

PAPER

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One silicon atom of bis(silylene) functions as a selective Lewis base under adduct formation with a Lewis acid†

Yi Ding,^{a,b} Mohd Nazish,^b Paul Niklas Ruth,^b Regine Herbst-Irmer,^b Dietmar Stalke^{*b} and Herbert W. Roesky^b

Herein, we describe the facile and selective one-pot synthetic route to silylene-aluminum and silylene-gallium adducts. Reduction of silylene LSiCl ($\text{L} = \text{PhC}(\text{N}^t\text{Bu})_2$) with KC_8 in the presence of bulky and sterically hindered cyclopentadienyl aluminum Cp^*AlCl_2 ($\text{Cp}^* = 1,2,4\text{-}t\text{Bu}_3\text{C}_5\text{H}_2$) and gallium $[\eta^1\text{-Cp}^*\text{Ga}(\mu\text{-Cl})\text{Cl}]_2$ to afford the Lewis acid–base adducts $\eta^1\text{-Cp}^*\text{M}(\text{Cl})_2 \leftarrow \text{Si}(\text{L})\text{-SiL}$ ($\text{M} = \text{Al}$, **1**; $\text{M} = \text{Ga}$, **3**). To confirm the formation of the Lewis acid–base adduct, the bis(silylene) $\text{LSi}(\text{l})\text{-Si}(\text{l})\text{L}$ reacts with Cp^*AlI_2 to form $\eta^1\text{-Cp}^*\text{Al}(\text{I})_2 \leftarrow \text{Si}(\text{L})\text{-SiL}$ (**2**). These are the first examples where one Si atom in the bis(silylene) is a Lewis base and coordinates with aluminum or gallium to form a Lewis acid–base adduct, while the other Si atom in the bis(silylene) still maintains the characteristics of silylene. Compound **3** was heated to 70 °C in toluene for 4 hours and decomposed into the silylene LSiCl and $\text{Cp}^*\text{Ga}^{\text{I}}$. Compounds **1–3** are well characterized with NMR spectroscopic methods and single-crystal X-ray structural analysis.

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Introduction

As a silicon analog of carbene, silylene has a relatively large $\Delta E_{\text{S-T}}$ energy gap and displays fascinating reactivity.¹ Bearing vacant orbitals as well as reactive lone pairs of electrons at silicon results in the silylene that can act as a Lewis acid as well as a Lewis base. Silylenes have been widely explored for the formation of transition metal complexes.² In contrast, the subject of main group metals with silylene or bis(silylene) adducts are not extensively explored. Intrinsically group 13 compounds possess Lewis acidity. Silylene is reported to form Lewis acid–base adducts with organoboron compounds. A number of literature reports on silylene-boron adducts are well documented.^{3–10}

In comparison with silylene-boron adducts, reports on silylene-aluminum, silylene-gallium, and silylene-indium are rare (Fig. 1). In 2016, Tacke and co-workers reported the first silylene-aluminum adduct (**A**) with a Si–Al bond derived from a

Chart A: Compounds of Silylene-aluminum or Bis(silylene)-aluminum

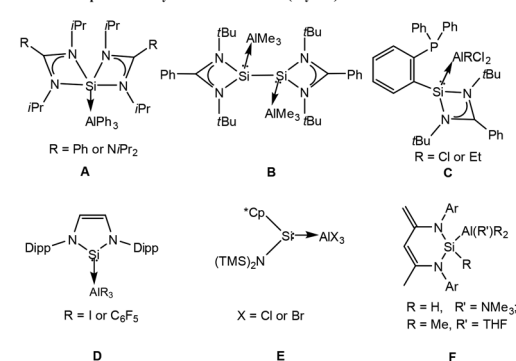
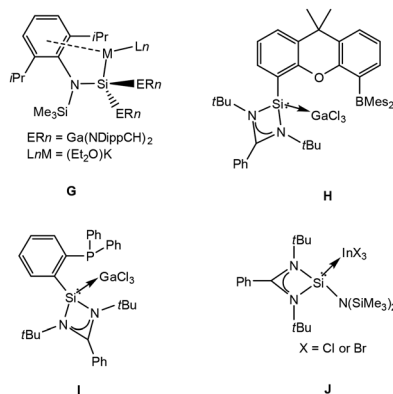


Chart B: Compounds of Silylene-gallium or Silylene-indium

**Fig. 1** Adducts of silylene-aluminum, silylene-gallium or silylene-indium.

^aCollege of Chemistry and Chemical Engineering, State Key Laboratory of High-Efficiency Utilization of Coal and Green Chemical Engineering, Ningxia University, Yinchuan 750021, China. E-mail: yiding@nxu.edu.cn

^bInstitute of Inorganic Chemistry, Georg-August-Universität Göttingen, Göttingen Tammannstrasse 4, D-37077, Germany. E-mail: dstalke@chemie.uni-goettingen.de, hroesky@gwdg.de

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bis(guanidinato)silylene.^{4b} In 2019, we treated LSi-SiL with AlMe₃ to afford the adduct LSi(AlMe₃)₂-Si(AlMe₃)L (L = PhC(N^tBu)₂) (**B**).¹¹ In addition to that we have also reported adduct **C** containing an organoaluminum dichloride of a mixed-donor ligand LSiC₆H₄PPh₂.^{5a} In 2021, Radius and co-workers reported the adducts **D**, which were derived from the reactions with N-heterocyclic silylene (Dipp₂NHSi) and AlI₃ or Al(C₆F₅)₃.¹² Recently, Khan and co-workers reported the reaction of disilene (TMS)₂N(η¹-Cp*)Si=Si(η¹-Cp*)N(TMS)₂ with AlX₃ (X = Cl or Br) to form adduct **E**.¹³ However, the reactions of the stable N-heterocyclic silylene L'Si: (L' = (ArN)C(=CH₂)CH=C(Me)-(NAr), Ar = 2,6-*t*Pr₂C₆H₃) with AlMe₃ or AlH₃·NMe₃ leads directly to the 1,1-addition product **F**.¹⁴ In 2013, Aldridge and co-workers reported the silylene-gallium adduct **G** with metathesis steps from the Si(IV) precursor Si{N(SiMe₃)Dipp}Br₃.¹⁵ In 2017, Driess and co-workers treated LSi-R-BMes₂ (L = PhC(N^tBu)₂; R = 1,12-xanthendiyl spacer; Mes = 2,4,6-Me₃C₆H₂) with equivalent amounts of GaCl₃, which resulted in the Si^{II} → GaCl₃ adduct (**H**).¹⁶ We have also reported a silylene-gallium adduct **I**.^{5a} In 2018, Sen and co-worker prepared the first silylene-indium complex **J**.¹⁷

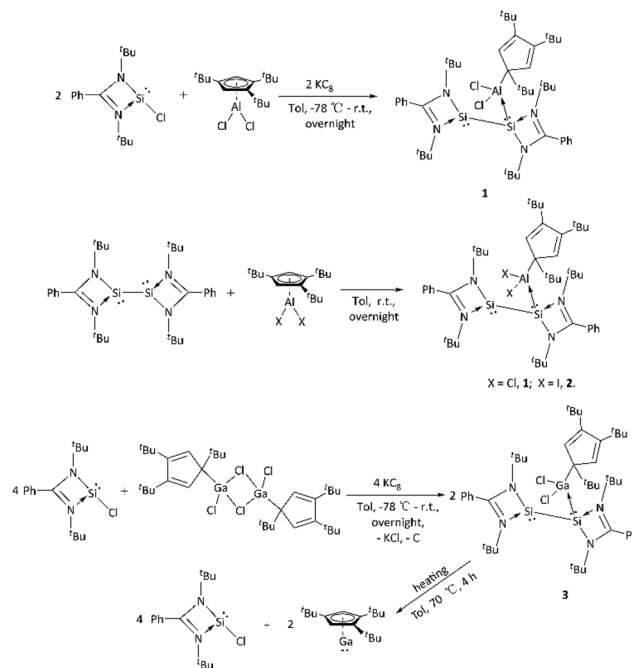
Since we report on the silylene LSiCl,¹⁸ many groups have used this precursor for preparing a number of unprecedented compounds.¹⁹ Later on, we reported the bis(silylene) LSi-SiL,²⁰ which displayed a silicon(i) dimer, that comprises of a Si-Si single bond with a lone pair of electrons on each silicon center showing very high reactivity.²¹ Since then this high reactivity of silylene and bis(silylene) were explored by our group and others. However, the reports of the Lewis acid-base adducts based on the silylene or bis(silylene) are limited.

In this report, we reduced the silylene LSiCl with an equivalent amount of KC₈ in the presence of half equivalent of bulky and sterically hindered cyclopentadienyl Cp^{'''}MCl₂ (M = Al or Ga) to afford interesting Lewis acid-base adducts η¹-Cp^{'''}M(Cl₂) ← Si(L)-SiL. To confirm the formation of this type of novel Lewis acid-base adducts, bis(silylene) LSi-SiL was treated with equivalent amounts of Cp^{'''}AlI₂ to get η¹-Cp^{'''}Al(I₂) ← Si(L)-SiL. The new compounds are well characterized by NMR spectroscopic and single-crystal X-ray analyses.

Results and discussion

Reduction of LSiCl proceeds with equivalent amounts of KC₈ in the presence of 0.5 equivalents of Cp^{'''}AlCl₂ in the toluene at -78 °C. Then the reaction was slowly warmed up to room temperature and stirring was continued overnight to afford the Lewis acid-base adduct η¹-Cp^{'''}Al(Cl₂) ← Si(L)-SiL (**1**) as colorless crystals in 52% yield (Scheme 1).

The ¹H NMR spectrum of **1** shows two singlets at δ 1.25 and 1.36 ppm for the ^tBu of amidinato ligand, two singlets at δ 1.64 and 1.75 ppm for the ^tBu of cyclopentadienyl ligand. One broad resonance at δ 6.79–6.85 ppm for cyclopentadienyl, and two broad resonances at δ 6.92–7.02 and 7.23–7.25 ppm for phenyl protons. The ²⁹Si NMR shows two resonances at 49.2 and 57.0 ppm caused by the different chemical environments



Scheme 1 Synthesis of compound 1–3.

of the two Si atoms in the compound **1**, both shift up-field in comparison to the bis(silylene) (76.3 ppm).

Compound **1** crystallizes in the triclinic space group *P* $\bar{1}$ with one molecule and two half toluene solvent molecules in the asymmetric unit. The X-ray crystallography of **1** clearly shows the coordination of the Lewis acid Cp^{'''}AlCl₂ with bis(silylene) LSi-SiL to form the Lewis acid-base adduct (Fig. 2). It is noteworthy that in the bis(silylene) LSi-SiL, one Si atom adopts a four-coordinate arrangement as a Lewis base, while another Si atom also holds a lone pair of electrons with a

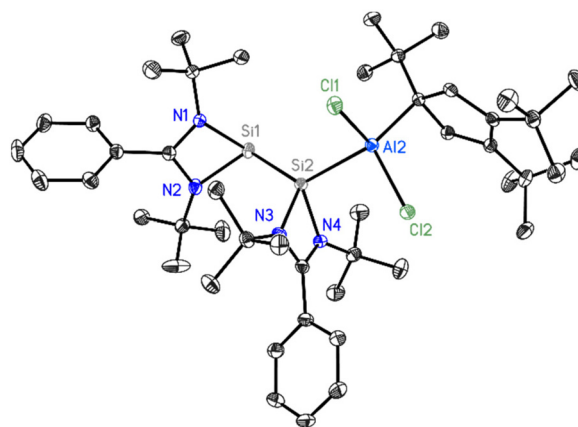


Fig. 2 Molecular structure of **1**. Anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.4245(10), Si2–Al2 2.5413(9), Si1–N1 1.8667(12), Si1–N2 1.8691(11), Si2–N3 1.8295(11), Si2–N4 1.8522(11), Al2–Cl1 2.2005(7), Al2–Cl2 2.1745(7), N1–Si1–N2 69.50(5), N3–Si2–N4 71.08(5).



three-coordinate character. However, the two Si atoms are in an oxidation state I, this is a very rare situation. In the Lewis acid part, the Al atom adopts a four-coordinate oxidation state III. The Al2–Si2 (2.5413(9) Å) bond length is significantly longer than the reported Al–Si covalent bond in compounds [LAlHSiH₂Mes]₂ (2.4602(8) Å)¹¹ and LAl(SiH₂SiH₂)₂AlL (2.4473(9)–2.4545(9) Å).¹¹ Furthermore, other selected examples with Si–Al bonds are mentioned in brackets (F (2.487(1) Å),¹⁴ NacnacAlHSiH₂Ph (2.4522(8) Å), and NacnacAlHSiHMePh (2.4548(7) Å)).²² However, the Al–Si coordination bond length which is reported in the following examples is longer in LSi(AlMe₃)–Si(AlMe₃)L (2.5921(7) and 2.5799(8) Å),¹¹ [PhC(N^tPr)₂]₂Si → AlPh₃ (2.5293(14) Å) and [C(N^tPr)₃]₂Si → AlPh₃ (2.5544(17) Å).^{4b} This indicates that the Al–Si bond in compound **1** is a coordination bond. The Si1–Si2 bond length is 2.4244(10) Å, which is longer than the corresponding compound in LSi–SiL (2.413(2) Å),²⁰ LSi(AlMe₃)–Si(AlMe₃)L (2.3937(7) Å),¹¹ and LSi(M)–Si(M)L (M = Ir, 2.376(5) Å; M = Rh, 2.388(2) Å).²³ Since only Si2 in LSi–SiL is coordinated with Al from the Cp^{'''}Al(Cl)₂, the Si–N bond lengths and the N–Si–N bond angles in the two amidinato silicon four-membered rings are different. The Si2–N bond length (Si2–N3 1.8295(11) Å, Si2–N4 1.8522(11) Å) are shorter than Si1–N (Si1–N1 1.8667(12) Å, Si1–N2 1.8691(11) Å), which makes the bond angle N3–Si2–N4 (71.08(5)°) to be slightly bigger than N1–Si1–N2 (69.50(5)°). It is also noteworthy that the Cp^{'''}AlCl₂ changes from η⁵ to η¹.

To confirm the formation of Lewis acid–base adduct, we also tried the reaction of bis(silylene) LSi–SiL with Cp^{'''}AlI₂ at room temperature overnight, and then isolated the light yellow crystals η¹-Cp^{'''}Al(I₂) ← Si(L)–SiL (**2**) in the yield of 45% (Scheme 1). The ¹H NMR spectrum of **2** shows four singlets at δ 1.21, 1.42, 1.66, and 1.76 ppm for the ^tBu of amidinato and cyclopentadienyl ligand. One broad resonance at δ 6.88–6.95 ppm for cyclopentadienyl, two broad resonances at δ 6.97–7.06 and 7.20–7.25 ppm for phenyl protons. The ²⁹Si NMR shows two resonances at 47.8 and 54.4 ppm for the two Si atoms in compound **2**, which shift to up-field in comparison to compound **1** (49.2 and 57.0 ppm) and the starting material bis(silylene) (76.3 ppm).

2 crystallizes isostructurally to **1** (Fig. 3) in the triclinic space group *P* $\bar{1}$ with one molecule and two toluene solvent molecules. Due to the larger radius of the two iodine atoms connected to Al in the Lewis acid part, the bond lengths of Al–Si (2.5505(9) Å) and Si–Si (2.4399(8) Å) are both slightly longer than those in compound **1**, while all other features mentioned above for **1** are identical.

To further elaborate the formation of Lewis acid–base adduct, we repeated the reaction of LSiCl with equivalent amounts of KC₈ and 0.25 equivalents of [η¹-Cp^{'''}Ga(μ-Cl)Cl]₂ in toluene at –78 °C. From this reaction we obtained as a Lewis acid–base adduct η¹-Cp^{'''}Ga(Cl)₂ ← Si(L)–SiL (**3**) as colorless crystals in 65% yield. The ¹H NMR spectrum of **3** shows two singlets at δ 1.25 ppm and 1.37 ppm for the ^tBu of amidinato ligand, two singlets at δ 1.63 ppm and 1.72 ppm for the ^tBu of cyclopentadienyl ligand. One broad resonance at δ 6.81–6.87 ppm for cyclopentadienyl, two broad resonances at δ

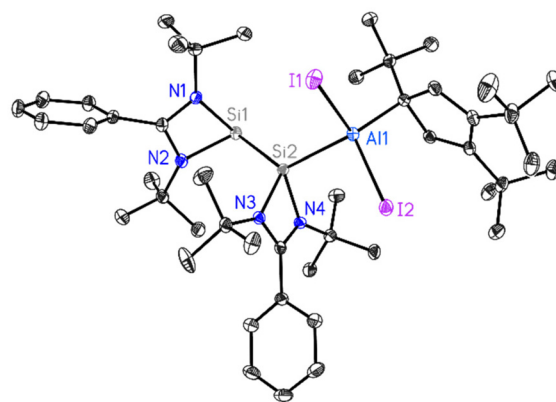


Fig. 3 Molecular structure of **2**. Anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity. Si1–Si2 2.4399(8), Si2–Al1 2.5505(9), Si1–N1 1.8659(15), Si1–N2 1.8669(15), Si2–N3 1.8396(14), Si2–N4 1.8492(13), Al1–I1 2.6040(8), Al1–I2 2.5740(7), N1–Si1–N2 69.73(7), N3–Si2–N4 70.77(7).

6.92–7.01, 7.10–7.13, and 7.22–7.24 ppm for phenyl protons. The ²⁹Si NMR shows two resonances at 41.1 and 54.7 ppm for the two Si atoms with the different chemical environments in compound **3**, which also shift to up-field in comparison to the aluminum compound **1** and starting material bis(silylene) (76.3 ppm).

Compound **3** crystallizes again isostructurally to **1** (Fig. 4) in the triclinic space group *P* $\bar{1}$, however with two molecules and four toluene solvent molecule in the asymmetric unit. Interestingly, the dimer gallium [η¹-Cp^{'''}Ga(μ-Cl)Cl]₂ was split into the monomers Cp^{'''}GaCl₂ by the bis(silylene) to form compound **3**. In the Lewis acid part, the Ga atom is four-coordinated in oxidation state III. The Si2–Ga1 bond length (2.4910(7) Å) is longer than those in adducts of **G** (2.438(1) and 2.452(1) Å),¹⁵ **H** (2.3963(17) Å),¹⁶ and **I** (2.3904(6) Å),^{5a} but

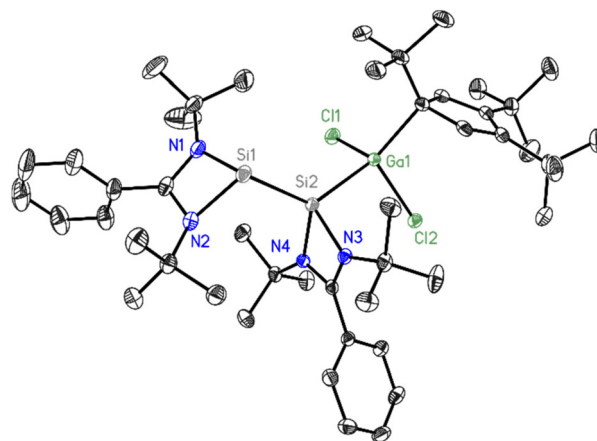


Fig. 4 Molecular structure of **3**. Anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity. Si1–Si2 2.4339(7), Si2–Ga1 2.4910(7), Si1–N1 1.8621(16), Si1–N2 1.8755(16), Si2–N3 1.8427(15), Si2–N4 1.8271(14), Ga1–Cl1 2.2788(8), Ga1–Cl2 2.2368(6), N1–Si1–N2 69.60(7), N3–Si2–N4 71.33(6).



shorter than the Si–Al bond length in compounds **1** (2.5413(9) Å) and **2** (2.5506 Å). However, the Si1–Si2 bond length (2.4339(7) Å) is longer than in the compound of LSi–SiL (2.413(2) Å),²⁰ the adduct LSi(AlMe₃)–Si(AlMe₃)L (2.3937(7) Å),¹¹ LSi(M)–Si(M)L (M = Ir, 2.376(5) Å; M = Rh, 2.388(2) Å).²³ The above mentioned differences in the two amidinato silicon rings are again valid.

We heated compound **3** in toluene to 70 °C and kept it for 4 hours, hoping to get some novel structures through rearrangement, but it was found to be decomposed into the silylene LSiCl and Cp^{'''}Ga^I according to the NMR spectroscopic methods (Scheme 1).

Conclusions

In summary, we reported the reduction of silylene LSiCl with KC₈ in the presence of large sterically hindered cyclopentadienyl aluminum or gallium dichloride to form three novel silylene-aluminum or silylene-gallium Lewis acid–base adducts. In the adducts, one silicon atom in the bis(silylene) is a Lewis base coordinated with large sterically hindered cyclopentadienyl aluminum dihalide or gallium dichloride. One silicon atom in bis(silylene) acts as a Lewis base, while another silicon atom also maintains the characteristics of silylene, making the two amidino silicon four-membered rings in bis(silylene) showing regular changes.

Experimental section

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high-purity dinitrogen. THF, hexane, and toluene, respectively, were distilled over Na/K alloy (25 : 75), while diethyl ether was distilled over potassium mirror. Deuterated NMR solvent C₆D₆ was dried by stirring for 2 days over Na/K alloy followed by distillation in a vacuum and degassing. ¹H, ¹³C{¹H}, and ²⁹Si NMR spectra were recorded on Bruker Avance 400 MHz NMR spectrometer and were referenced to the resonances of the solvent used. Microanalyses were performed by the Analytisches Labor für Anorganische Chemie der Universität Göttingen. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. The starting material LSiCl,¹⁸ LSi–SiL,²⁰ η⁵–Cp^{'''}AlX₂ and [η¹–Cp^{'''}Ga(μ–Cl)Cl]₂ were synthesized by following the literature procedure.²⁴ All other reagents were used as received.

Synthesis of η¹–Cp^{'''}Al(Cl₂) ← Si(L)–SiL (**1**)

To a mixture of LSiCl (294 mg, 1.0 mmol), KC₈ (135 mg, 1.0 mmol) and η⁵–Cp^{'''}AlCl₂ (166 mg, 0.5 mmol) or Cp^{'''}AlBr₂ (210 mg, 0.5 mmol) was added toluene (30 mL) at –78 °C, and the resulting mixture was allowed to warm to room temperature slowly and stirred at room temperature overnight. After filtration, the solvent was concentrated to 10 mL under vacuum. The orange solution was stored in a freezer at –30 °C for 7 days to isolate X-ray quality colorless block-shaped crystals of **1**

(yield: 247 mg, 52%). ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ 7.25–7.23, 7.02–6.92 (m, 10H, Ar–H), 6.85–6.79 (m, 2 H, C₅H₂(^tBu)₃), 1.75 (s, 18 H, C₅H₂(^tBu)₃), 1.64 (s, 9 H, C₅H₂(^tBu)₃), 1.36 (s, 18 H, N^tBu), 1.25 (s, 18 H, N^tBu); ¹³C NMR (126 MHz, C₆D₆, 298 K, ppm): δ 163.6 (NCN), 154.1, 152.3 (PhCN), 133.7, 131.8, 131.1, 130.5, 130.1, 129.7, 129.0, 128.5, 128.4, 127.5, 126.8 (Ar–C, Cp–C), 53.9, 53.2 (C(CH₃)), 35.4, 33.9, 33.5, 32.6, 31.9, 31.7, 31.6, 31.0, 28.8 C(CH₃); ²⁹Si NMR (99 MHz, 298 K, C₆D₆, ppm): δ 57.0, 49.2. Mp: 208 °C (dec). Anal. (%) calcd for C₄₇H₇₅AlCl₂N₄Si₂C₇H₈ (940.3): C, 68.83; H, 8.88; N, 5.95 Found: C, 69.11; H, 9.01; N, 5.54.

Synthesis of η¹–Cp^{'''}Al(I₂) ← Si(L)–SiL (**2**)

To a mixture of LSi–SiL (259 mg, 0.5 mmol) and η⁵–Cp^{'''}AlI₂ (258 mg, 0.5 mmol) were added toluene (30 mL) at room temperature and stirred overnight. After filtration, the solvent was concentrated to 10 mL under vacuum. The red solution was stored in a freezer at –30 °C for 3 days to get X-ray quality colorless block-shaped crystals of **2** (yield: 247 mg, 43%). ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ 7.25–7.20, 7.06–6.93 (m, 10H, Ar–H), 6.92–6.88 (m, 2 H, C₅H₂(^tBu)₃), 1.76 (s, 18 H, C₅H₂(^tBu)₃), 1.66 (s, 9 H, C₅H₂(^tBu)₃), 1.42–1.21 (m, 36 H, N^tBu); ¹³C NMR (100 MHz, C₆D₆, 298 K, ppm): δ 170.1 (NCN), 164.9, 164.8 (PhCN), 133.4, 131.6, 131.4, 130.3, 130.1, 129.8, 129.1, 129.0, 128.5, 128.4, 128.2, 126.9, 125.3 (Ar–C, Cp–C), 54.4, 53.1 (C(CH₃)), 35.9, 34.0, 33.7, 33.5, 32.2, 32.2, 32.0, 31.5 C(CH₃); ²⁹Si NMR (99 MHz, 298 K, C₆D₆, ppm): δ 54.4, 47.8. Mp: 219 °C (dec). Anal. (%) calcd for C₄₇H₇₅AlI₂N₄Si₂C₇H₈ (1217.33): C, 60.18; H, 7.53; N, 4.60 Found: C, 60.31; H, 7.73; N, 4.39.

Synthesis of η¹–Cp^{'''}Ga(Cl₂) ← Si(L)–SiL (**3**)

To a mixture of LSiCl (294 mg, 1.0 mmol), KC₈ (135 mg, 1.0 mmol) and [η¹–Cp^{'''}Ga(μ–Cl)Cl]₂ (188 mg, 0.25 mmol) was added toluene (30 mL) at –78 °C, and the resulting mixture was allowed to warm to room temperature slowly and stirred at room temperature overnight. After filtration, the solvent was concentrated to 10 mL under vacuum. The yellow solution was stored in a freezer at –30 °C for 2 weeks to get X-ray quality yellow block shaped crystals of **3** (yield: 315 mg, 65%). ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ 7.24–6.89 (m, 10 H, Ar–H), 6.89–6.84 (m, 2 H, C₅H₂(^tBu)₃), 1.72 (s, 18 H, C₅H₂(^tBu)₃), 1.63 (s, 9 H, C₅H₂(^tBu)₃), 1.37 (s, 18 H, N^tBu), 1.25 (s, 18 H, N^tBu). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K, ppm) δ 166.2 (NCN), 155.5, 152.3 (PhCN), 133.3, 131.4, 130.9, 130.3, 129.9, 128.8, 128.5, 128.2, 127.8, 127.5, 126.8 (Ar–C, Cp–C), 54.1, 53.4 (C(CH₃)), 35.8, 34.6, 33.9, 33.4, 31.7, 31.5, 31.0, 30.5 (C(CH₃)). ²⁹Si NMR (99 MHz, C₆D₆, 298 K, ppm): 54.7, 41.1. Mp: 187 °C (dec). Anal. (%) calcd for C₄₇H₇₅GaCl₂N₄Si₂C₇H₈ (1077.17): C, 68.01; H, 8.52; N, 5.20 Found: C, 68.25; H, 8.81; N, 5.14.

Conflicts of interest

There are no conflicts to declare.



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References

- (a) R. S. Grev, H. F. Schaefer and P. P. Gaspar, *J. Am. Chem. Soc.*, 1991, **113**, 5638–5643; (b) M. C. Holthausen, W. Koch and Y. Apeloig, *J. Am. Chem. Soc.*, 1999, **121**, 2623–2624; (c) M. Haaf, T. A. Schmedake and R. West, *Acc. Chem. Res.*, 2000, **33**, 704–714; (d) B. Gehrhus and M. F. Lappert, *J. Organomet. Chem.*, 2001, **617–618**, 209–223; (e) P. P. Gaspar, M. Xiao, D. H. Pae, D. J. Berger, T. Haile, T. Chen, D. Lei, W. R. Winchester and P. Jiang, *J. Organomet. Chem.*, 2002, **646**, 68–79; (f) M. Yoshida and N. Tamaoki, *Organometallics*, 2002, **21**, 2587–2589; (g) Y. Apeloig, R. Pauncz, M. Karni, R. West, W. Steiner and D. Chapman, *Organometallics*, 2003, **22**, 3250–3256; (h) Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479–3511; (i) M. Kira, *Chem. Commun.*, 2010, **46**, 2893–2903; (j) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354–396; (k) M. Kosa, M. Karni and Y. Apeloig, *J. Am. Chem. Soc.*, 2013, **135**, 9032–9040.
- (a) L. Alvarez-Rodriguez, J. A. Cabeza, P. Garcia-Alvarez and D. Polo, *Coord. Chem. Rev.*, 2015, **300**, 1–28; (b) Y.-P. Zhou and M. Driess, *Angew. Chem., Int. Ed.*, 2019, **58**, 3715–3728; (c) C. Shan, S. Yao and M. Driess, *Chem. Soc. Rev.*, 2020, **49**, 6733–6754; (d) W. Yang, Y. Dong, H. Sun and X. Li, *Dalton Trans.*, 2021, **50**, 6766–6772; (e) M. Ghosh and S. Khan, *Dalton Trans.*, 2021, **50**, 10674–10688.
- M. P. Luecke, E. Pens, S. Yao and M. Driess, *Chem. – Eur. J.*, 2020, **26**, 4500–4504.
- (a) R. Tacke and T. Ribbeck, *Dalton Trans.*, 2017, **46**, 13628–13659; (b) F. M. Mück, J. A. Baus, R. Bertermann, C. Burschka and R. Tacke, *Organometallics*, 2016, **35**, 2583–2588.
- (a) M. Nazish, M. M. Siddiqui, S. K. Sarkar, A. Münch, C. M. Legendre, R. Herbst-Irmer, D. Stalke and H. W. Roesky, *Chem. – Eur. J.*, 2021, **27**, 1744–1752; (b) J. Li, Y. Liu, S. Kundu, H. Keil, H. Zhu, R. Herbst-Irmer, D. Stalke and H. W. Roesky, *Inorg. Chem.*, 2020, **59**, 7910–7914; (c) A. Jana, D. Leusser, I. Objartel, H. W. Roesky and D. Stalke, *Dalton Trans.*, 2011, **40**, 5458–5463; (d) R. Azhakar, G. Tavčar, H. W. Roesky, J. Hey and D. Stalke, *Eur. J. Inorg. Chem.*, 2011, 475–477; (e) A. Jana, R. Azhakar, S. P. Sarish, P. P. Samuel, H. W. Roesky, C. Schulzke and D. Koley, *Eur. J. Inorg. Chem.*, 2011, 5006–5013; (f) R. S. Ghadwal, H. W. Roesky, S. Merkel and D. Stalke, *Chem. – Eur. J.*, 2010, **16**, 85–88.
- (a) G. Dübek, D. Franz, C. Eisenhut, P. J. Altmann and S. Inoue, *Dalton Trans.*, 2019, **48**, 5756–5765; (b) S. Inoue and K. Leszczyńska, *Angew. Chem., Int. Ed.*, 2012, **51**, 8589–8593.
- (a) H. Braunschweig, T. Bruckner, A. Deißberger, R. D. Dewhurst, A. Gackstatter, A. Gartner, A. Hofmann, T. Kupfer, D. Prieschl, T. Thiess and S. R. Wang, *Chem. – Eur. J.*, 2017, **23**, 9491–9494; (b) A. Gackstatter, H. Braunschweig, T. Kupfer, C. Voigt and N. Arnold, *Chem. – Eur. J.*, 2016, **22**, 16415–16419.
- Y. Suzuki, S. Ishida, S. Sato, H. Isobe and T. Iwamoto, *Angew. Chem., Int. Ed.*, 2017, **56**, 4593–4597.
- S. Khoo, Y. L. Shan, M. C. Yang, Y. Li, M. D. Su and C. W. So, *Inorg. Chem.*, 2018, **57**, 5879–5887.
- (a) M. K. Bisai, V. S. V. S. N. Swamy, K. V. Raj, K. Vanka and S. S. Sen, *Inorg. Chem.*, 2021, **60**, 1654–1663; (b) S. Pahar, S. Karak, M. Pait, K. V. Raj, K. Vanka and S. S. Sen, *Organometallics*, 2018, **37**, 1206–1213.
- J. Li, M. Zhong, H. Keil, H. Zhu, R. Herbst-Irmer, D. Stalke, S. De, D. Koley and H. W. Roesky, *Chem. Commun.*, 2019, **55**, 2360–2363.
- M. J. Krahfuss and U. Radius, *Eur. J. Inorg. Chem.*, 2021, 548–561.
- N. Sen, N. Parvin, S. Tothadi and S. Khan, *Organometallics*, 2021, **40**, 1874–1883.
- Y. Xiong, S. Yao and M. Driess, *Chem. – Eur. J.*, 2012, **18**, 3316–3320.
- A. V. Protchenko, A. D. Schwarz, P. M. Blake, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *Angew. Chem., Int. Ed.*, 2013, **52**, 568–571.
- Z. Mo, T. Szilvási, Y. P. Zhou, S. Yao and M. Driess, *Angew. Chem., Int. Ed.*, 2017, **56**, 3699–3702.
- S. Pahar, S. Karak, M. Pait, K. V. Raj, K. Vanka and S. S. Sen, *Organometallics*, 2018, **37**, 1206–1213.
- (a) C. W. So, H. W. Roesky, J. Magull and R. B. Oswald, *Angew. Chem., Int. Ed.*, 2006, **45**, 3948–3950; (b) S. S. Sen, H. W. Roesky, D. Stern, J. Henn and D. Stalke, *J. Am. Chem. Soc.*, 2010, **132**, 1123–1126.
- (a) S. Nagendran and H. W. Roesky, *Organometallics*, 2008, **27**, 457–492; (b) S. Yao, Y. Xiong and M. Driess, *Organometallics*, 2011, **30**, 1748–1767; (c) S. S. Sen, S. Khan, P. P. Samuel and H. W. Roesky, *Chem. Sci.*, 2012, **3**, 659–682.
- S. S. Sen, A. Jana, H. W. Roesky and C. Schulzke, *Angew. Chem., Int. Ed.*, 2009, **48**, 8536–8538.
- S. S. Sen, S. Khan, S. Nagendran and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 578–587.
- T. Chu, I. Korobkov and G. I. Nikonov, *J. Am. Chem. Soc.*, 2014, **136**, 9195–9202.
- S. Khoo, H. X. Yeong, Y. Li, R. Ganguly and C. W. So, *Inorg. Chem.*, 2015, **54**, 9968–9975.
- Y. Ding, P. N. Ruth, R. Herbst-Irmer, D. Stalke, Z. Yang and H. W. Roesky, *Dalton Trans.*, 2021, **50**, 2067–2074.

