

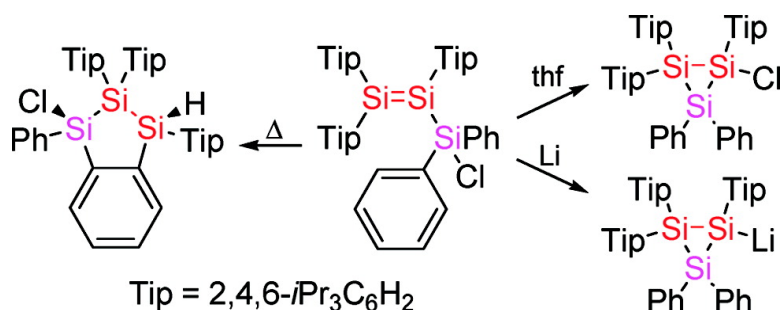
Article

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Syntheses of Trisila Analogues of Allyl Chlorides and Their Transformations to Chlorocyclotrisilanes, Cyclotrisilanides, and a Trisilaindane

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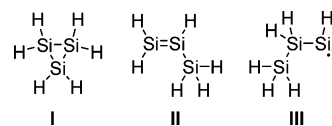
Abstract: The rearrangements of (chlorosilyl)disilenes $R_2(Cl)Si-(Tip)Si=SiTip_2$ (**5a,b**: Tip = 2,4,6-*i*-Pr₃C₆H₂, **a**: R = Me, **b**: R = Ph) quantitatively yield the isomeric chlorocyclotrisilanes (**6a,b**). The disilene precursors **5a,b** are, in turn, accessible from the reactions of the disilene $Tip_2Si=Si(Tip)Li$ (**1**), that is, a disila analogue to vinyl anions, with dichlorosilanes R_2SiCl_2 . This novel approach to cyclotrisilanes potentially allows for the facile variation of the substitution pattern and grants access to the first anionic derivatives; while the rearrangement of **5a,b** to **6a,b** is slow at room temperature and additionally requires the presence of THF or other *n*-donors, reduction of **5b** with lithium instantly yields the corresponding cyclotrisilanide (**7b**) without detection of any open-chained isomer. Heating of a neat sample of **5b** to 150 °C provides a completely characterized 1,2,3-trisilaindane derivative (**13**), strongly supporting the intermediacy of a disilanyl silylene species that inserts into an *ortho*-CH bond of the phenyl substituents. The X-ray diffraction studies on single crystals of **6a,b** and **7b** reveal that the Si–Si bond distance in cyclotrisilanes depends significantly on the electronegativity of the opposing silicon atom's substituents, which is rationalized by density functional theory (DFT) calculations on model systems.

Introduction

Since the synthesis of the first stable derivative by Masamune et al. in 1983,¹ cyclotrisilanes have attracted considerable interest as the smallest homonuclear silacycles, both from a fundamental and applied point of view.² Due to the inherent ring strain, cyclotrisilanes usually fragment easily under photochemical or thermal conditions and are therefore valuable precursors for the generation of silylenes and disilenes, as has been shown by the groups of Masamune, Weidenbruch, Belzner, and others in various contributions.^{1,3} Mechanistic studies using combined experimental and theoretical approaches investigated the formation of elemental silicon films by pyrolysis of silane SiH₄ and disilane Si₂H₆ and the possible involvement of the parent cyclotrisilane **I** as an intermediate.⁴ Computational efforts have been devoted to neutral and the (experimentally elusive) anionic cyclotrisilanes,⁵ particularly as examples of small hydrogenated silicon clusters, which are assumed to be band-gap-determining components of amorphous silicon.^{5b,d}

In sharp contrast to the cyclopropane–propene case, cyclotrisilane **I** (see Chart 1) is considered the global minimum of the Si₃H₆ hypersurface.⁶ It was found to be 7.8 kcal mol^{−1} lower

Chart 1. Some Isomers of Si₃H₆



in energy than the open-chained silyl disilene **II**. A plausible intermediate for the interconversion of **I** and **II** could be disilanyl silylene **III**, which is, in turn, 18.8 kcal mol^{−1} higher in energy than **I**.^{6d} While a large number of stable disilenes bearing silyl

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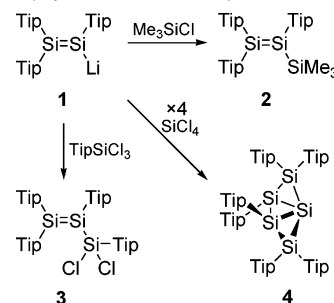
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substituents is known,⁷ the silyl disilene–cyclotrisilane rearrangement, to the best of our knowledge, has never been observed experimentally, unlike the related silyl silylene–disilene interconversion.⁸ In fact, the synthesis of cyclotrisilanes is usually accomplished by means of Wurtz-type reductive coupling of substituted dihalosilanes.⁹ Since this approach is evidently restricted to homoleptic systems in most cases, only a few unsymmetrical derivatives have been prepared from unsaturated cyclotrisilenes¹⁰ or dianionic disilanes¹¹ as starting materials.

Recently, disilenides, that is, disila analogues to vinyl anions, have become available in pure form.¹² In the meantime, a number of applications of such disilenides as reagents for the transfer of Si=Si double bonds to organic and inorganic substrates has emerged.¹³ First evidence for the nucleophilicity of disilenide **1** was derived from its quantitative conversion to monosilyl disilene **2** by treatment with Me₃SiCl.^{12a} While reaction of **1** with bulkily substituted TipSiCl₃ yielded **3**, a compound featuring a difunctionalized trisila allyl moiety,^{13b} addition of 4 equiv of **1** to silicon tetrachloride led to the

Scheme 1. Diverging Reactivity of Disilenide **1** toward Chlorosilanes^{13b,c} (Tip = 2,4,6-*i*Pr₃C₆H₂)



formation of the unusual cluster **4** exhibiting one vertex free of additional substituents.^{13c} These diverging results (open chain vs tricyclic derivative) gave a hint at the importance of the substitution pattern of the electrophile employed and prompted us to investigate the reactivity of disilenide **1** toward chlorosilanes bearing substituents with intermediate steric demand (see Scheme 1).

Here, we report on the synthesis of trisila analogues of allyl chlorides, that is, chlorosilyl disilenes, and their reduction with lithium to cyclotrisilanides, the first anionic homonuclear three-membered silacycles,¹⁴ rather than open-chained allylic anions. Moreover, the tetrahydrofuran-promoted rearrangement of chlorosilyl disilenes yields chlorocyclotrisilanes, not only allowing the first observation of the silyl disilene–cyclotrisilane isomerism but also the full characterization of both isomers. Additionally, the thermal isomerization of the diphenyl-substituted chlorosilyl disilene affords a trisilaindane derivative, providing firm evidence for a transient disilanylsilylene that undergoes intramolecular CH insertion. To complement the experimental data, the structural features of neutral and anionic cyclotrisilanes are rationalized by DFT calculations on model systems.

Experimental Section

General. All manipulations were carried out under a protective atmosphere of argon applying standard Schlenk techniques or in a dry box. Etheral solvents were refluxed over sodium/benzophenone; toluene over sodium; pentane, hexane, and (deuterated) benzene over sodium/potassium alloy. All solvents were distilled and stored under argon and degassed prior to use. Tip₂Si=Si(Tip)Li (**1**) was prepared following our published procedure.^{12a} Chlorosilanes were purchased from Aldrich, stored over Mg turnings, and distilled prior to use. Finely dispersed lithium powder was prepared by melting lithium rods (Aldrich) in paraffin oil under argon, dispersing it with an Ultra Turrax (Ika) for 3 min, filtering the cooled suspension, and rinsing three times with pentane before drying in vacuum. The NMR spectra were recorded on a Bruker Avance 200 (¹H, 200.13 MHz), on a Bruker DRX 300 (⁷Li, 116.64 MHz), and on a Bruker AV 500 (¹H, 500.13 MHz; ¹¹B, 160.46 MHz; ¹³C, 125.76 MHz; ²⁹Si, 99.36 MHz) FT-NMR spectrometer. ¹H and ¹³C{¹H} NMR spectra were referenced to external TMS via the residual protons of the deuterated solvent (¹H) or the solvent itself (¹³C). ⁷Li{¹H} NMR spectra were referenced to external LiCl(aq) and ²⁹Si{¹H} NMR spectra to external TMS. Microanalyses for C, H, and N were performed on a Leco CHNS-932 elemental analyzer. UV–vis spectra were recorded on a Shimadzu UV-Mini 1240. Melting points were determined under argon in closed NMR tubes and are uncorrected.

1-Chloro-1,1-dimethyl-2,3,3-tris(2,4,6-triisopropylphenyl)-2-trisilene, 5a. Via a cannula, 10 mL of hexane is added to 2.00 g (2.344

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mmol) of disilenide **1**. The orange solution is cooled to $-45\text{ }^{\circ}\text{C}$, and 0.33 g (2.557 mmol) of Me_2SiCl_2 is added. After 5 min, the reaction mixture is brought to $-10\text{ }^{\circ}\text{C}$ and left stirring for another 10 min. Following subsequent warming to room temperature, the solution is separated from precipitated LiCl by filtration. All volatiles are removed in vacuum, and the solid residue is dissolved with approximately 5 mL of hexane. After 16 h at $0\text{ }^{\circ}\text{C}$, 0.58 g of **6a** is separated from the mother liquor, the volume of which is slightly reduced, leading to a second crop of crystals predominantly composed of **6a** (0.20 g). The remaining solution is evaporated to dryness in vacuum, yielding 0.98 g (55%) of **5a** as an orange powder of 90–95% purity (contains 5–10% of **6a**), as estimated from the NMR spectra. ^1H NMR (500 MHz, C_6D_6 , 298 K): δ 7.09, 7.06, 6.99 (each s, each 2H, Tip-H), 4.29, 4.00, 3.78 (each hept., each 2H, *i*Pr-CH), 2.744, 2.736, 2.64 (each hept., each 1H, *i*Pr-CH), 1.34, 1.30 (br), 1.18, 1.17, 1.07, 0.96 (each d, altogether 54H, *i*Pr-CH₃), 0.45 (s, 6H, SiCH₃). ^{13}C NMR (125 MHz, C_6D_6 , 298 K): δ 156.55, 155.36, 155.15, 151.86, 151.16, 150.84 (Tip- C_{op}), 134.81, 134.20, 129.38 (Tip- C_i), 122.51, 122.27, 121.96 (Tip-CH), 38.32, 36.76, 34.83, 34.78, 34.44 (*i*Pr-CH), 25.44 (br), 24.65, 24.13, 24.08, 23.87 (*i*Pr-CH₃), 6.92 (SiCH₃). ^{29}Si NMR (99.36 MHz, C_6D_6 , 298 K): δ 103.0 ($^1J(\text{Si},\text{Si}) = 123\text{ Hz}$, *SiTip*), 39.9 ($^1J(\text{Si},\text{Si}) = 123$ and 84 Hz, *SiTip*), 26.2 ($^1J(\text{Si},\text{Si}) = 84\text{ Hz}$, *SiMe*₂).

1-Chloro-1,1-diphenyl-2,3,3-tris(2,4,6-triisopropylphenyl)-2-trisilene, 5b. Via a syringe, 1.74 g (6.87 mmol) of neat Ph_2SiCl_2 is added to a solution of 5.00 g (5.86 mmol) of disilenide **1** in 40 mL of toluene at $-78\text{ }^{\circ}\text{C}$. The color of the reaction mixture gradually intensifies to deep red while it is brought to room temperature overnight. Toluene is removed under vacuum and replaced by 70 mL of pentane. The solution is filtered, and solvents are distilled off, affording an orange oil, which is crystallized at $0\text{ }^{\circ}\text{C}$ from a saturated pentane solution, yielding 3.35 g (65%) of **5b** as orange blocks (mp $134\text{ }^{\circ}\text{C}$, dec). ^1H NMR (500 MHz, C_6D_6 , 298 K): δ 7.72 (t, 2H, Ph-H), 7.70 (d, 2H, Ph-H), 7.00–6.90 (m, 12H, Tip, and Ph-H), 4.15, 3.97, 3.74 (each hept., each 2H, *i*Pr-CH), 2.70, 2.68, 2.66 (each hept., each 1H, *i*Pr-CH), 1.30–0.96 (br, 24H, *i*Pr-CH₃), 1.144, 1.142, 1.095 (each d, each 6H, *i*Pr-CH₃), 0.93 (d, 12H, *i*Pr-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 298 K): δ 156.06, 155.05, 154.50, 151.41, 150.99, 150.98 (Tip- C_{op}), 136.67 (Ph- C_i), 135.93 (Ph-CH), 135.26, 134.73 (Tip- C_i), 130.18 (Ph-CH), 129.21 (Tip- C_i), 127.97 (Ph-CH), 122.52, 122.24, 121.91 (Tip-CH), 38.55, 37.83, 37.70, 34.74, 34.62, 34.40 (*i*Pr-CH), 24.73, 24.49 (each br, each *i*Pr-CH₃), 24.06, 24.00, 23.86 (*i*Pr-CH₃). ^{29}Si NMR (99.36 MHz, C_6D_6 , 298 K): δ 109.1 ($^1J(\text{Si},\text{Si}) = 120\text{ Hz}$, *SiTip*), 35.5 ($^1J(\text{Si},\text{Si}) = 120$ and 82 Hz, *SiTip*), 11.8 ($^1J(\text{Si},\text{Si}) = 82\text{ Hz}$, *SiPh*₂). UV-vis (hexane) λ_{max} (ϵ): 427 nm ($24800\text{ L mol}^{-1}\text{ cm}^{-1}$). Anal. Calcd for $\text{C}_{57}\text{H}_{79}\text{Si}_3\text{Cl}$: C, 77.45; H, 9.01. Found: C, 77.22; H, 9.06.

1-Chloro-2,2-dimethyl-1,3,3-tris(2,4,6-triisopropylphenyl)cyclotrisilane, 6a. Via a syringe, 0.93 g (7.21 mmol) of neat Me_2SiCl_2 is added to a solution of 4.00 g (4.69 mmol) of disilenide **1** in 40 mL of toluene at $-78\text{ }^{\circ}\text{C}$. The color of the reaction mixture quickly intensifies to deep red. After stirring at room temperature overnight, the color of the product mixture changes to light yellow. The solution is filtered, and the volatile components are distilled off. Crystallization at room temperature from a hexane solution saturated at $60\text{ }^{\circ}\text{C}$ yields 2.18 g (61%) of **6a** as light-yellow blocks (mp $184\text{ }^{\circ}\text{C}$). ^1H NMR (400.2 MHz, C_6D_6 , 298 K): δ 7.20, 7.18, 7.15, 7.02, 6.95 (each s, altogether 6H, Tip-H), 4.21 (br), 4.09, 3.74 (br), 3.61, 3.43 (br), 2.79, 2.76, 2.70 (each hept., altogether 9H, *i*Pr-CH), 1.51 (br), 1.49, 1.42 (br), 1.41, 1.39, 1.37, 1.31, 1.24 (br), 1.17, 1.14, 1.13 (each d, altogether 45H, *i*Pr-CH₃), 0.83 (s, 3H, SiCH₃), 0.67 (br, 3H, *i*Pr-CH₃), 0.51 (br, 6H, *i*Pr-CH₃), 0.23 (s, 3H, SiCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 298 K): δ 156.77, 156.67, 156.00, 155.94, 155.75, 154.18, 152.23, 150.57, 150.23 (Tip- C_{op}), 132.91, 131.20, 130.80 (Tip- C_i), 122.59, 122.22, 121.98, 121.79, 121.73, 121.00 (Tip-CH), 37.78, 36.90, 36.57, 36.34, 35.67, 34.90, 34.83, 34.59, 34.49 (*i*Pr-CH), 27.74, 27.68, 26.98, 26.85, 26.45, 24.77, 24.63, 24.51, 24.05, 24.02, 23.99, 23.60, 22.50 (*i*Pr-CH₃), -2.48, -4.43 (SiCH₃). ^{29}Si NMR (99.36 MHz, C_6D_6 , 298 K):

δ -26.5 (*SiTip*), -35.4 (*SiMe*₂), -64.2 (*SiTip*₂). Exact Mass (ESI-MS) (m/z) calcd for $\text{C}_{47}\text{H}_{76}\text{Si}_3\text{Cl}^+$ (MH^+): 759.49379; found: 759.49374. Anal. Calcd for $\text{C}_{47}\text{H}_{75}\text{Si}_3\text{Cl}$: C, 74.30; H, 9.95. Found: C, 74.10; H, 9.88.

1-Chloro-2,2-diphenyl-1,3,3-tris(2,4,6-triisopropylphenyl)cyclotrisilane, 6b. A solution of 500 mg (0.57 mmol) of **5b** in 5 mL of THF is left at room temperature overnight, leading to quantitative conversion to **6b**. Crystallization from a hexane solution saturated at $50\text{ }^{\circ}\text{C}$ affords 325 mg (65%) of slightly yellow crystals (mp $158\text{--}61\text{ }^{\circ}\text{C}$) of **6b**. Single crystals are grown at $-30\text{ }^{\circ}\text{C}$ from THF solution. ^1H NMR (500 MHz, C_6D_6 , 298 K): δ 8.18 (d, 2H, Ph-H), 7.26–7.20 (m, 4H, Tip- and Ph-H), 7.11–6.82 (m, 10H, Tip- and Ph-H), 4.04, 3.96, 3.89, 3.55 (each hept., altogether 6H, *i*Pr-CH), 2.79, 2.74, 2.71 (each hept., each 1H, *i*Pr-CH), 1.59, 1.48, 1.43, 1.41 (each d, each 3H, *i*Pr-CH₃), 1.29 (d, 6H, *i*Pr-CH₃), 1.23, 1.22, 1.17, 1.16, 1.15, 1.14, 1.09, 0.96, 0.75, 0.61, 0.56, 0.52 (each d, each 3H, *i*Pr-CH₃). ^{13}C NMR (125 MHz, C_6D_6 , 298 K): δ 156.96, 156.45, 156.19, 154.12, 152.40, 151.44, 150.54 (Tip- C_{op}), 138.68, 138.12 (Ph-CH), 135.94, 135.01 (Ph- C_i), 132.34, 131.10, 130.22 (Tip- C_i), 129.45, 128.95, 128.27, 127.67 (Ph-CH), 123.20, 122.97, 122.11, 122.08, 122.06, 121.39 (Tip-CH), 37.43, 36.84, 36.82, 36.68, 36.32, 34.74, 34.70, 34.62, 34.46 (*i*Pr-CH), 28.00, 27.79, 27.18, 26.97, 25.81, 25.42, 24.64, 24.61, 24.48, 24.31, 24.11, 24.07, 23.97, 23.93, 23.48, 21.63 (*i*Pr-CH₃). ^{29}Si NMR (99.36 MHz, C_6D_6 , 298 K): δ -28.4 (*SiTip*), -45.8 (*SiPh*₂), -62.6 (*SiTip*₂). Anal. Calcd for $\text{C}_{61}\text{H}_{87}\text{ClSi}_3$: C, 76.63; H, 9.17. Found: C, 76.43; H, 9.23.

1-Lithio-2,2-diphenyl-1,3,3-tris(2,4,6-triisopropylphenyl)cyclotrisilane, 7b·Li⁺·Et₂O. Via a cannula, 10 mL of Et₂O is added to 1.50 g (1.70 mmol) of **5b** and 0.15 g (21.6 mmol) of lithium powder at $-80\text{ }^{\circ}\text{C}$. The resulting mixture is stirred overnight. All volatiles are removed in vacuum, and the solid is residue digested with hot hexane ($50\text{ }^{\circ}\text{C}$). The solution is filtered while warm, and its volume reduced to 15 mL. Prematurely precipitating product is dissolved by gentle heating. Keeping the temperature at $25\text{ }^{\circ}\text{C}$ for 24 h yields 1.04 g (72%) of orange crystals. Slightly yellow crystals of pure **7b·Li⁺·Et₂O** (mp $199\text{ }^{\circ}\text{C}$ dec) are obtained by a second crystallization from hexane (0.73 g, 50%). ^1H NMR (500 MHz, C_6D_6 , 298 K): δ 8.34 (d, 2H, Ph-H), 7.34 (t, 2H, Ph-H), 7.28–7.22 (m, 5H, Tip- and Ph-H), 7.07 (br, 1H, Tip-H), 7.02 (d, 1H, Tip-H), 6.96–6.88 (m, 5H, Tip- and Ph-H), 4.64, 4.59 (br), 4.38, 4.21, 4.14, 3.88, 2.88, 2.85 (each hept., altogether 8H, *i*Pr-CH), 2.70 (q, 4H, Et₂O), 2.59 (hept., 1H, *i*Pr-CH), 1.69 (br), 1.51 (br), 1.39, 1.380 (br), 1.377, 1.34 (each d, each 3H, *i*Pr-CH₃), 1.31 (d, 6H, *i*Pr-CH₃), 1.279, 1.275, 1.15, 1.07, 1.06, 0.89 (br), 0.64 (br) (each d, each 3H, *i*Pr-CH₃), 0.63 (t, 6H, Et₂O), 0.56, 0.52, 0.35 (each d, each 3H, *i*Pr-CH₃). ^{13}C NMR (125 MHz, C_6D_6 , 298 K): δ 158.48 (br), 156.61 (br), 155.56, 155.16, 154.84, 154.15 (br), 150.05 (br), 149.79, 146.51 (Tip- C_{op}), 144.49, 142.87, 139.78 (br), 139.77 (Tip and Ph- C_i), 138.74 (Ph-CH), 138.30 (br, Tip- or Ph- C_i), 137.79, 127.66, 127.60, 127.05, 126.98 (Ph-CH), 123.69, 122.89, 122.68, 121.10, 120.65 (br), 119.03 (br) (Tip-CH), 65.64 (THF), 36.40, 36.39, 36.05 (br), 35.74, 34.84, 34.79, 34.45 (br), 34.32, 33.58 (*i*Pr-CH), 27.04 (br), 26.82, 26.79, 26.09, 24.91, 24.80, 24.60, 24.53, 24.47, 24.44, 24.32, 24.06, 23.91, 23.75 (br), 23.74, 23.50, 22.37 (br) (*i*Pr-CH₃), 14.05 (THF). ^{29}Si NMR (99.36 MHz, C_6D_6 , 298 K): δ -47.8 (1Si, *SiPh*₂), -76.4 (1Si, *SiTip*₂), -128.0 (1Si, $^1J(\text{Si},\text{Li}) \approx 50\text{ Hz}$, *SiTipLi*). MS-Cl, negative mode (isobutane) (m/z): 849 ($\text{M}^- - \text{Li}^+ \cdot \text{Et}_2\text{O} + \text{H}^+$).

[Lithium(C2.2.1)]-2,2-diphenyl-1,3,3-tris(2,4,6-triisopropylphenyl)cyclotrisilane-1-ide, 7b·[Li⁺(C2.2.1)]. A solution of 124 mg (0.43 mmol) of cryptand 2.2.1 in 1 mL of toluene is added to 350 mg (0.41 mmol) of **7b·Li⁺·Et₂O** in 1 mL of toluene. About 0.5 mL of hexane is added by a pipet. The resulting precipitate is dissolved by gentle warming to $60\text{ }^{\circ}\text{C}$ in an oil bath. Heating is turned off, and the clear orange solution is left to cool down to room temperature overnight. Decanting the mother liquor and drying in vacuum yields **7b·[Li⁺(C2.2.1)]** as orange crystals. ^1H NMR (500 MHz, C_6D_6 , 298 K): δ

Table 1. Selected Crystallographic Details for Compounds **5b**, **6a**, **6b**, **7b**·Li⁺·Et₂O, **7b**·[Li⁺ (C2.1.1)], and **13**

	5b	6a	6b	7b ·Li ⁺ ·Et ₂ O	7b ·[Li ⁺ (C2.1.1)]	13
formula	C ₂₃₃ H ₃₂₈ Cl ₄ Si ₁₂	C ₄₇ H ₇₅ ClSi ₃	C ₆₁ H ₈₇ ClOSi ₃	C ₆₄ H ₉₆ LiOSi ₃	C ₇₈ H ₁₁₅ LiN ₂ O ₄ Si ₃	C ₇₅ H ₁₁₅ ClSi ₃
temperature	98(2) K	173(2) K	193(2) K	173(2) K	97(2) K	173(2) K
crystal system	monoclinic	triclinic	orthorhombic	triclinic	triclinic	triclinic
space group	P2 ₁ /c	P-1	P 2 ₁ 2 ₁ 2 ₁	P-1	P-1	P-1
<i>a</i> , Å	31.0675(8)	14.135(1)	10.8740(5)	12.9877(9)	13.0569(4)	13.3185(8)
<i>b</i> , Å	18.4074(5)	17.7858(13)	15.4908(8)	13.6085(10)	16.6258(4)	15.7123(9)
<i>c</i> , Å	39.2606(9)	20.6446(15)	34.2768(17)	19.7857(14)	17.0696(5)	18.0837(11)
α , °	90°	69.997(1)°	90°	99.423(2)°	84.847(1)°	78.6948(14)°
β , °	99.287(1)°	75.569(1)°	90°	100.153(2)°	86.065(1)°	75.7526(13)°
γ , °	90°	89.749(2)°	90°	112.956(1)°	85.138(1)°	76.4736(13)°
<i>V</i> , Å ³	22157.7(10)	4704.4(6)	5773.8(5)	3063.6(4)	3670.28(18)	3527.4(4)
<i>Z</i>	4	4	4	2	2	2
<i>d</i> , g cm ⁻³	1.082	1.073	1.100	1.054	1.118	1.070
μ , mm ⁻¹	0.168	0.187	0.166	0.115	0.113	0.144
<i>F</i> (000)	7848	1664	2080	1066	1348	1248
θ_{\max}	25.03°	25.03°	25.03°	26.37°	26.37°	25.03°
refl. _{total}	427594	37758	46564	27554	232386	28117
refl. _{unique} reflections	39112	16623	10194	12481	14989	12409
<i>S</i>	1.054	1.123	1.307	1.031	1.025	1.107
<i>R</i> ₁ (<i>I</i> > 2 σ)	0.0508	0.0645	0.0671	0.0524	0.364	0.0696
<i>wR</i> ₂ (all data)	0.1376	0.1483	0.1548	0.1307	0.0901	0.1660

8.66 (d, 2H, Ph-H), 7.44–7.28 (m, 6H, Tip- and Ph-H), 7.12–6.82 (m, 8H, Tip- and Ph-H), 4.96, 4.93 (br), 4.66, 4.49, 4.28 (each hept., altogether 6H, *i*Pr-CH), 2.99–2.92 (m, 6H, *i*Pr-CH and OCH₂), 2.91 (s, 4H, OCH₂), 2.84–2.72 (m, 9H, *i*Pr-CH and OCH₂), 1.96 (ddd, 4H, NCHH), 1.90 (t, 4H, NCH₂), 1.81 (ddd, 4H, NCHH), 1.66, 1.63 (br), 1.57, 1.49, 1.38 (br), 1.37, 1.28–1.20 (br), 1.05 (br), 1.03, 0.74, 0.72, 0.68 (each d, altogether 54H, *i*Pr-CH₃). ⁷Li NMR (194.37 MHz, C₆D₆, 298 K): δ -1.11. ¹³C NMR (125 MHz, C₆D₆, 298 K): δ 155.26, 155.15, 154.87, 154.84, 154.64, 149.26, 148.70, 148.07, 147.74, 146.69, 146.21, 145.50, 143.19 (Tip-C_{ip}), 139.80, 137.94, 128.00, 126.63, 126.28, 125.88, 124.83 (Ph-CH), 121.67, 121.17, 120.59, 120.51, 118.93, 118.47 (Tip-CH), 68.30, 66.46, 65.37 (OCH₂), 51.41, 50.04 (NCH₂), 36.42, 36.19, 35.92, 35.0 (br), 34.99, 34.92, 34.74, 34.62, 34.54, 34.5 (br) (*i*Pr-CH), 27.60, 27.40, 27.24, 26.87 (br), 25.22, 25.19, 25.05, 24.93, 24.90, 24.71, 24.56, 24.44, 23.76, 23.61 (*i*Pr-CH₃). ²⁹Si NMR (99.36 MHz, v): δ -42.0 (1Si, *S*iPh₂), -74.1 (1Si, *S*iTip₂), -123.0 (1Si, *S*iTip).

1-Chloro-1-phenyl-2,2,3-tris(2',4',6'-triisopropylphenyl)-1,2,3-trisilaindane, 13. A neat sample of **5b** (200 mg, 0.226 mmol) is heated under vacuum to 150 °C for 30 min. The colorless residue is dissolved in a minimum amount of hexane at 60 °C and left at room temperature overnight. Decanting of the mother liquor and drying in vacuum yields 170 mg of **9** (85%) as colorless plates (mp. 136 °C). Single crystals are grown from cyclohexane at 25 °C. ¹H NMR (500 MHz, C₆D₆, 298 K): δ 8.05 (m, 2H, Ph-H), 7.80, 7.40 (each d, 1H, Ph-H), 7.36, 7.32 (each s, 1H, Tip-H), 7.23 (m, 3H, Ph-H), 7.07, 7.04, 7.01 (each s, each 1H, Tip-H), 7.00 (m, 1H, Ph-H), 6.91 (m, 1H, Ph-H), 6.80 (s, 1H, Tip-H), 6.41 (s, 1H, ¹J(Si,H) = 194 Hz, SiH), 4.54, 4.04, 3.62, 3.44, 3.07, 2.79, 2.78, 2.63, 2.40, (each hept., each 1H, *i*Pr-CH), 1.91, 1.63, 1.59, 1.43, 1.22, 1.20, 1.14, 1.08, 1.05, 0.96, 0.94, 0.67, 0.41, 0.19, 0.17 (each d, altogether 54H, *i*Pr-CH₃). ¹³C NMR (125 MHz, C₆D₆, 298 K): δ 157.54, 157.46, 156.38, 156.19, 154.69, 152.41, 151.25, 150.19, 149.89 (Tip-C_{ip}), 147.63, 143.59 (Ph-C_i), 137.63, 136.55, 134.24 (Ph-CH), 133.53 (Tip-C_i), 133.30 (Ph-C_i), 132.19 (Tip-C_i), 130.45, 129.85, 128.95, 127.87 (Ph-CH), 127.15 (Tip-C_i), 123.53, 123.22, 123.19, 122.76, 122.19, 121.45 (Tip-CH), 39.48, 38.39, 37.70, 36.62, 35.70, 34.61, 34.49, 34.40, 34.25 (*i*Pr-CH), 31.91 (hexane), 27.67, 26.70, 25.92, 25.78, 25.28, 25.17, 24.84, 24.74, 24.68, 24.08, 24.06, 24.04, 24.01, 23.95, 23.94, 23.78, 23.66 (*i*Pr-CH₃), 23.00, 14.33 (hexane). ²⁹Si NMR (99.36 MHz, v): δ 5.7, (*S*iCl), -42.0 (1Si, *S*iH), -50.6 (1Si, *S*iTip₂). Anal. Calcd for C₆₃H₉₃ClSi₃: C, 78.00; H, 9.66. Found: C, 77.37; H, 9.44.

Crystallography. Single crystals of **5b**, **6a**, **6b**, **7b**·Li⁺·Et₂O, **7b**·[Li⁺ (C2.2.1)], and **13** were coated with perfluorinated polyether and

transferred to the cold nitrogen stream at the goniometer. A sphere of data was collected on a Bruker Smart Apex II with CCD detector (**5b** and **7b**·[Li⁺ (C2.1.1)]): Bruker Smart Apex II with rotating anode source and CCD detector). The cells were determined accurately on a representative set of frames. Data reduction was carried out with SAINT+ 6.22, and a semiempirical absorption correction was applied with SADABS. Structures were solved by direct methods or Patterson synthesis. The disorder of some isopropyl groups and/or cocrystallized solvent molecules in **5b**, **6a**, **6b**, and **7b**·Li⁺·Et₂O was modeled by applying split positions and appropriate positional restraints. H atoms attached to silicon were located in the difference electron map and refined isotropically; all other H-atom positions were calculated and refined using a riding model. Refinements (ShelXL-97) proceeded smoothly to yield the crystallographic parameters summarized in Table 1.

Theoretical Calculations. All calculations were carried out with the Gaussian 98 program package.¹⁵ The B3LYP functional was applied with the 6-31G(d,p) basis set. The natural bond orbital (NBO) analyses were done with NBO 5.0 as implemented in Gaussian.¹⁶ The molecular orbitals were visualized and plotted with the MOLEKEL program.¹⁷

Results and Discussion

Disilene **1** reacts with dichlorosilanes R₂SiCl₂ in toluene or THF at room temperature in 2 h to yield the chlorosilyl-substituted disilenes **5a,b** (**a**: R = Me, **b**: R = Ph) in essentially quantitative yield. Both **5a** and **5b** were fully characterized by multinuclear NMR spectroscopy; only the diphenyl derivative **5b**, however, was isolated as orange blocks (mp 134 °C) in 65% yield by crystallization from a concentrated pentane solution at 0 °C (see Scheme 2).

The chemical shifts in the ²⁹Si NMR spectra compare well to those of monosilyl-substituted disilenes **2** and **3**, recently reported by us (Table 2).^{12a,13b} The well-resolved ²⁹Si–²⁹Si coupling constants together with 2D NMR spectra (²⁹Si, ¹H) allow for the unambiguous assignment of the signals of **5a,b**; the resonances at intermediate field show two sets of ²⁹Si

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Scheme 2. Syntheses of Chlorosilyl Disilenes **5a,b** and Their Rearrangement and Reduction to Cyclotrisilanes **6a,b** and Cyclotrisilanides **7a,b** (Tip = 2,4,6-*i*Pr₃C₆H₂)

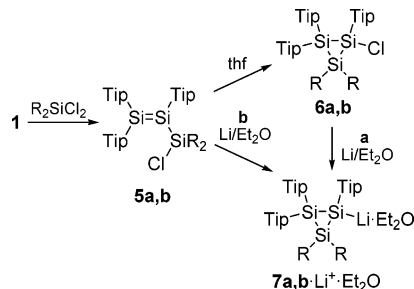


Table 2. Comparison of ²⁹Si NMR and UV–Vis Data of Chlorosilyl Disilenes **5a** and **5b** with **2**, **12a**, **3**, **13b** and **11**²¹

	5a	5b	2 ^{12a}	3 ^{13b}	11 ²¹
$\delta^{29}\text{Si1}$, ppm ^d	103.0	109.1	97.7	99.1	102.7 ^d
$\delta^{29}\text{Si2}$, ppm ^b	39.9	35.5	50.9	54.7	96.0 ^d
$\delta^{29}\text{Si3}$, ppm ^c	26.2	11.8	−8.3	11.7	−3.2
¹ <i>J</i> _{Si1, Si2} , Hz	123	120	116		
¹ <i>J</i> _{Si2, Si3} , Hz	84	82	75		
λ_{max} , nm		427			411
ϵ , L mol ^{−1} cm ^{−1}		24800			46820

^a *S*Tip₂. ^b *S*Tip. ^c Si3 = Silyl–Si. ^d Tentatively assigned.

satellites and are hence attributable to the silyl-substituted silicon atoms of the Si=Si double bonds. The coupling constants derived from the ²⁹Si satellites of the low-field signals are approximately 1.5 times larger than those for the high-field shifts, which reflects the higher s character of the Si=Si double bond compared to that of the Si–Si single bond. Both **5a** and **5b** show very similar ²⁹Si resonances for the corresponding double bond atoms, with considerable differences between the chemical shifts of the two silicon atoms of one double bond. This difference is significantly more pronounced than that in (dichloro)silyl-substituted **3**^{13b} and trimethylsilyl disilene **2**^{12a} (**5a**: $\Delta\delta = 63.1$; **5b**: $\Delta\delta = 73.6$; **2**: $\Delta\delta = 46.8$, **3**: $\Delta\delta = 44.4$ ppm) but less than that in disilyldiaryl disilenes of the A₂-Si=SiB₂ type.¹⁸ The underlying large chemical shift anisotropies of unsymmetrically substituted disilenes were subject to detailed theoretical studies.¹⁹

Because **5a** could not be isolated in sufficiently pure form, meaningful UV–vis spectroscopic data could only be obtained for **5b**. Its longest wavelength absorption is observed at $\lambda_{\text{max}} = 427$ nm ($\epsilon = 24800$ L mol^{−1} cm^{−1}), which is considerably red shifted compared to λ_{max} values of symmetrical (aryl)(silyl)-disilenes ((*E*)-**10**: 394 nm; (*Z*)-**10**: 398 nm)²⁰ but similar to that of bis(chlorosilyl)-substituted disilene **11**²¹ (Table 2 and Chart 2).

An X-ray diffraction study on single crystals of **5b** proved the constitution deduced from the spectroscopic data (Figure 1). Remarkably, **5b** crystallizes as four independent molecules in the asymmetric unit, which show significantly differing Si=Si bond lengths ranging from 217.23(8) to 219.00(8) pm. The Si–Si single bond distances (231.60(8)–232.70(8) pm) are

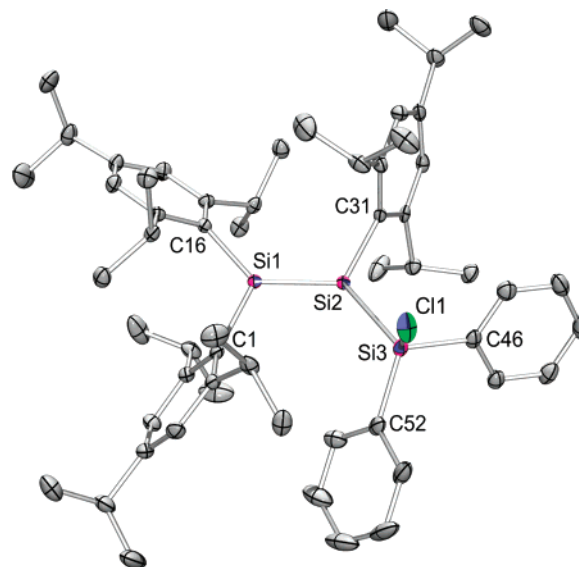
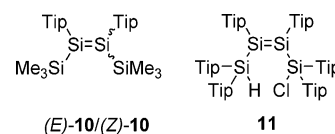


Figure 1. Molecular structure of **5b** in the solid state at the 50% probability level. Only one of four independent molecules is displayed. Cocrystallized pentane, disordered *i*Pr groups, and protons were removed for clarity.

Chart 2. Symmetrical Disilyl Disilenes (*E*)-**10**, (*Z*)-**10**,²⁰ and Chlorosilyl Disilene **11**²¹ (Tip = 2,4,6-*i*Pr₃C₆H₂) for Comparison



slightly shorter than the usual single bond (234 pm),²² which could be attributed to π back donation into the silyl group's σ^* orbitals. As expected in terms of higher group electronegativity and lesser steric bulk,⁷ the trans-bent angles θ (defined as the angle between the Si=Si bond vector and the normal vector to the plane given by the sp² silicon atom and the pending substituent atoms) are higher for the chlorosilyl-substituted silicon atoms ($\theta = 9.5, 17.6, 16.6,$ and 25.0°) compared to those of the SiTip₂ moieties of the same molecule ($\theta = 3.9, 10.8, 4.5,$ and 17.3°).

Both chlorosilyl disilenes **5a,b** isomerize to chlorocyclotrisilanes **6a,b** at room temperature, albeit under differing rates and conditions. While a solution of diphenyl(chloro)silyl-substituted **5b** in C₆D₆ does not show any significant changes of the NMR spectroscopic data for several weeks, its rearrangement to **6b** is complete after 2 h in *n*-donating tetrahydrofuran. Presumably due to the less bulky dimethyl(chloro)silyl group, the derivative **5a** is much more prone to cyclization even in the absence of donor solvents, which explains our failure to obtain it as a pure sample. While **5b** is unaffected by excess Ph₂SiCl₂, the presence of excess Me₂SiCl₂ accelerates the rearrangement of **5a** to such an extent that the stoichiometry of the reaction of the dichlorosilane with disilene **1** has to be carefully respected in order to be able to isolate **5a** at all.

The ²⁹Si NMR spectra of the rearrangement products cyclotrisilanes **6a,b**, show signals between −26.5 and −64.2 ppm at a relatively high field, as typically observed for cyclotrisilanes (Table 3).^{2c} While the chemical shifts for the Si(Cl)Tip and

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Table 3. Comparison of ^{29}Si NMR and Structural Data of Cyclotrisilanes **6a,b** and Cyclotrisilanides **7a,b**·Li⁺·Et₂O

	6a	6b	7a ·Li ⁺ ·Et ₂ O ^e	7b ·Li ⁺ ·Et ₂ O	7b ·[Li ⁺ (C2.1.1)]
$\delta^{29}\text{Si1}$, ppm ^a	-64.2	-62.6	-78.2 ^d	-76.4	-74.1
$\delta^{29}\text{Si2}$, ppm ^b	-26.5	-28.4	-121.6 ^d	-128.0	-123.0
$\delta^{29}\text{Si3}$, ppm ^c	-35.4	-45.8	-39.0 ^d	-47.8	-42.0
Si1–Si2, pm	235.8(1) ^f	236.1(1)		237.27(7)	238.32(5)
Si1–Si3, pm	230.7(1) ^f	233.9(1)		230.24(6)	232.18(5)
Si2–Si3, pm	237.7(1) ^f	240.9(1)		233.60(7)	233.87(5)

^a SiTip₂. ^b SiTip. ^c Si3 = SiR₂. ^d Tentatively assigned. ^e Prepared by reduction of **6a**, not isolated. ^f Intermediate value.

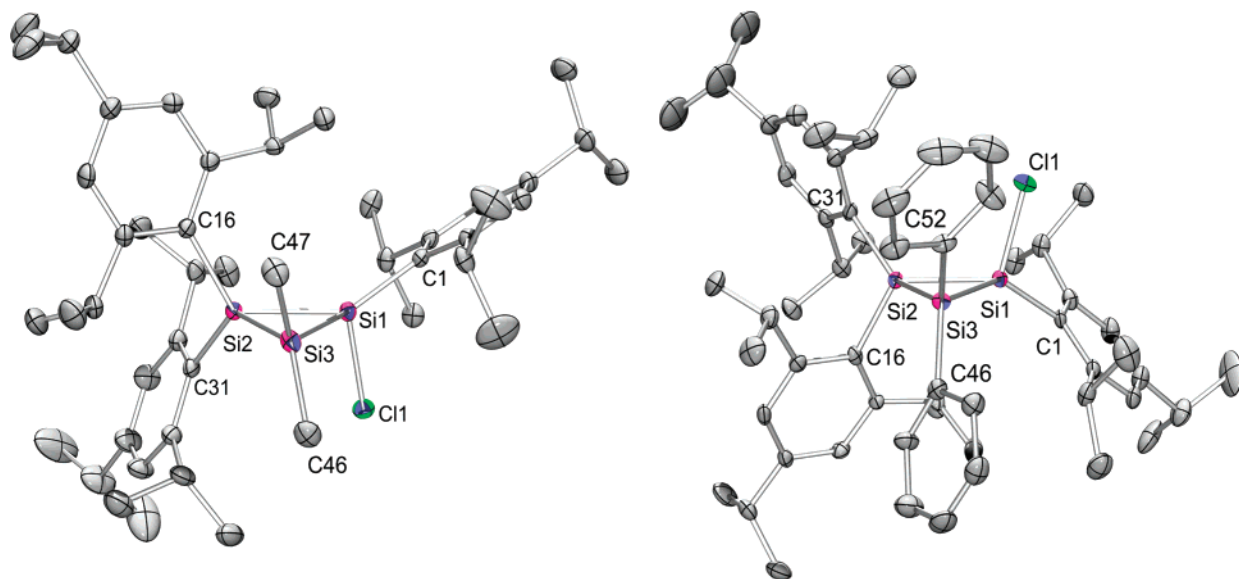


Figure 2. Molecular structures of **6a** (left) and **6b** (right) in the solid state at the 30% probability level. Only one of two independent molecules is displayed (**6a**). Cocrystallized THF (**6b**), disordered *i*Pr groups, and protons were removed for clarity.

SiTip₂ moieties are almost identical for **6a** and **6b**, the resonances of the SiR₂ fragments differ significantly, which was also observed in the case of **5a,b**.

The structural features of neutral cyclotrisilanes **6a,b** as determined by X-ray diffraction studies on single crystals (Figure 2) exhibit highly varying endocyclic Si–Si bond distances from 230.67(11) to 240.95(13) pm. The bond lengths of homoleptic cyclotrisilanes were subject to discussion due to relatively large variations depending on the substitution pattern; it has been suggested that these variations are mainly attributable to large steric strain induced by the bulky substituents.^{1,9a} In a detailed theoretical study on substituted derivatives of the carbon congener, that is, cyclopropane C₃H₅X, by Schleyer and Clark et al., a significant effect of the electronic nature of the substituent X was demonstrated.²³ They convincingly showed that σ -accepting groups lengthen the opposing and, at the same time, shorten the adjacent endocyclic C–C bonds of cyclopropanes. Apparently, a similar trend can be observed in the case of cyclotrisilanes as the longest bond in both cases, **6a** and **6b**, is the one opposing the chlorine-substituted silicon atom (Table 3).

Given the slow isomerization of chlorosilyl disilene **5b**, a trisila analogue of allyl chlorides, we investigated its reduction with finely dispersed lithium powder in Et₂O at room temperature. Contrary to our expectations, the anticipated trisila analogue to allyl lithiums could not be observed. Instead, the

first example of an anionic cyclotrisilanide^{14,24} was formed as the only detectable product and isolated as its lithium salt **7b**·Li⁺·Et₂O in 50% yield. The structure determination by single-crystal X-ray diffraction (Figure 3) reveals the presence of a close contact ion pair, in which Li1 strongly coordinates to the negatively charged silicon atom and shows additional contacts to Si2 and one *ipso*-carbon atom (Si1–Li1 258.0(4), Si2–Li1 289.8(4), Li1–C31 245.5(4) pm). This contact ion pair clearly remains intact in C₆D₆ solution, as proven by the quartet splitting of the ^{29}Si NMR signal at -128.0 ppm due to coupling to the ^7Li nucleus ($^1J(^{29}\text{Si}, ^7\text{Li}) \approx 50$ Hz).

In contrast to the corresponding chlorocyclotrisilane **6b**, the endocyclic Si–Si bond lengths of **7b**·Li⁺·Et₂O are all in the range expected for single bonds (Table 3), corroborating the above assumption that more σ -donating substituents should lead to shorter opposing Si–Si bonds in cyclotrisilanes. However, not only the Si2–Si3 bond distances of **7b**·Li⁺·Et₂O are shorter than the corresponding bond length of **6b**, but also, the Si1–Si3 distance is shorter. In order to eliminate the possibility that the coordination of the Li⁺ counterion is responsible for the observed relatively short endocyclic bonds of **7b**, we also prepared the solvent-separated ion pair by addition of cryptand 2.2.1 (C2.2.1) to a benzene solution of **7b**·Li⁺·Et₂O. The solid-state structure (Figure 3) of **7b**·[Li⁺ (C2.2.1)] shows no close contact of the cation to the anion **7b**. While the Si1–Si3 bond length of **7b**·[Li⁺ (C2.2.1)] is

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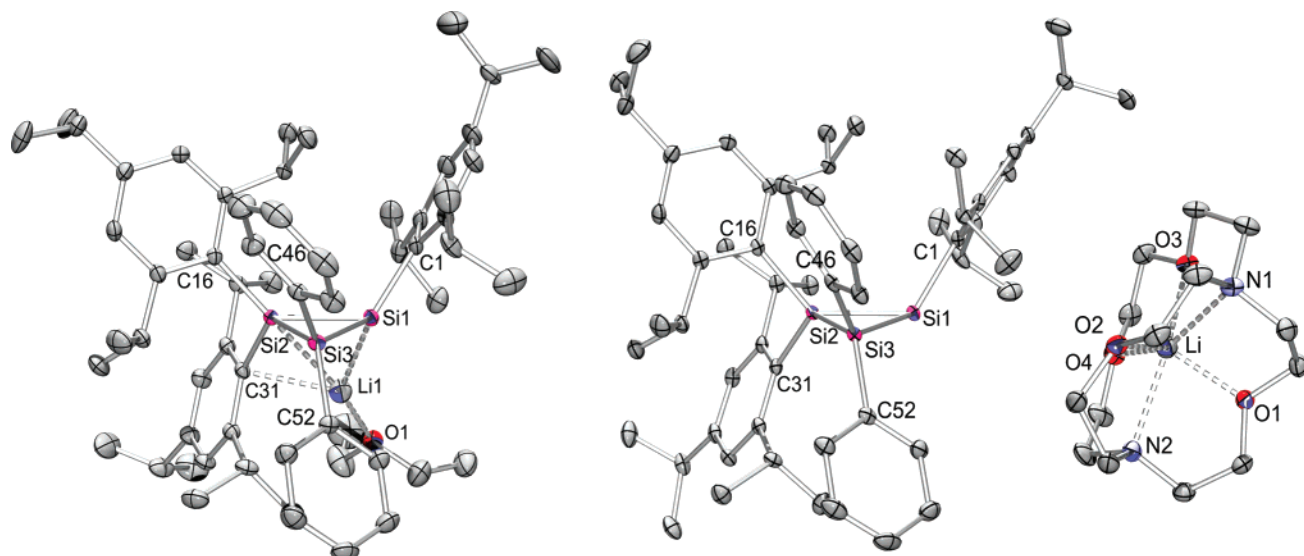


Figure 3. Molecular structures of **7b**·Li⁺·Et₂O (left) and **7b**·[Li⁺(C2.2.1)] (right) in the solid state at the 30 and 50% probability levels, respectively. CocrySTALLIZED hexane (**7b**·Li⁺·Et₂O), disordered *i*Pr groups, disordered coordinating Et₂O, and protons were removed for clarity.

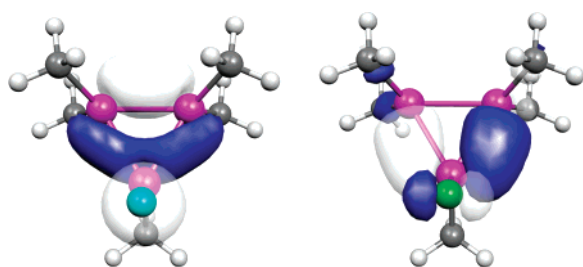


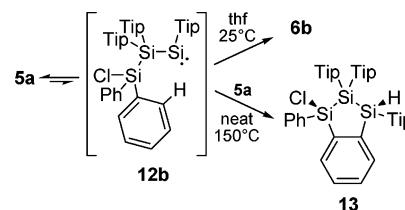
Figure 4. Contour plots of the HOMOs of model cyclotrisilanes Me₃Si₃X, with X = Li (left) and Cl (right). Color coding: Si (pink), Cl (green), Li (light-blue), C (dark gray), H (white).

indeed much closer to that of **6b**, the Si₂–Si₃ is practically unaffected by the detachment of the counterion.

In order to clarify the bonding situation in cyclotrisilanes **6** and **7** in a manner independent of the steric strain induced by the bulky ligand set, we carried out DFT calculations on the permethylated model compounds Me₃Si₃X (X = Li, Cl) at the B3LYP/6-31G(d,p) level of theory. The Si₂–Si₃ bond opposing the heterosubstituted silicon atom is considerably shorter for X = Li (232.7 pm) than that for X = Cl (237.5 pm). Conversely, the adjacent Si–Si bonds are shorter in the case of the more electronegative chloro substituent (Si₁–Si_{2/3} (X = Li): 238.3; (X = Cl): 235.3 pm). As can be seen from the plots in Figure 4, the HOMO with respect to Si₂–Si₃ is bonding for the lithiated and antibonding cases of the chlorinated cyclotrisilane. Consequently, the increase in electronegativity amended by the chloro substituent reduces the Wiberg bond indices of the Si₂–Si₃ bond from 0.9718 for X = Li to 0.9240 for X = Cl, as well as the NLMO/NPA indices from 1.0648 for X = Li to 1.0117 for X = Cl. Indeed, the few crystallographically characterized chlorinated cyclotrisilanes apart from **6a,b** all exhibit longer endocyclic Si–Si bonds opposing the chlorinated silicon atoms as well.¹⁰

Although the formation mechanism of the cyclotrisilanes **6a,b** remains speculative for now, we tentatively interpret the solvent dependency of the rearrangement in terms of the formation of transient disilanyl silylene **12** by 1,2-migration of the diphenyl(chloro)silyl moiety.²⁵ The silylene **12** would likely insert into the Si–Cl bond, keeping in mind that such insertion reactions

Scheme 3. Proposed Mechanisms for Thermal and THF-Promoted Isomerizations of Chlorosilyl Disilenes (Tip = 2,4,6-*i*Pr₃C₆H₂)



have been reported for both stable and transient silylenes.²⁶ As an aryl–silyl-substituted silylene, **12** most certainly would have a singlet ground state,²⁷ which should be further stabilized by a Lewis acid–base interaction of the vacant p_z orbital with THF or other *n*-donors. An *n*-donating solvent would thereby not only catalyze the formation of cyclotrisilanes **6** but possibly lower the reactivity of **12** to such an extent that competing reactions such as CH insertions would be disfavored.

Not too surprisingly, all attempts to trap a silylene intermediate **12b** with bis(trimethylsilyl)acetylene in either the presence or absence of THF were unsuccessful, the intramolecular reaction likely being much more rapid than the intermolecular one with the trapping agent (Scheme 3). Heating of **5b** slightly above its melting point (mp 134 °C) in the absence of *n*-donors, however, yields a single product without the Si=Si double bond but contrary to cyclotrisilane **6b** with a silicon-bonded proton, as evidenced by a signal in the ¹H NMR spectrum at δ = 6.41 ppm with a typical ¹J(Si,H) coupling constant of 194 Hz.²⁸ The constitution of the product as a 1,2,3-trisilaindane^{29,30} derivative

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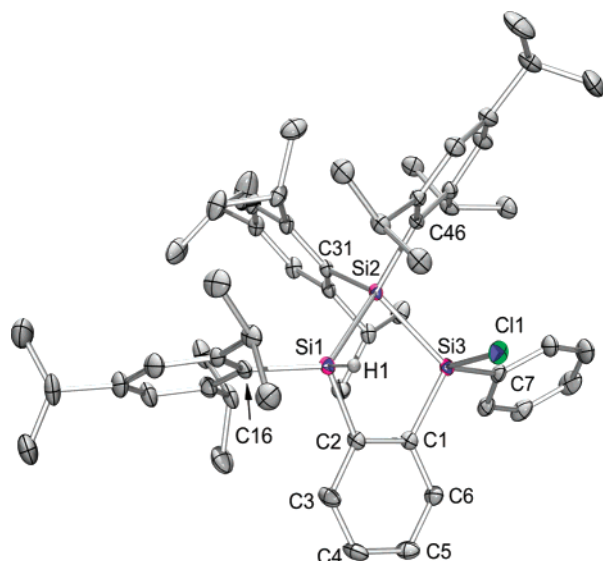


Figure 5. Molecular structure of 1,2,3-trisilaindane **13** in the solid state at the 30% probability level. Cocrystallized cyclohexane, disordered *iPr* groups, and most protons were removed for clarity.

13 is determined by X-ray diffraction on single crystals isolated in 85% yield (mp 136 °C) by crystallization from a concentrated solution in cyclohexane at room temperature (Figure 5).

While the intermediacy of silylene **12** in the formation of cyclotrisilane **6a,b** is hypothetical, the connectivity of **13**, in which the phenyl- and chloro-substituted silicon atom is attached to the SiTip₂ rather than to the SiTip moiety, as in the precursor disilene **5b**, provides strong evidence for a transient silylene **12b**.³¹ Both Si–Si bond distances (Si1–Si2, 240.36(10); Si2–Si3, 237.38(10) pm) are slightly longer than the usual Si–Si single bond presumably due to the sterically demanding substitution pattern. The structure in the solid state also reveals the stereochemistry of the trisilaindane, in which the proton H1 is located on the same side of the five-membered ring as the

chlorine atom Cl1. The almost exclusive formation of the *cis* stereoisomer **13** is proven by the NMR spectra of the crude product mixture showing only very minor impurities apart from the signals belonging to **13**. This preference can be explained by a pronounced staggering of the five-membered ring (dihedral angles: Si1–Si2–Si3–C1 25.67(9)°; C2–Si1–Si2–Si3–C2 26.50(9)°), which avoids the unfavorable 1,3-diaxial interactions that would necessarily be present in the *trans* stereoisomer.

Conclusion

We have described the synthesis of chlorosilyl disilenes **5a,b** from the reaction of a disilene **1** with dichlorosilanes. While **5a,b** rearrange to the isomeric cyclotrisilanes **6a,b** in the presence of THF (or possibly other *n*-donors), heating of **5b** above its melting point exclusively yields a trisilaindane derivative **13**. We propose that both rearrangements, thermal and THF-promoted, proceed via a transient disilanyl silylene, the reactivity of which might be tamed through stabilization of its vacant p_z orbital by a Lewis base. The reductions of **5b** and **6a** do not provide the anticipated open-chained trisila allylic anions but furnish the first anionic cyclotrisilanes **7a,b**. The solid-state structures of neutral **6a,b** and anionic **7b** show that bond lengths in cyclotrisilanes apart from steric strain also depend significantly on the electronic properties of the substituents. Supported by DFT calculations, we conclude that the endocyclic bond distances of cyclotrisilanes are longer when the σ -acceptor strength of the opposing substituent is high.

Given that various disilenes have been reported in the last couple of years,¹² the reactions described in this article should be of broad applicability for the preparation of a large variety of tailor-made asymmetric cyclotrisilanes, cyclotrisilanides, and silaindane derivatives.

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Supporting Information Available: Crystallographic data in CIF format, plots of NMR spectra, and computational details with complete ref 15. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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