–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. Schnockel, *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. Scheschkewitz, *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. Stammler, M. J. Cowley, P. Jutzi and D. Scheschkewitz, *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, D. L. 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. Scheschkewitz, *Science*, 2010, **327**, 564–566; (*b*) K. Abersfelder, A. J. P. White, R. J. F. Berger, H. S. Rzepa and D. Scheschkewitz, *Angew. Chem., Int. Ed.*, 2011, **50**, 7936–7939; (*c*) D. Kratzert, D. Leusser, J. J. Holstein, B. Dittrich, K. Abersfelder, D. Scheschkewitz 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. Scheschkewitz, *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. Habereder 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(N*t*Bu)$_2$) and AlHCl$_2$.
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-Álvare 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 *BrukerApex 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.