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Silicon-carbon hybrid [2]-ladderanes

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The first silicon-carbon hybrid ladderanes consisting of trisila and tricarbonyl ladder rails were obtained by the reactions of lithium disilene $R_2Si=SiRLi$ ($R=2,4,6$ -triisopropylphenyl) with allylchlorosilanes. The steric strain in the 1,2,6-trisilabicyclo[2.2.0]hexanes imposed by the bulky substituents

leads to highly distorted ring systems with extreme puckering and long silicon-carbon bridgehead bonds. All 1,2,6-trisilabicyclo[2.2.0]hexanes show strong absorptions in the UV/vis and the rigidity of the [2]-ladderane framework gives rise to turquoise fluorescence.

Introduction

Oligo- and polymeric chains of fused cyclobutane motifs have been intensely investigated due to their structural rigidity and the resulting potential as rod-like building blocks for materials.^[1] In 1988, the term [n]-ladderane was introduced by Miller and Schulman, where n is the number of linearly fused four-membered rings (Figure 1),^[2] Ladder polymers in general^[3,4] and [n]-ladderanes in particular^[5] have been considered as linkers for the energy transfer antenna in light harvesting systems that minimize the formation of excimers due to their rigidity thus improving the efficiency of the energy transfer. In general, ladderanes are mostly obtained via photodimerization^[6] or reduction of halogenated precursors.^[7] They have been synthesized in chain lengths of up to 13 repeat units as early as 1994.^[8] [n]-Ladderanes even occur in nature as structural element of lipid building blocks for ultra-dense diffusion-resistant membranes of certain bacteria.^[9,10]

Heavier group 14 ladderanes have been synthesized in case of Si,^[11] Ge^[12] and Sn.^[13] In contrast to their carbon analogues, ladder polysilanes have only been synthesized up to the octacyclic system.^[14] Due to pronounced σ -conjugation of

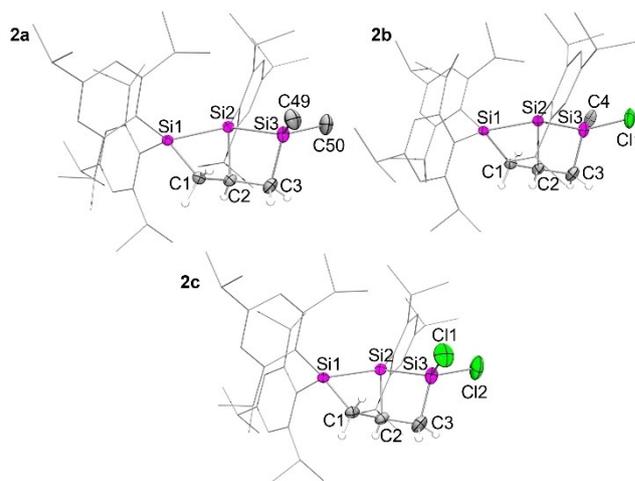


Figure 1. Molecular structures of **2a**, **2b** and **2c** in the solid state. Thermal ellipsoids at 50%, hydrogen atoms at the wireframe. Selected bond lengths [Å] and angles [°]: **2a**: Si1–Si2 2.3663(7), Si2–Si3 2.3733(8), Si1–C1 1.892(2), Si2–C2 1.976(2), Si3–C3 1.888(2), C1–C2 1.554(3), C2–C3 1.550(3); 74.28(7), Si1–Si2–C2 75.65(6), C2–Si2–Si3 73.76(6), C3–Si3–Si2 80.77(7), C1–C2–Si2 94.1(1), C2–C1–Si1 101.8(1), C2–C3–Si3 99.3(1). **2b**: Si1–Si2 2.3645(6), Si2–Si3 2.3615(7), Si1–C1 1.890(2), Si2–C2 1.976(2), Si3–C3 1.868(2), C1–C2 1.551(2), C2–C3 1.547(2); C1–Si1–Si2 74.15(6), Si1–Si2–C2 75.95(5), C2–Si2–Si3 72.56(5), C3–Si3–Si2 82.13(6), C2–C1–Si1 102.3(1), C1–C2–Si2 93.9(1), C2–C3–Si3 98.0(1). **2c**: Si1–Si2 2.3660(8), Si2–Si3 2.3557(8), Si1–C1 1.896(2), Si2–C2 1.981(2), Si3–C3 1.857(3), C1–C2 1.555(3), C2–C3 1.553(3); C1–Si1–Si2 74.28(7), Si1–Si2–C2 76.14(7), C2–Si2–Si3 71.29(7), C3–Si3–Si2 83.87(8), C2–C1–Si1 102.4(1), C1–C2–Si2 93.9(1), C2–C3–Si3 96.1(1).

oligosilanes in general,^[15] they show absorptions in the near UV/visible region. Longer chained silicon ladderanes show a bathochromic shift from 310 nm for [2]-ladderane up to 414 nm for a [4]-ladderane.^[16] Ladder polysilanes are mostly synthesized by reductive coupling of halosilane chains.^[11,17] Hybrid silicon-carbon ladderanes with distinct ladder stringers are unknown at present. Here, we report the synthesis of a series of silicon-carbon bicycles with 1,2,6-trisilabicyclo[2.2.0]hexane scaffold and thus the first examples of Si–C hybrid [2]-ladderanes.

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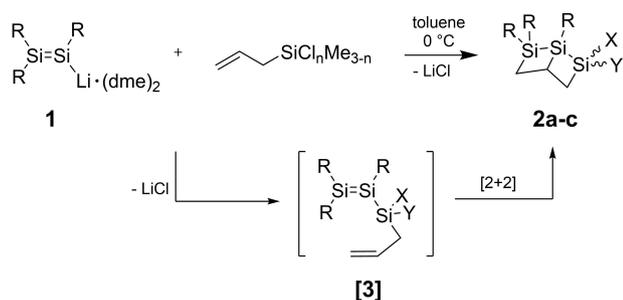
Results and Discussion

Treatment of a toluene solution of lithium disilene **1**^[18] with the appropriate allylchlorosilanes $R^1R^2Si(Cl)C_3H_5$ results in a rapid change in color from orange to light yellow and yields the hybrid [2]-ladderanes **2a–c** (**2a**: $R^1 = R^2 = Me$; **2b**: $R^1 = Me$, $R^2 = Cl$; **2c**: $R^1 = R^2 = Cl$) in near-quantitative manner (Scheme 1). Pale-yellow single crystals are obtained in average to mediocre yields (**2a**: 42 % **2b**: 51 % **2c**: 45 %).

At first glance, the ²⁹Si NMR spectra of **2a–c** show characteristic signals in the region of saturated silicon atoms. While the hybrid [2]-ladderanes **2a** and **2c** give rise to three signals, the diastereomeric mixture of **2b** exhibits two sets of three signals each in an approximate 2:1 ratio. Apparently, the steric discrimination between the methyl and chloro groups at silicon is only moderate so that the diastereoselectivity remains low. In the chiral **2a**, the methyl groups at silicon are diastereotopic and hence give rise to two resonances each in the ¹H (0.67 and 0.28 ppm) and ¹³C NMR spectra (3.62 and 2.95 ppm). While the signals for the SiTip₂ unit are observed in the same range for **2a–c** (**2a**: –15.5 ppm; **2b**: –14.1 (minor), –15.5 (major) ppm, **2c**: –14.1 ppm), the signals for SiTip are increasingly shifted downfield from **2a** to **2c** (**2a**: 6.8 ppm, **2b**: 17.7 (major), 17.5 (minor) ppm, **2c**: 34.5 ppm), which may reflect the inductive effect of the additional chlorine atoms in **2b** and **2c**. In contrast, the signals attributed to the SiXY vertex do not show any discernible trend with chemical shifts at 17.0 ppm (**2a**), 46.0 (minor), 41.7 (major) ppm (**2b**) and 36.1 ppm (**2c**).

The trisilabicyclo[2.2.0]hexanes **2a–c** are presumably formed by nucleophilic substitution at the chloro-substituted silicon atom of the allyl substrate. The plausible, yet undetected open-chained intermediates [**3a–c**] would subsequently undergo intramolecular [2+2]-cycloaddition to form the final bicyclic products. Intramolecular [2+2]-cycloadditions between Si=Si and C=C double bonds have previously been reported by our group.^[19]

The molecular structures **2a–c** in the solid state as determined by single crystal x-ray diffraction (Figure 1)^[20] show the anticipated 1,2,6-trisilabicyclo[2.2.0]hexane backbones with differing number of chloro substituents at the terminal silicon atom Si3. The derivative with one chloro and one methyl group



Scheme 1. Synthesis of **2a–c** via the proposed intermediate [**3**] ($R = Tip = 2,4,6$ -triisopropylphenyl; **2a**: $n = 1$, $X = Y = Me$; **2b**: $n = 2$, $X = Cl$, $Y = Me$; **2c**: $n = 3$, $X = Y = Cl$).

at Si3 crystallized as mixture of diastereomers with an occupational disorder in an approximate 50:50 ratio.

The difference in covalent radii between silicon and carbon gives rise to pronounced distortions of the two annulated four-membered rings in all three derivatives prepared during this study. While the inner angles of the four-membered rings of full carbon analogues are close to 90°, ^[21] the corresponding angles at the silicon atoms of **2a–c** are more acute (**2a**: C1–Si1–Si2 74.28(7)°, C2–Si2–Si3 73.76(6)°, C3–Si3–Si2 80.77(7)°; **2b**: C1–Si1–Si2 74.16(6)°, C2–Si2–Si3 72.56(5)°, C3–Si3–Si2 82.13(6)°, **2c**: C1–Si1–Si2 74.28(7)°, C2–Si2–Si3 71.29(7)°, C3–Si3–Si2 83.87(8)°). Conversely, the endocyclic angles at the carbon atoms are widened reflecting the smaller covalent radius of carbon compared to silicon (**2a**: C1–C2–Si2 94.1(1)°, C2–C1–Si1 101.8(1)°, C2–C3–Si3 99.3(1)°; **2b**: C2–C1–Si1 102.3(1)°, C1–C2–Si2 93.9(1)°, C2–C3–Si3 97.9(1)°; **2c**: C2–C1–Si1 102.4(1)°, C1–C2–Si2 93.9(1)°, C2–C3–Si3 96.1(1)°). The number of chloro substituents at Si3 does not significantly impact the distortion of the concerned four-membered ring (largest deviation from mean plane through C2/Si2/Si3/C3 for **2a**: 0.168(2) Å, C3; **2b**: –0.175(2) Å, C2; **2c**: –0.189(3) Å, C2). The rigid geometry forces the two four-membered rings to twist significantly against each other as manifest in the dihedral angles C1–Si1–Si3–C3 (**2a**: 29.7(1)°, **2b**: 29.47(9)°, **2c**: 28.9(1)°), which are markedly differing from the 0° of an idealized bicyclo[2.2.0]hexane. Again, the number of chloro substituents does not significantly affect this distortion.

The cyclobutane parent is strongly puckered by approximately 27° according to theoretical calculations and experimental studies,^[22] and so are 1,2-disilacyclobutanes with dihedral angles Si–Si–C–C of a similar magnitude.^[23] In contrast, monocyclic cyclotetrasilanes are completely planar as a consequence of the low tendency of silicon towards hybridization.^[24] The puckering angles in **2a–c** (i.e. the angles between the normal of the two triangles constituting the cyclobutene motif) cannot be defined unambiguously due to lack of symmetry, but nonetheless clearly differ for the two annulated rings containing Si1/Si2/C2/C1 (average values; **2a**: 40.0(1), **2b**: 39.3(1)°, **2c**: 38.7(1)°) and Si2/Si3/C3/C2, respectively (**2a**: 16.7(1)°, **2b**: 17.1(1)°, **2c**: 16.6(2)°). Obviously, any flattening of the constituting four-membered rings upon catenation is minimal, if present at all. In contrast, a significant decrease of the puckering angle (8.1°) in comparison to an monocyclic cyclobutane was experimentally confirmed by Andersen and Srinivasan through a gas phase electron diffraction study on bicyclo[2.2.0]hexane.^[25] Similarly, the puckering of the individual rings of persila[n]-ladderane equally decreases with increasing number of catenated rings according to theoretical calculations.^[26] We can therefore conclude that the strong puckering in hybrid [2]-ladderanes **2a–c** is attributed to the fact that the two “ladder rails” consist exclusively of one sort of atom each. The thus caused distortion of the bicyclic ring system is also visible in lengthened bridgehead bonds (Si2–C2, **2a**: 1.976(2) Å, **2b**: 1.975(2) Å, **2c**: 1.981(2) Å) in comparison to the Si–C bond lengths of the perimeter of the ladder motif (e.g. for Si1–C1; **2a**: 1.891(2) Å, **2b**: 1.890(2) Å, **2c**: 1.896(2) Å).

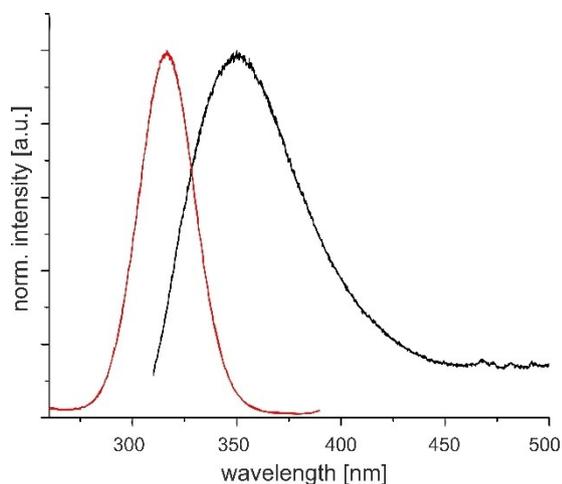


Figure 2. Fluorescence spectrum (black = emission, red = excitation) of **2c**.

Similar to ladder polysilanes^[16] and oligosilanes in general,^[15] the 1,2,6-trisilabicyclo[2.2.0]hexanes show two absorptions in the UV with maxima at 286, 259 nm for **2a**; 285, 258 nm for **2b** and 283, 259 nm for **2c**. The extinction coefficients vary between 16600 and 21270 Lcm⁻¹mol⁻¹. The incorporation of chloro substituents only leads to an insignificant blue-shift of the longest wavelength absorption.

The rigid framework results in a turquoise fluorescence in the solid state upon excitation with UV light (**2a**, $\lambda_{\text{ex}}=314$ nm, $\lambda_{\text{em}}=354$ nm; **2c** $\lambda_{\text{ex}}=316$ nm, $\lambda_{\text{em}}=351$ nm), although it is apparently quenched in solution by non-radiative relaxation processes based on the additional degrees of freedom of the Tip substituents. The Stokes shifts are unremarkable with $\Delta\lambda=40$ nm for **2a** and $\Delta\lambda=35$ nm for **2c**. The determined quantum yields for **2a** and **2c** are low, but significant (**2a**: $\Phi=7.2\%$, **2c**: $\Phi=7.0\%$). A typical fluorescence spectrum is depicted in Figure 2 showing the emission and excitation spectra of **2c**.

Conclusions

A series of trisilabicyclo[2.2.0]hexanes were synthesized by reaction of disilenide **1** with allylchlorosilanes H₂C=CHCH₂SiMe_nCl_{3-n}. The products were characterized by NMR spectroscopy and X-Ray diffraction. In comparison to the well-known carbon and silicon ladderane analogues, the structure of these novel silicon-carbon hybrid [2]-ladderanes is considerably more distorted by the strain induced due to the two ladder rails being of significantly differing length. The rigid structure gives rise to a turquoise fluorescence in the solid state.

Experimental Section

General Methods: All experiments were carried out under an inert atmosphere of argon 5.0 using standard Schlenk techniques. All

solvents were dried and deoxygenated by distillation from sodium/benzophenone (Et₂O, thf) or sodium/benzophenone/tetraglyme (hydrocarbons, toluene, benzene) before use. NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. ¹H and ¹³C NMR spectra were referenced to residual signals of the deuterated solvent. ²⁹Si was referenced to external SiMe₄. UV-Vis spectra were obtained using a Shimadzu UV-2600 in quartz cells with a path length of 0.1 cm. Melting points were determined under argon in a sealed NMR tube. Elemental analysis was performed with a Leco CHN-900 analyzer. Lithium disilene **1** was prepared according to the published procedure.^[21] Allylsilanes were purchased from Sigma Aldrich and distilled prior to use.

2,2-Dimethyl-1,6,6-tris(2,4,6-triisopropylphenyl)-1,2,6-trisilabicyclo [2.2.0]hexane: Allylchlorodimethylsilane (187 μ L, 1.28 mmol) was added to a solution of **1** (1.00 g, 1.17 mmol) in 15 mL toluene at 0 °C. The mixture was stirred overnight in the thawing ice bath. After removing all the volatiles under reduced pressure, the residue was digested in 20 mL hexane and the solids were filtered off. The remaining solution was concentrated and kept at -20 °C to obtain 0.378 g of **2a** as light-yellow crystals (yield: 42%, m.p. > 220 °C). ¹H NMR (400.13 MHz, C₆D₆, 300 K) δ 7.51–7.31 (m, 2H, Tip-CH); 7.29–7.16 (m, 5H, Tip-CH overlapping with C₆D₆); 4.55 (br. s, 1H, *i*Pr-CH), 3.93 (br. s, 2H, *i*Pr-CH); 3.78–3.45 (m, 4H, *i*Pr-CH); 3.00–2.80 (m, 4H, *i*Pr-CH); 2.10–2.00 (m, 2H, *i*PrCH₃); 1.78–1.46 (m, together 18H, *i*PrCH₃); 1.39–1.36 (m, 7H, *i*PrCH₃); 1.32–1.29 (each m, together 13H, *i*PrCH₃); 1.28–1.22 (br. s, 10H, *i*PrCH₃, CH); 0.82 (br., 5H, CH₂); 0.67, 0.28 (each s, 3H, SiCH₃). ¹³C{¹H} NMR (100.61 MHz, C₆D₆, 300 K) δ 155.42 (Tip-C); 150.09, 149.96, 149.61 (Tip-C); 133.97, 132.04, 131.80, 129.26, 128.49 (Tip-CH); 125.63, 122.44, 122.02 (Tip-CH); 121.16 (Tip-CH); 35.55 (*i*Pr-CH); 34.53, 34.48, 34.44 (*i*Pr-CH); 33.53 (*i*Pr-CH); 33.29 (*i*Pr-CH); 32.55, 29.96 (CH₂); 26.09, 25.22 (CH); 24.07, 24.05, 24.02, 23.96, 23.78 (*i*Pr-CH₃); 3.62, 2.95 (SiCH₃). ²⁹Si{¹H} NMR (79.49 MHz, C₆D₆, 300 K): δ 17.0 (SiMe₂); 6.8 (STip); -15.5 (STip₂). **UV-Vis** (hexane) λ_{max} (ϵ): 256 nm (17970 M⁻¹cm⁻¹), 286 nm (17010 M⁻¹cm⁻¹). C₅₀H₈₀Si₃; calc. C 78.46; H 10.54%; found: C 73.46, H 9.34%.

2-Chloro-2-methyl-1,6,6-tris(2,4,6-triisopropylphenyl)-1,2,6-trisilabicyclo[2.2.0]hexane: Allyldichloromethylsilane (186 μ L, 1.28 mmol) was added to a solution of **1** (1.00 g, 1.17 mmol) in 15 mL toluene at 0 °C. The mixture was stirred overnight in the thawing ice bath. After removing all the volatiles under reduced pressure, the residue was digested in 20 mL hexane and the solids were filtered off. The remaining solution was concentrated and kept at -20 °C to obtain 0.437 g of **2b** as yellow-white crystals of the diastereomeric mixture (yield: 51%, m.p. > 220 °C). ¹H NMR (400.13 MHz, C₆D₆, 300 K) δ 7.34 (s, 1H, Tip-CH); 7.25–7.16 (m, 4H, Tip-CH overlapping with C₆D₆); 4.40 (br. s, 1H, *i*Pr-CH); 3.85–3.84 (m, 2H, *i*Pr-CH); 3.67–3.39 (m, 4H, *i*Pr-CH); 3.03–2.80 (m, 4H, *i*Pr-CH); 2.55–2.48 (m, 1H, *i*PrCH); 2.21–2.12 (m, 2H, *i*PrCH); 1.78–1.51 (m, together 14H, *i*PrCH₃); 1.40–1.36 (m, together 8H, *i*PrCH₃); 1.32–1.30 (m, together 13H, *i*PrCH₃, CH); 1.25–1.23 (bs, 10H, *i*PrCH₃); 1.07 (hexane); 0.96 (s, 3H, SiCH₃); 0.77 (br. s, 4H, CH₂); 0.62 (s, 3H, CH₃). ¹³C{¹H} NMR (100.61 MHz, C₆D₆, 300 K) δ 155.56, 155.44, 154.72 (Tip-C); 150.69, 150.46, 150.42, 150.07, 150.01 (Tip-C); 133.06, 132.63, 130.81, 130.58, 129.39 (CH₂); 122.58, 122.13, 121.39 (Tip-CH); 36.85 (CH) 36.27 (*i*Pr-CH); 35.21, 34.86 (CH); 34.52, 34.49, 34.47, 34.44 (*i*Pr-CH); 33.44 (CH); 33.36, 33.07, 32.62 (*i*Pr-CH); 32.29, 31.91 (CH); 26.03, 25.16, 25.10, 24.94, 24.84, 24.78, 24.62, 24.02, 23.96, 23.91, 23.89, 23.75, 23.70, 23.63, 23.59, 23.58, 23.00, 23.43, 14.01 (unassigned alkyl signals); 8.20, 7.09 (SiCH₃). ²⁹Si{¹H} NMR (79.49 MHz, C₆D₆, 300 K): δ = 46.0, 41.7 (SiClMe); 17.6, 17.5 (STip); -14.1, -15.5 (STip₂) ppm. **UV-Vis** (hexane) λ_{max} (ϵ): 258 nm (20370 M⁻¹cm⁻¹), 285 nm (21270 M⁻¹cm⁻¹). C₄₉H₇₇ClSi₃; calc. C 74.89; H 9.88%; found: C 75.26, H 10.19%.

2,2-Dichloro-1,6,6-tris(2,4,6-triisopropylphenyl)-1,2,6-trisilabicyclo-[2.2.0]hexane: Allyltrichlorosilane (186 μL , 1.28 mmol) was added to a solution of **1** (1.00 g, 1.17 mmol) in 15 mL toluene at 0 °C. The mixture stirred overnight in the thawing ice bath. After removing all the volatiles under reduced pressure, the residue was digested in 20 mL hexane and the solids were filtered off. The remaining solution was concentrated and kept at $-20\text{ }^\circ\text{C}$ to obtain 0.425 g of **2c** as light-yellow crystals (yield: 45%, m.p. $>220\text{ }^\circ\text{C}$). ^1H NMR (400.13 MHz, C_6D_6 , 300 K) δ 7.36–7.31 (bs, 3H, Tip-CH); 4.37 (bs, 0.8H, *i*Pr-CH); 3.79 (bs, 2H, *i*Pr-CH); 3.64 (bs, 1H, *i*Pr-CH); 3.51–3.44 (m, 1H, *i*Pr-CH); 3.27 (bs, 1H, *i*Pr-CH); 2.99–2.76 (m, 4H, *i*Pr-CH); 2.71–2.65 (m, 1H, *i*Pr-CH); 2.47–2.15 (bs, 3H, *i*PrCH₃); 1.95 (bs, 1H, *i*PrCH₃); 1.66–1.54 (bs, 10H, *i*PrCH₃); 1.45–1.37 (m, 10H, *i*PrCH₃); 1.32–1.29 (m, 14H, *i*PrCH₃, CH₃); 1.23 (bs, 11H, *i*PrCH₃); 0.78 (bs, 4H, CH₂) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, C_6D_6 , 300 K) δ 155.60, 155.51, 155.34, 154.65, 151.36, 150.84, 150.50 (Tip-C); 131.79, 129.75, 129.27, 128.51, 128.43 (Tip-CH); 125.64, 122.73, 122.24, 121.74 (Tip-CH); 42.83 (CH₂); 36.70, 35.01, 34.51, 34.48, 33.43(*i*Pr-CH); 33.11 (CH₂); 31.90, 28.11, 26.39, 25.92 (CH); 25.35 (CH); 25.06, 23.98, 23.88 (CH); 23.83, 23.70, 22.49 (*i*Pr-CH₃) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, C_6D_6 , 300 K) δ 36.0 (*Si*Cl₂); 34.5 (*Si*Tip); -14.1 (*Si*Tip₂) ppm. UV-Vis (hexane) λ_{max} (ϵ): 259 nm (16600 $\text{M}^{-1}\text{cm}^{-1}$), 283 nm (16780 $\text{M}^{-1}\text{cm}^{-1}$). $\text{C}_{48}\text{H}_{74}\text{Cl}_2\text{Si}_3$; calc. C 71.51; H 9.25%; found: C 70.99, H 8.84%.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Ladderanes · silicon · carbon · fluorescence · cycloaddition

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