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Siloxane-bridged [*n*]Troticenophanes: Syntheses, Structures and Ring-Opening Reactions

Alain C. Tagne Kuate, Mihaela Alexandru, Matthias Freytag, Carmen Racles, Maria Cazacu, Peter G. Jones, Matthias Tamm

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- Siloxane-bridged [*n*]troticenophanes were synthesized and fully characterized.
- Thermal behaviors were studied by DSC and resistance to ROP at high temperature was observed.
- In the presence of initiators, redistribution reactions occurred with detection of oligotroticenylsiloxanes, ring-opened and ring-expanded troticenes.

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Siloxane-bridged [*n*]Troticenophanes: Syntheses,

Structures and Ring-Opening Reactions

Alain C. Tagne Kuate,^a Mihaela Alexandru,^b Matthias Freytag,^a Carmen Racles,^b Maria Cazacu,^b

Peter G. Jones,^a Matthias Tamm^a*

^aInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig,

Hagenring 30, 38106 Braunschweig, Germany

^b "Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41 A, Iasi 700487,

Romania

*Corresponding author. Tel.: +49(0) 531 391 5309; Fax: +49(0) 531 391 5387.

Email-address. m.tamm@tu-bs.de

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Graphical abstract



Troticenophanes containing siloxane bridges were prepared by metathesis of dilithiated troticene with 1,3dichlorotetramethyl-, 1,5-dichlorohexamethyl-, 1,7-dichlorooctamethylsiloxane in a one pot reaction at -78°C. The compounds exhibit thermal resistance to ring-opening polymerization (ROP) at elevated temperature indicated by differentials scanning calorimetry (DSC) studies. However, investigations of the ROP in the presence of potassium polysiloxanolate or *n*-butyllithium induce a redistribution reaction with formation of oligotroticenylsiloxane incorporating two to four troticenyl units.

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Abstract

Salt elimination reactions between dilithiotroticene $[(\eta^7 \Box C_7 H_6 Li)Ti(\eta^5 \Box C_5 H_4 Li)]$ ·pmdta (1) (pmdta = N, N', N', N', N''-pentamethyldiethylenetriamine) and siloxane dichlorides ClMe₂Si-(OSiMe₂)_m-Cl $(m = 1 \square 3)$ at low temperature allowed the synthesis and isolation of the siloxane-bridged [n]troticenophanes $[(\eta^7 \Box C_7 H_6)Ti(\eta^5 \Box C_5 H_4)](OSiMe_2)_m(SiMe_2)$ (2, m = 1; 3, m = 2; 4, m = 3) as blue crystalline solids in moderate yield. The compounds were characterized by ¹H, ¹³C and ²⁹Si NMR spectroscopy, elemental and single crystal X-ray diffraction analyses. The molecular structures of 2 and 3 showed a low degree of strain indicated by the dihedral ($\alpha = 4.8^{\circ}$ for 2; 4.9/3.7° for 3) and distortion ($\delta = 176.2^\circ$ for 2; 174.3/176.3° for 3) angles between the two rings. The structure of 4 was severely disordered. Compounds $2\Box 4$ are thermally resistant to ring-opening polymerization, as revealed by differential scanning calorimetry studies, with 2 exhibiting the higher melting temperature. Moreover, the observation of two endotherms in the DSC spectrum of 2 suggests a solid state transition as a result of polymorphism. The reactions of $2\Box 4$ with basic initiators such as potassium siloxanolate, ammonium siloxanolate or nBuLi and analysis of the product distribution by electron ionization mass spectrometry revealed the formation of oligotroticenylsiloxanes incorporating one or more troticenyl units, ring-opened troticenes and ringexpanded troticenophanes $[(\eta^7 \Box C_7 H_6)Ti(\eta^5 \Box C_5 H_4)](OSiMe_2)_r(SiMe_2)$ (r > m). Similar cleavage and extension of the ring were observed by treatment of $2\Box 4$ with the acidic initiator Purolite CT-175, and ring-opened troticenes having mixed terminal –OH and –SiMe₃ groups were detected. Attempts to copolymerize $2\Box 4$ and cyclotrisiloxane with *n*BuLi afforded essentially the monomeric and polymeric siloxanes $[Me_2SiO]_w$ (w = 7, 8), $Me_2(nBu)Si[OSiMe_2]_vOSiMe_2$ (y = 3 \square 6) and $Me_2(nBu)Si[OSiMe_2]_OH$ (z = 1 \Box 7), together with the ring-opened and ring-expanded products mentioned above.

1. Introduction

Polysiloxanes (silicones) represent a polymer class characterized by a repetition of the ($-R_2SiO$ -) unit along the main chain. They are some of the most widely studied polymeric inorganic materials and display properties such as heat resistance, high elasticity and stability. Silicones are also inert, non-toxic and exhibit a high gas permeability, which makes them attractive for applications e.g. in sealants or coatings, in contact lenses and in biomedicine generally. These materials are accessible by polycondensation of dichlorosilane, which is hydrolyzed to linear siloxane via hydroxy intermediates. However, this approach has been progressively replaced by the ring-opening polymerization (ROP) of cyclic siloxane trimers and tetramers, which now appears to be the most convenient and versatile route to polysiloxanes and allows a better control of the molecular weight [1 \square 6].

During the last two decades, there has been an increasing interest in the incorporation of other metals or elements in the main chain of polysiloxanes. The resulting polymers are expected to exhibit new properties with interesting potential applications. Heterocyclosiloxanes, in which one silicium atom is replaced by a main group element (B, Sn, S, P, As) [7 \Box 11] or by a transition metal (Ti, Zr, Ni, Co) [11 \Box 14], have been synthesized and structurally characterized, but very few have been the subjects of polymerization studies. The boracyclotrisiloxane (PhBO)(Ph₂SiO)₂ was reported to undergo ring-ring transformation reactions at elevated temperature in the presence of K[OSiMe₃],⁷ and the polystannasiloxane [(*t*BuSnO)(Ph₂SiO)₂]_n was generated in the solid state by condensation of [Ph₂(OH)Si]₂O with *t*Bu₂SnCl₂ [8c].

Polysiloxanes with ferrocenyl side groups or in which the ferrocene moiety is part of the main chain have attracted attention because of the additional redox, optical, magnetic and electronic properties that the materials are expected to display. Several authors have reported the synthesis of linear or cyclic siloxane precursors with substituted ferrocenyl fragments and investigated their oligo- and/or polymerization reactions including dendronisation [15 \Box 22]. Relevant examples are the homo- and copolymers (Me₃SiO)(MeSi(CH₂CH₂Fc)O)_n(SiMe₃) (I, n ~ 35) and

 $(Me_3SiO)(MeSiFcO)_n$ - $(Me_3SiO)_m(SiMe_3)$ (**II**, n = 30 \Box 35%, m = 65 \Box 70%, Fc = ferrocene), containing pendant ferrocenyl moieties, which were synthesized by hydrosilation of ferrocenylvinylsilane with polysiloxanes containing terminal Si \Box H bonds [23]. The linear polyferrocenylsiloxanes **III** \Box **V** with ferrocene as part of the main polymer chain were obtained by condensation reactions of 1,1'-bis(chlorocarbonyl)ferrocene with appropriate siloxane precursors and by dehydrogenative coupling of 1,1'-bis(dimethylsilyl)ferrocene (Chart 1) [24 \Box 26]. ROP of siloxane-bridged [*n*]ferrocenophanes (**VI**) (Chart 2) was also attempted, but instead of polymerization, redistribution and skeletal cleavage reactions occurred [27].



Chart 1. Examples of polysiloxanes with pendant ferrocenyl ligands or with ferrocene as the main part of the polymer chain.

Compounds of type **VI** are known for more than five decades $[28 \square 30]$ and belong to the family of the related *ansa*-ferrocenes $[(\square^5 \square C_5H_4)Fe(\square^5 \square C_5H_4)](ER_x)_n$, (**VII**, Chart 2) from which ROP studies with formation and isolation of ring-opened polymers were pioneered by Manners [31]. One derivative of precursor **VI** is the disiloxane-bis(1-indenyl)-*ansa*-ferrocene, Fe(\square^5 -inden-1-yl-SiMe₂)₂O, which was reported to copolymerize with octamethylcyclotetrasiloxane to afford a green material [32]. Other non-iron *ansa* compelexes, for instance group 4 (Ti, Zr, Hf) [33 \square 37] and group 6 (Mo W) [38] metallocenes with bridged siloxanes, have been reported, but the studies were limited to their structural characterization and/or use as catalysts in olefin polymerization. In

contrast, to the best of our knowledge, there are no reports on the synthesis of *ansa*-bridged siloxane compounds containing cycloheptatrienyl-cyclopentadienyl (Cht \Box Cp) sandwich complexes or on their incorporation into the chains of polymeric siloxanes. The only related work involving siloxanes and Cht \Box Cp sandwich units is the synthesis and structural elucidation of the disiloxane-bridged bitrovacene [($\Box^7 \Box C_7 H_7$)V($\Box^5 \Box C_5 H_4$)]₂(Me₂SiOSiMe₂), which aimed at studying the intermetallic communication between the two paramagnetic groups across the Si \Box O \Box Si bridge [39].



Chart 2. Ansa-metallocenophanes.

In the course of a systematic study of the functionalization of $[(\Box^7 \Box C_7 H_7)M(\Box^5 \Box C_5 H_5)]$ (M = Ti, troticene; V; trovacene, Cr, trochrocene), we and other research groups recently reported the first examples of the *ansa*-Cht Cp complexes $[(\Box^7 \Box C_7 H_7)M(\Box^5 \Box C_5 H_5)](ER_x)_n$ (VIII, Chart 2) with phosphorus, boron, silicon, germanium and tin in the bridge. These complexes were obtained by selective lithiation of troticene, trovacene or trochrocene, respectively, with a mixture of *n*-butyllithium/tmeda (tmeda = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) or *n*-butyllithium/pmdta and subsequent treatment with the appropriate Cl₂(ER_x)_n reagent [40 \Box 42]. For the sila-, germa- and stanna[1]troticenophanes, studies of their thermal behavior by DSC revealed exotherms at 130, 170 and 233 °C, which were assigned to ring-opening reactions and formation of poly(troticenylsilane), poly(troticenylstannane) of moderate molecular weight ($M_w = 14113$ g.mol^{\Box 1}) [41b] was

synthesized by living anionic ROP of stanna[1]troticenophane with *n*BuLi as initiator, while transition-metal-catalyzed ROP of sila[1]troticenophane and sila[1]trochrocenophane was achieved by reaction with Pt^0 at elevated temperature to give low-molecular-weight polymers ($M_w = 1301$ and 6400 g.mol⁻¹, respectively) [41f,42e]. In a continuation of our work on the ROP of *ansa*-troticenes, we have synthesized and structurally characterized siloxane-bridged [*n*]troticenophanes (**IX**, Chart 2). Herein, we present results on the investigations of their thermal behavior by DSC and their ring- opening reactions under conditions similar to those used for cyclic siloxanes.

2. Experimental Section

2.1. General procedures

All reactions were performed in a glove-box under dry argon (MBraun 200B) or on a high vacuum line using Schlenk techniques. Commercial-grade solvents were purified using a system from MBraun GmbH and stored over molecular sieves (4 Å) prior to use. Tetrahydrofuran was additionally dried with sodium/benzophenone, distilled, degassed and stored under argon. NMR spectra were recorded with Bruker DPX 200, DRX 400 and AV 300 devices. Chemical shifts (δ) are given in ppm and referenced to tetramethylsilane. Coupling constants (*J*) are reported in Hertz (Hz) and splitting patterns are indicated as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), pt (pseudo triplet) and m (multiplet). Elemental analyses (C, H, N) were performed by combustion and gas chromatographic analysis with an Elementar Vario MICRO elemental analyser. DSC experiments were performed with a Netzsch 203 DSC instrument under a continuous flow of nitrogen at a heating rate of 10 K/min. Electron ionization mass spectrometry (EI-MS) was performed on a Finnigan MAT 90 device (resolution: 2000, 10% valley definition). The samples were prepared in the GloveBox by impregnating the sharp point of a needle with the substance and introducing in a crucible, which is directly introduced in the EI-MS device for analysis.

2.2. Materials

n-Butyllithium (1.6 M in hexane) purchased from Aldrich was used as received. Trimethylchlorosilane (Me₃SiCl), purchased from Aldrich, was distilled, degassed and stored under argon prior to use. 1,3-Dichlorotetramethyldisiloxane, 1,5-dichlorohexamethyltrisiloxane and 1,7dichlorooctamethyltetrasiloxane were purchased from ABCR and used as received. Styrenedivinylbenzene ion exchange with -SO₃H groups, commonly called Purolite CT-175, was ordered from Viromet S.A. and dehydrated by azeotrope distillation with toluene under vacuum at 110°C/10 mm Hg. Dilithiotroticene $[(\Box^7 \Box C_7 H_6 Li)Ti(\Box^5 \Box C_5 H_4 Li)]$ ·pmdta was prepared as previously reported [41e]. Tetramethylammonium hydroxide solution was purchased from Fluka. Hexamethyldisiloxane, hexamethylcyclotrisiloxane (D₃), and octamethylcyclotetrasiloxane (D₄) were purchased from ABCR and used as received.

2.3. Single-crystal X-ray structure determinations

Numerical details are summarized in Table 1. Crystals were mounted in inert oil on glass fibres. Intensities were recorded on Oxford Diffraction diffractometers using monochromated Mo *Ka* (2) or mirror-focussed Cu *K*a radiation (3). Absorption corrections were based on multi-scans. Structures were refined anisotropically on F^2 using the program SHELXL-97 [43]. Hydrogen atoms were either refined freely (H atoms of seven-membered rings, using restraints for 2), as part of idealized methyl groups allowed to rotate but not tip, or using a riding model. The crystal of 2 was a non-merohedral twin (by 180° rotation about *a*); untwinning routines automatically merge all equivalent reflections, so that *R*(int) becomes meaningless; the number of reflections includes both components of overlapped reflections. The structure was refined using the "HKLF 5" option, whereby the scale factor refined to 0.4416(6) for the minor component.

Table 1	
Crystal and structure refinement data for 2 and	d 3.

	2	3
Empirical formula	$C_{16}H_{22}OSi_2Ti$	$C_{18}H_{28}O_2Si_3Ti$
Formula weight	334.42	408.57

Temperature (K)	100(2)	100(2)	
Wavelength λ (Å)	0.71073	1.54184	
Crystal system	monoclinic	monoclinic	
Space group	$P2_1$	$P2_1/n$	
<i>a</i> [Å]	6.5601(5)	18.7698(4)	
<i>b</i> [Å]	8.2580(6)	9.10194(15)	
<i>c</i> [Å]	15.1392(11)	24.2942(5)	
α[°]	90	90	
β [°]	96.201(6)	95.548(2)	
γ[°]	90	90	
Volume [Å ³]	815.35(10)	4131.02(14)	
Ζ	2	8	
Reflections collected	3761	104682	
Independent reflections	3761	8603 [$R_{\rm int} = 0.053$]	
Goodness of fit on F^2	0.90	1.03	
$\rho_{calcd} [g cm^{-3}]$	1.362	1.314	
μ [mm ⁻¹]	0.66	5.2	
Flack parameter	0.00(2)	-	
$R(F_{o}), [I > 2\sigma(I)]$	0.031	0.026	
$R_{\rm w} (F_{\rm o}^{2})$	0.041	0.070	
Δρ [e Å ⁻³]	0.39/-0.26	0.32/-0.49	

2.4. Synthesis of $[(\eta^7 - C_7 H_6)Ti(\eta^5 - C_5 H_4)](OSiMe_2)(SiMe_2)(2)$

A solution of 1,3-dichlorotetramethyldisiloxane (0.59 g, 2.9 mmol) in hexane (15 mL) was added dropwise to a suspension of $[(\eta^7 \square C_7 H_6 Li)Ti(\eta^5 \square C_5 H_4 Li)]$ ·pmdta (1.02 g, 2.6 mmol) in hexane (20 mL) at $\square 78$ °C. The reaction mixture was stirred for 1 h at this temperature and then slowly warmed up to room temperature and stirred overnight. The solution was filtered to remove LiCl, and all volatiles were removed in vacuum. The remaining blue oily residue was dissolved in 1.5 mL pentane and the solution was stored at $\square 30$ °C. A blue crystalline solid deposited after few days. Separation of the solid from the pentane solution and drying in vacuum afforded 0.41 g (47%) of pure **2**. Anal.

ZY '

Calcd (%) for C₁₆H₂₂OSi₂Ti (334.42): C 57.47, H 6.63, Found. C 56.53, H 6.60. ¹H NMR (400 MHz, C₆D₆, 297K) δ : 5.43 (m, 2H, C₇H₆), 5.32 (m, 4H, C₇H₆), 4.89 (pt, ³*J*(¹H \square ¹H) = 2.6 Hz, 2H, C₅H₄), 4.82 (pt, ³*J*(¹H \square ¹H) = 2.6 Hz, 2H, C₅H₄), 0.28 (s, ²*J*(¹H \square ²⁹Si) = 6.6 Hz, 6H, C₅H₄Si*Me*₂), 0.0 (s, ²*J*(¹H \square ²⁹Si) = 6.9 Hz, C₇H₆Si*Me*₂). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 297K) δ : 110.5 (s, *i*-C₅H₄), 103.6 (s, C₅H₄), 100.4 (s, C₅H₄), 95.9 (s, *i*-C₇H₆), 90.9 (s, C₇H₆), 90.4 (s, C₇H₆), 87.4 (s, C₇H₆), 0.3 (s, C₅H₄Si*Me*₂), 0.0 (s, C₇H₆Si*Me*₂). ²⁹Si NMR (300 MHz, C₆D₆, 297K) δ : 4.1 (C₅H₄SiMe₂), \square 5.6 (C₇H₆SiMe₂).

2.5. Synthesis of $[(\eta^7 - C_7 H_6)Ti(\eta^5 - C_5 H_4)](OSiMe_2)_2(SiMe_2)$ (3)

A solution of 1,5-dichlorohexamethyltrisiloxane (0.39 g, 1.4 mmol) in hexane (15 mL) was added dropwise to a suspension of $[(\eta^7 \square C_7H_6Li)Ti(\eta^5 \square C_5H_4Li)]$ -pmdta (0.50 g, 1.3 mmol) in hexane (20 mL) at \square 78 °C. The reaction mixture was stirred for 1 h at this temperature and then slowly warmed up to room temperature and stirred overnight. Insoluble LiCl was filtered off and the clear solution was vacuum dried to leave a blue oily residue, which solidified on standing. Recrystallization from pentane at \square 30 °C gave 0.26 g (49%) of pure **3** as blue crystalline solid. Anal. Calcd (%) for C₁₈H₂₈O₂Si₃Ti (408,54): C 52.92, H 6.91, Found. C 52.27, H 7.57. ¹H NMR (300 MHz, C₆D₆, 297K) δ : 5.62 (pt, ${}^{3}J({}^{1}H\square{}^{1}H) = 0.8$ Hz, 1H, C₇H₆), 5.59 (pt, ${}^{3}J({}^{1}H\square{}^{1}H) = 0.8$ Hz, 1H, C₇H₆), 5.36 (m, 2H, C₇H₆), 5.24 (m, 2H, C₇H₆), 5.0 (pt, ${}^{3}J({}^{1}H\square{}^{1}H) = 2.6$ Hz, 2H, C₅H₄), 4.91 (pt, ${}^{3}J({}^{1}H\square{}^{1}H) = 2.6$ Hz, 2H, C₅H₄), 0.27 (s, ${}^{2}J({}^{1}H\square{}^{29}Si) = 6.8$ Hz, 6H, Osi*Me*₃O). ${}^{13}C{{}^{1}H}$ NMR (75.5 MHz, C₆D₆, 297K) δ : 109.9 (s, *i*-C₅H₄), 102.6 (s, C₅H₄), 99.8 (s, C₅H₄), 96.6 (s, *i*-C₇H₆), 91.0 (s, C₇H₆), 88.8 (s, C₇H₆), 86.2 (s, C₇H₆), 1.8 (s, C₅H₄SiMe₂), 1.6 (s, C₇H₆SiMe₂), 1.03 (s, OSiMe₂O).

2.6. Synthesis of
$$[(\eta^7 - C_7 H_6)Ti(\eta^5 - C_5 H_4)](OSiMe_2)_3(SiMe_2)$$
 (4)

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A solution of 1,7-dichlorooctamethyltetrasiloxane (0.70 g, 2.0 mmol) in hexane (15 mL) was added dropwise to a suspension of $[(\eta^7 \Box C_7 H_6 Li)Ti(\eta^5 \Box C_5 H_4 Li)]$ pmdta (0.70 g, 1.8 mmol) in hexane (20 mL) at \Box 78 °C. The reaction mixture was stirred for 1 h at this temperature and then slowly warmed up to room temperature and stirred overnight. Insoluble LiCl was filtered off and the clear solution was vacuum dried to leave a blue oily residue. Pentane (1.5 mL) was added and the solution was stored at 30 °C for one day. 0.35 g (40%) of pure 4 deposited as a blue crystalline solid. Anal. Calcd (%) for C₂₀H₃₄O₃Si₄Ti (482.69): C 49.77, H 7.10, Found. C 49.39, H 7.18. ¹H NMR (300 MHz, C₆D₆, 297K) δ : 5.66 (pt, ³J(¹H \square ¹H) = 0.8 Hz, 1H, C₇H₆), 5.63 (pt, ${}^{3}J({}^{1}H \Box {}^{1}H) = 0.8$ Hz, 1H, C₇H₆), 5.43 (m, 2H, C₇H₆), 5.29 (m, 2H, C₇H₆), 5.11 (pt, ${}^{3}J({}^{1}H \Box {}^{1}H) = 2.6$ Hz, 2H, C₅H₄), 4.95 (pt, ${}^{3}J({}^{1}H\Box{}^{1}H) = 2.6$ Hz, 2H, C₅H₄), 0.25 (s, ${}^{2}J({}^{1}H\Box{}^{29}Si) = 6.8$ Hz, 6H, $C_5H_4SiMe_2$, 0.04 (s, ${}^{2}J({}^{1}H\Box {}^{29}Si) = 7.4$ Hz, 6H, $C_7H_6SiMe_2$), 0.0 (s, ${}^{2}J({}^{1}H\Box {}^{29}Si) = 7.4$ Hz, 6H, OSiMe₃O), 0.0 (s, ${}^{2}J({}^{1}H \square {}^{29}Si) = 6.8$ Hz, 6H, OSiMe₃O, ${}^{13}C\{{}^{1}H\}$ NMR (75.5 MHz, C₆D₆, 297K) δ : 110.5 (s, *i*-C₅H₄), 102.6 (s, C₅H₄), 99.8 (s, C₅H₄), 96.1 (s, *i*-C₇H₆), 90.7 (s, C₇H₆), 89.1 (s, C₇H₆), 86.4 (s, C₇H₆), 2.1 (s, ${}^{1}J({}^{13}C \Box {}^{29}Si) = 62.6$ Hz, C₅H₄SiMe₂), 2.0 (s, ${}^{1}J({}^{13}C \Box {}^{29}Si) = 61.2$ Hz. $C_7H_6SiMe_2$), 1.07 (s, ${}^{1}J({}^{13}C \Box {}^{29}Si) = 74.7$ Hz $OSiMe_2O$), 1.06 (s, ${}^{1}J({}^{13}C \Box {}^{29}Si) = 74.7$ Hz, OSiMe₂O). ²⁹Si NMR (300 MHz, C₆D₆, 297K) δ : 0.3 (C₅H₄SiMe₂), \Box 5.7 (C₇H₆SiMe₂), \Box 21.2 (s, OSiMe₂O), \Box 21.3 (s, OSiMe₂O).

2.7. Synthesis of KO(Me₂SiO)_nK

Toluene, hexamethylcyclotrisiloxane (5 g, 33% wt) and powdered KOH (5% wt) were mixed and refluxed for 24 h. After this time, the mixture was cooled to room temperature and filtered to remove insoluble materials. The solution was then dried in vacuum to leave a white crystalline solid (16.1 g, 70%) as the pure product. ¹H-NMR (300 MHz, CDCl₃, 297 K) δ : 0.07 (s, 85H, SiMe₂). IR (MIR): 916 cm-1 (v(Si \square O \square K), 1022-1088 cm⁻¹ (v_{as}(Si-O-Si)), 1261 (v_s(Si-Me₂), 800 cm⁻¹ (v_{as}(Si-Me₂), 2963 (v_{as}(C-H)), and 2905 (v_s(C-H)). Based on ¹H-NMR signal ratios, the number of repeating Me₂SiO units is n = 14.

2.8. Synthesis of Me₄NO(Me₂SiO)_nNMe₄

In a reaction flask 1 mL of an aqueous solution of TMAH was mixed with 5 mL of benzene. The mixture was refluxed for 1 h followed by vacuum distillation until the appearance of a white product. Then, D₄ (4.76 g) was added and the mixture left to stir for 24 h at room temperature. In the next step, 5 mL of benzene were added and the reaction mixture was refluxed for 1 h. The benzene was distilled under vacuum ($p = 10^{-2}$ mbar) to remove the water azeotrope thus formed. The addition of benzene, reflux and evaporation was repeated twice more. Finally, the product was filtered and distilled under vacuum to remove the volatile fractions. The ⁻¹H NMR spectrum of tetramethylammonium siloxanolate showed peaks corresponding to the Me₄N⁺ end group protons at 2.92 ppm (24H) and to the dimethylsiloxane units at 0.37 ppm (364H). In the FTIR spectrum of the initiator, the presence of the dimethylsiloxane units was evidenced by the strong absorption bands at 1020-1092 cm⁻¹ v_{as}(Si-O-Si), 1261 v_s(Si-CH₃) and 798 cm⁻¹ v_{as}(SiMe₃), 2963 v_{as}(C-H from SiMe₃), 2905 v_s(C-H from SiMe₃). The presence of the shoulder at 3110 cm⁻¹ and of the sharp band at 1412 cm⁻¹ indicates the presence of the Me₄N⁺ groups. The number average (n) of the Me₂SiO repeating unit in tetramethylammonium siloxanolate Me₄NO[Me₂SiO]₆₀Me₄N was determined on the basis of the ¹H NMR signal ratio.

2.9. Homopolymerization of **2** with potassium siloxanolate

A solution of KO(Me₂SiO)₁₄K (0.021 g, 0.02 mmol, 13 mol%) in THF (10 mL) was added to a solution of **2** (0.050 g 0.15 mmol) in THF (10 mL) and the mixture was stirred while increasing the temperature. Near 100 °C, we observed a color change from blue to light-green, which changed again to dark green and to brown within 30 min. The mixture was stirred for 1.5 h at 100 °C and then cooled to room temperature, whereby the color of the solution turned again to green. The reaction was then quenched with few drops of Me₃SiCl and stirred for another 15 min. Filtration and removal of the solvent under high vacuum afforded a blue-green solid residue. The latter was analyzed by mass spectrometry without further purification. MS (EI, 70 eV, m/z up to 2000): m/z 334.1 {[(η^7 -C₇H₆)Ti(η^5 -C₅H₄)](OSiMe₂)(SiMe₂)}⁺, 1461.4 {[(η^7 -C₇H₆SiMe₂)Ti(η^5 -C₅H₄SiMe₂O)]

 $(SiMe_3)(OSiMe_2)_{13}(OSiMe_3)\}^+$,

 $(\Box^{5}\Box C_{5}H_{4}SiMe_{2}O)]_{2}(SiMe_{3})(OSiMe_{2})_{12}-(OSiMe_{3})\}^{+}.$

2.10. Homopolymerization of 3 with potassium siloxanolate

A solution of KO(Me₂SiO)₁₄K (0.013 g, 0.013 mmol, 11 mol%) in THF (10 mL) was added to a solution of **3** (0.048 g 0.12 mmol) in THF (10 mL) and the mixture was stirred while increasing the temperature. At about 70 °C, we observed a color change from blue to blue-green. The solution was heated up to 100 °C and stirred for 24h. After cooling to room temperature, the reaction mixture was quenched with few drops of Me₃SiCl and stirring was continued for another 1 h. Filtration and removal of the solvent under high vacuum afforded a green solid residue. The latter was analyzed by mass spectrometry without further purification. MS (EI, 70 eV, m/z up to 2000): m/z 408.0 {[($\eta^7 - C_7H_6$)Ti($\eta^5 - C_5H_4$)](OSiMe₂)₂(SiMe₂)]⁺, 1097.3 and 1245.2.

2.11. Homopolymerization of 4 with potassium siloxanolate

A solution of KO(Me₂SiO)₁₄K (0.011 g, 0.010 mmol, 10.5 mol%) in THF (10 mL) was added to a solution of **4** (0.049 g 0.10 mmol) in THF (10 mL) and the mixture was heated up to 100 °C. No relevant color change was observed when the solution reached this temperature. Stirring was continued at 100 °C for 24 h followed by cooling to room temperature and quenching with Me₃SiCl (six drops). At this time, the blue color switched to green. Filtration and removal of the solvent under high vacuum afforded a green solid residue. The latter was analyzed by mass spectrometry without further purification. MS (EI, 70 eV, m/z up to 2000): m/z 482.1 {[(η^7 -C₇H₆)Ti(η^5 -C₃H₄)](OSiMe₂)₃(SiMe₂)}⁺, 645.2 {[($\Box^7 \Box C_7 H_6 SiMe_2)Ti(\Box^5 \Box C_5 H_4(SiMe_2O)_3)](SiMe_3)(OSiMe_3)}^+.$

2.12. Homopolymerization of 2 with tetramethylammonium siloxanolate

A 50 mL Schlenk flask containing toluene (10 mL), 2 (0.043 g, 0.130 mmol), and $Me_4NO(Me_2SiO)_{60}Me_4N$ (0.06 g, 0.013 mmol, 10 mol%) was heated at 110 °C for one day. After this time, the solution was cooled to room temperature and DMSO (two drops) was added with stirring. The mixture was then heated to 120 °C and maintained at this temperature over the weekend. After cooling again to room temperature and quenching with hexamethyldisiloxane (seven drops), the mixture was heated at 140 °C for two hours followed by removal of all volatiles under vacuum. The remaining blue solid residue was dried and analyzed by mass spectrometry without further purification. MS (EI, 70 eV, m/z up to 2000): m/z 408.0 {[$(\eta^7 - C_7 H_6)Ti(\eta^5 C_{5}H_{4}$](OSiMe₂)₂(SiMe₂)⁺, 482.1 {[($\eta^{7}-C_{7}H_{6}$)Ti($\eta^{5}-C_{5}H_{4}$)](OSiMe₂)₃ (SiMe₂)⁺, 1075.2 {[($\eta^{7}-C_{7}H_{6}$)Ti($\eta^{5}-C_{5}H_{4}$)](OSiMe₂)⁺, 1075.2 {[($\eta^{7}-C_{7}H_{6}$)Ti($\eta^{5}-C_{7}H_{6}$)](OSiMe₂)⁺, 1075.2 {[($\eta^{7}-C_{7}H_{6}$)Ti($\eta^{5}-C_{7}H_{6}$)](OSiMe₂)](OSiMe₂)⁺, 1075.2 {[($\eta^{7}-C_{7}H_{6})$](OSiMe₂)]($\{[(\Box^7 \Box C_7 H_6 SiMe_2)Ti(\Box^5 \Box C_5 H_4 SiMe_2 O)]_3\}$ C_7H_6)Ti(η^5 - C_5H_4)](OSiMe₂)₁₁(SiMe₂)}⁺, 1741.3 {[($\Box^7 \Box C_7 H_6 SiMe_2$)Ti- ($\Box^5 \Box C_5 H_4 SiMe_2O$)]₂(SiMe₃)- $(SiMe_3)(OSiMe_2)_8[OSiMe_3]\}^+$, 1911.4 $(OSiMe_2)_{15}[OSiMe_3]\}^+$.

2.13. Homopolymerization of 2 with Purolite CT-175

In a reaction flask, **2** (0.034 g, 0.1 mmol), Purolite CT-175 (0.019 g, 2.5 w%) and toluene (5 mL) were mixed. The reaction mixture was heated to 80 °C and maintained at this temperature with stirring for 24 h. The next day, Me₃SiCl (six drops) was added to the blue solution, which did not induce a color change. After 6 h stirring at room temperature, the reaction was stopped by filtering off the catalyst, and the solvent was evaporated under high vacuum to leave a blue solid residue that was analyzed by mass spectrometry without further purification. MS (EI, 70 eV, m/z up to 2000): m/z 334.1 {[(η^7 -C₇H₆)Ti(η^5 -C₅H₄)](OSiMe₂)(SiMe₂)}⁺, 408.1{[(η^7 -C₇H₆)Ti(η^5 -C₅H₄)](OSiMe₂)₂-(SiMe₂)}⁺, 424.1{[(η^7 -C₇H₆)SiMe₂OSiMe₃)Ti(\square^5 -C₅H₄SiMe₂OH)]⁺, 482.1{[(η^7 -C₇H₆)Ti(η^5 -C₅H₄)](OSiMe₂)]⁺, 630.2 {[(η^7 -C₇H₆)Ti(η^5 -C₅H₄)](OSiMe₂)]⁺, 644.2 {[(\square^7 -C₇H₆SiMe₂OSiMe₃)Ti(\square^5 -C₅H₄SiMe₂ON]]⁺.

2.14. Homopolymerization of 2 with n-BuLi

To a solution of **2** (0.048 g, 0.075 mmol) in toluene (10 mL) seven drops of *n*-BuLi were added. We observed an immediate color change from blue to light-green. The mixture was stirred for 1 h and about six drops of Me₃SiCl were added to quench the reaction mixture, which turned dark-green. Filtration and removing the solvent under vacuum gave a viscous green oily residue. The latter was analyzed by mass spectrometry without further purification. MS (EI, 70 eV, m/z up to 2000): m/z 408.0 {[(η^7 -C₇H₆)Ti(η^5 -C₅H₄)](OSiMe₂)₂(SiMe₂)]⁺, 464.2 {[($\Box^7 \Box C_7H_6SiMe_2nBu$)Ti($\Box^5 \Box C_5H_4SiMe_2OSiMe_3$)]⁺, 482.1 {[η^7 -C₇H₆)Ti(η^5 -C₅H₄)](OSiMe₂)₂(SiMe₂)]⁺, 1204.3 {[($\Box^7 \Box C_7H_6SiMe_2$)Ti($\Box^5 \Box C_5H_4SiMe_2$ O)]₄(*n*Bu)(OSiMe₂)(SiMe₃)]⁺.

2.15. Homopolymerization of 3 with n-BuLi

To a solution of **3** (0.044 g, 0.11 mmol) in THF (10 mL) six drops of *n*-BuLi were added. We observed an immediate color change from blue to blue-green. The mixture was stirred for 4 h and quenched with Me₃SiCl (six drops), whereby the solution turned green. Filtration and removing the solvent under vacuum gave a viscous green oily residue. The latter was analyzed by mass spectrometry without further purification. MS (EI, 70 eV, m/z up to 2000): m/z 482.1 {[η^7 -C₇H₆)Ti(η^5 -C₅H₄)](OSiMe₂)₂(SiMe₂)]⁺,538.2

$$\{ [(\Box^7 \Box C_7 H_6 SiMe_2 nBu)Ti(\Box^5 \Box C_5 H_4 (SiMe_2 O)_2 SiMe_3)] \}^+, 1163.3$$

$$\{ [(\Box^7 \Box C_7 H_6 SiMe_2)Ti-(\Box^5 \Box C_5 H_4 (OSiMe_2)_2)]_2 (nBu)(OSiMe_2)_5 (SiMe_3) \}^+, 1296.3$$

$$\{ [(\Box^7 \Box C_7 H_6 SiMe_2)Ti-(\Box^5 \Box C_5 H_4 (OSiMe_2)_2)]_3 (nBu)(OSiMe_2) (SiMe_3) \}^+.$$

2.16. Homopolymerization of 4 with nBuLi

To a solution of 4 (0.046 g, 0.10 mmol) in THF (10 mL), six drops of *n*-BuLi were added. We observed an immediate color change from blue to green. The mixture was stirred for 24 h, whereby the solution turned brown. Addition of Me₃SiCl after cooling, filtration and evaporation of the solvent under vacuum afforded a green solid residue. The latter was analyzed by mass spectrometry purification. without further MS (EI, 70 eV, 2000): 612.2 m/z up to m/z

 $\{[(\Box^7 \Box C_7 H_6 SiMe_2 nBu)Ti(\Box^5 \Box C_5 H_4 (SiMe_2 O)_3 SiMe_3)]\}^+, \qquad 758.3\{[(\Box^7 \Box C_7 H_6 SiMe_2)Ti-(\Box^5 \Box C_5 H_4 (OSiMe_2)_3)](nBu)(OSiMe_2)_2 (SiMe_3)\}^+.$

2.17. Copolymerization of 2 and D_3 with nBuLi

A 10 mL THF solution of **2** (0.041 g, 0.12 mmol) was gradually mixed with *n*-BuLi (six drops) at room temperature. The color of the solution changed from blue to green. After stirring for about 2 h, 10 mL of a THF solution of D₃ (0.049 g, 0.22 mmol) was added and the reaction mixture was stirred overnight. The next day, the solution looked brown but immediately turned green after addition of Me₃SiCl (six drops). Stirring was continued for another 2 h and after this time, the solution was concentrated to one quarter. Hexane (20 mL) was added and the solution was filtered to remove insoluble solids. Evaporation of the solvent under vacuum left a slightly viscous green oily residue. The latter was analyzed by mass spectrometry without further purification. MS (EI, 70 eV, m/z up to 2000): m/z 408.1 {[(η^7 -C₇H₆)Ti(η^5 -C₅H₄)](OSiMe₂)₂(SiMe₂)}⁺, 464.2 {[(\Box^7 -C₇H₆SiMe₂nBu)Ti(\Box^5 -C₅H₄SiMe₂OSiMe₃)]}⁺, 518.2 [Me₂SiO]₇⁺, 592.3 [Me₂SiO]₈⁺.

2.18. Copolymerization of 3 and D_3 with n-BuLi

A 10 mL THF solution of **3** (0.043 g, 0.11 mmol) was gradually mixed with *n*BuLi (six drops) at room temperature. A color change from blue to green was observed. After stirring for about 2 h, 10 mL of a THF solution of D₃ (0.041 g, 0.18 mmol) were added, and the reaction mixture was stirred overnight. The next day, the solution was green. Six drops of Me₃SiCl were added and the reaction mixture stirred for another 2 h, followed by filtration and removal of the solvent under vacuum. A blue-green solid residue remained in the flask and was analyzed by mass spectrometry without further purification. MS (EI, 70 eV, m/z up to 2000): m/z 482.1 {[η^7 -C₇H₆)Ti(η^5 -C₅H₄)](OSiMe₂)₂(SiMe₂)}⁺, 464.1 {[($\Box^7 \Box C_7H_6SiMe_2nBu$)Ti- ($\Box^5 \Box C_5H_4SiMe_2OSiMe_3$)]}⁺, 538.2 {[($\Box^7 \Box C_7H_6SiMe_2nBu$)Ti($\Box^5 \Box C_5H_4(SiMe_2O)_2$ -SiMe₃)]}⁺, 426.1 {Me₂(nBu)Si(OSiMe₂)₃OSiMe₃}⁺, 500.1 { $Me_2(nBu)Si(OSiMe_2)_4OSiMe_3$ }⁺, 574.1{ $Me_2(nBu)Si(OSiMe_2)_5OSiMe_3$ }⁺, 648.2 { $Me_2(nBu)Si(OSiMe_2)_6OSiMe_3$ }⁺.

2.19. Copolymerization of 4 and D_3 with n-BuLi

A 10 mL toluene solution of **4** (0.036 g, 0.075 mmol) was gradually mixed with *n*-BuLi (six drops) at room temperature. A color change from blue to green was observed. After stirring for about 2 h, 10 mL of a toluene solution of D₃ (0.039 g, 0.17 mmol) were added and the reaction stirred overnight. The next day, the solution appeared brown and immediately turned green upon addition of Me₃SiCl (six drops). The reaction mixture was stirred for another 2 h followed by evaporation of the solvent under vacuum. A viscous green oily residue was obtained and analyzed by mass spectrometry without further purification. MS (EI, 70 eV, m/z up to 2000): m/z 538.2 {[($\Box^7 \Box C_7H_6SiMe_2nBu$)Ti($\Box^5 \Box C_5H_4(SiMe_2O)_2SiMe_3$)]}⁺, 206.1 $\Box 652.2 Me_2(nBu)Si(OSiMe_2)_zOH$ (z = 1 \Box 7).

3. Results and Discussion

3.1. Synthesis and Structural Characterization of the Siloxa[n]troticenophanes 2 4

The siloxane-bridged [*n*]troticenophanes $2\Box 4$ were synthesized starting from the previously reported dilithiated troticene [$(\eta^7-C_7H_6Li)Ti(\eta^5-C_5H_4Li)$]·pmdta (1) [41e]. Thus, salt metathesis reactions between 1 and a slight excess of the corresponding siloxane dichloride, 1,3dichlorotetramethyldisiloxane, 1,5-dichlorohexamethyltrisiloxane and 1,7dichlorooctamethyltetrasiloxane, in hexane at $\Box 78$ °C afforded the siloxa[3]-, siloxa[5]- and siloxa[7]troticenophanes $2\Box 4$, respectively (Scheme 1). Compounds $2\Box 4$ were isolated as blue crystalline solid in yields of 47% (2), 49% (3) and 40% (4). They are highly soluble in common organic solvents and are air- and moisture-sensitive. However, they can be stored in a glove box atmosphere of argon and used for months without any risk of decomposition.



Scheme 1. Synthesis of the siloxane-bridged [n] troticenophanes $2\Box 4$.

The siloxa[n] troticenophanes were fully characterized by NMR spectroscopy and elemental analysis. As expected, the ¹H NMR spectra of $2 \Box 4$ displayed two pseudo triplets in the range $\delta =$ 4.82 \Box 5.11 ppm for the hydrogen atoms of the five-membered rings. The C₇H₆ protons appeared as two multiplets (ratio 2:4) in the spectrum of 2, whereas four multiplets (ratio 1:1:2:2) were observed in the spectra of **3** and **4**. These splitting patterns are in accordance with substitution at both the Cp and Cht rings. The methyl groups of the siloxane units in $2\Box 4$ gave rise to two, three or four singlet signals at high field (between 0.00 and 0.28 ppm) depending on the number of the bridging elements. The ²⁹Si NMR spectrum of **2** showed two singlets at $\delta = 4.1$ and $\Box 5.6$ ppm, which are assigned to the Cp- and Cht-bound silicon atoms, respectively. The former is shifted to lower field in comparison with the signal reported for tetramethyldisiloxane-bridged ferrocenophane ($\delta = 1.1$ ppm) and with those reported for disiloxane-bis(1-indenyl)-ansa-ferrocene ($\delta = 1.3$ and 1.6 ppm) [27,32]. Both resonances are also at lower field than that of $[Me_2SiO]_3$ ($\delta = \Box 9.0$ ppm).⁷ The ²⁹Si NMR spectra of compounds 3 and 4 display respectively three or four singlets at $\delta = 1.7$, $\Box 5.6$, $\Box 21.4$ (3) and 0.3, \Box 5.7, \Box 21.2, \Box 21.3 ppm (4). The signals at $\delta = \Box$ 5.6 and \Box 5.7 are very similar to the value $\delta = \Box$ 5.6 found for 2 and are therefore assigned to the Cht-bound silicon atom. The signals at $\delta = 1.7$ and 0.3 ppm in **3** and **4** correspond to the Cp-bound silicon atom. They appeared at higher field with respect to the signal in 2, but are slightly shifted to low field compared with those reported for hexamethyltrisiloxane- and octamethyltetrasiloxane-bridged ferrocenophanes ($\delta = \Box 0.5$ and 0.0 ppm).²⁷ The signals of the Cht-bound ($\delta = \mathbb{2}5.6$ (2), $\mathbb{2}5.6(3)$ and $\mathbb{2}5.7(4)$ ppm) and of the O $\mathbb{2}Si$ silicon atoms ($\delta = \Box 21.4$ (3), $\Box 21.2$ and $\Box 21.3$ (4) ppm) in the troticenophanes are very similar and

only marginally affected by the ring expansion, in contrast to the signals of the Cp-bound silicon atoms.

The structures of compounds $2\Box 4$ were also confirmed by X-ray diffraction analysis of single crystals grown from saturated solutions of pentane at $\Box 30$ °C. Compound 3 crystallized with two independent molecules, which display very similar structural parameters except for slight conformational differences of the siloxane bridges; a least-squares fit of all other non-H atoms gave an r.m.s. deviation of 0.10 Å. The molecular structures of 2 and of one molecule of 3 are shown in Figures 1 and 2; selected bond lengths and angles are summarized in Table 2. The molecular structure of 4 suffered from severe disorder of the siloxane units and will not be discussed here. A Figure of its structure is presented in the Supporting Information (Figure S1).



Fig. 1. ORTEP diagram of 2 with thermal displacement parameters drawn at the 50% probability level.



Fig. 2. ORTEP diagram of one molecule of 3 with thermal displacement parameters drawn at the 50% probability level.

Table 2

Selected Bond Lengths [Å] and Angles [°]	for compounds 2 and 3.
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	2		3
$Ti \square C_{Cht}$	2.180(2) 2.212(2)	$Ti \square C_{Cht}$	2.1956(14) 2.2320(14)
$Ti \square C_{Cp}$	2.306(2) 2.326(2)	$Ti \square C_{Cp}$	2.3121(13) 2.3497(13)
$Ti \square Cht_{ct}$	1.476	$Ti \square Cht_{ct}$	1.482, 1.488
$Ti\squareCp_{ct}$	1.983	$Ti \square Cp_{ct}$	1.990, 1.998
Si1 🗆 O1	1.6424(17)	Si1 01	1.6348(10), 1.6350(10)
Si2□O1	1.6397(17)	Si2 01	1.6282(10), 1.6335(10)
Si1□C1	1.858(2)	Si2 O2	1.6328(10), 1.6219(10)
Si2□C8	1.860(2)	Si3 02	1.6328(10), 1.6330(10)
Si1 01 Si2	135.93(10)	Si1□C1	1.8650(14), 1.8695(13)
		Si3□C8	1.8549(14), 1.8638(14)
		Si1 O1 Si2	146.27(7), 145.85(7)

Si2 O2 Si3 151.64(7), 156.03(7)

Table 3

Comparison of Selected Angles in Siloxane-Bridged [*n*]Troticenophanes and Siloxane-Bridged [*n*]Ferrocenophanes.^a

ansa complex	α (deg)	$\beta_{\rm cht/cp}$ (deg)	$\beta_{\rm cp}$ (deg)	δ (deg)
$[(\eta^7 - C_7 H_6)Ti(\eta^5 - C_5 H_4)](OSiMe_2)(SiMe_2)$ (2)	4.8	11.9	1.8	176.2
$[(\eta^7 - C_7 H_6)Ti(\eta^5 - C_5 H_4)](OSiMe_2)_2(SiMe_2) (3)$	4.9/3.7	1.5/3.0	4.3/2.0	174.3/176.3
$[(\eta^5 - C_5 H_4)Fe(\eta^5 - C_5 H_4)](OSiMe_2)(SiMe_2)^{27}$	≤2.5	average 4.1(7)/4.5(values: (8)/3.3(8)	
$[(\eta^{5}-C_{5}H_{4})Fe(\eta^{5}-C_{5}H_{4})](OSiMe_{2})_{2}(SiMe_{2})^{27}$	< 1.5	average 1.5(3)/	values: 1.7(2)	

^{a]} Definition of the angles: α is the dihedral angle between the Cht and Cp rings; β indicates the angle $Cht_{ct}/Cp_{ct}\square C_{ipso}\square Si$; δ denotes the angle $Cht_{ct}\square Ti\square Cp_{ct}$.

As a result of a stronger metal-ligand interaction with the seven-membered ring in group 4 mixed Cht \Box Cp sandwich complexes [41a], the Ti \Box C₇H₆ bonds in 2 (2.180(2) \Box 2.212(2) Å) and 3 (2.1956(14) \Box 2.2320(14) Å) are shorter than the Ti \Box C₅H₄ bonds (2.306(2) \Box 2.326(2) (2), 2.3121(13) \Box 2.3497(13) (3)). Both compounds exhibit some degree of strain, as indicated by the interplanar angles α between the two rings (4.8° for 2; 4.9/3.7 for 3) and the distortion angles δ of 176.2° (2) and 174.3/176.3° (3). In the family of *ansa*-troticenes reported so far, the strain in 2 and 3 is significantly less pronounced than observed in analogous compounds with only one bridging element, as in sila-, germa, and stanna[1]troticenophanes ($\alpha = 24.1^\circ$, 22.9° and 16.3(3)°; $\delta = 160.5^\circ$, 161.0°, 166.6°, respectively) [41b,d,g,h]. However, 2 and 3 display a slightly greater deviation from parallel Cht and Cp rings than does disila[2]troticenophane, with a (Me₂Si)₂ bridge ($\alpha = 4.2^\circ$, $\delta =$ 178.5°), Sn \Box S \Box Sn ($\alpha = 2.7^\circ$, $\delta = 177.4^\circ$), and Si \Box C \Box Si ($\alpha = 0.7^\circ$, $\delta = 179.5^\circ$) bridges [41d]. Comparison of the structural parameters of 2 and 3 with those reported for analogous siloxanebridged ferrocenophanes [27] demonstrate a higher degree of strain for the troticenophanes (see Table

3). This is particularly manifested by the value of the angle (β) between the plane of the rings and the Si C bond. Indeed, the β_{cht} value in **2** ($\beta_{cht} = 11.9^{\circ}$) is greater than that found in tetramethyldisiloxane-bridged ferrocenophane (av. $\beta = 4.1(7)/4.5(8)/3.3(8)^{\circ}$), while the β_{cht} and β_{cp} values in **3** ($\beta_{cp} = 4.3/2.0^{\circ}$ (av. 3.58), $\beta_{cht} = 1.5/3.0^{\circ}$ (av 2.18°)) are greater than those measured in hexamethyltrisiloxane-bridged ferrocenophanes (av. $\beta = 1.5(2)/1.7(2)^{\circ}$). The average Si–O distances in **2** (1.643 Å) and **3** (1.632 Å) are comparable to the value found in [Ph₂SiO]₃ (1.64 Å) [44], but slightly longer than those found in disiloxa[3]- and trisiloxa[5]ferrocenophanes (1.613/1.622 and 1.620/1.612 Å) [27]. The Si \Box O \Box Si bond angles of 135.8(9)° in **2** and between 146.27(7) and 156.03(7)° in **3** are greater than the values 125.05(5)° and 131.8(8)° reported for [Me₂SiO]₃ [45] and [Ph₂SiO]₃ [44], but lie below those measured for the corresponding ferrocenophanes (143.1(7)° and 155.4(2) \Box 165.7(2)°) [27].

3.2. Ring-Opening Reactions of the Siloxa[n]troticenophanes 2 4

Although compounds $2 \Box 4$ are relatively unstrained in comparison with related [1]troticenophanes, we were interested in studying their ability to ring-open and/or polymerize by breaking the Si \Box O bond in the presence of cationic or anionic initiators. ROP was used as the method of choice to attempt these reactions, and the conditions were based on those generally used for the polymerization of cyclic siloxanes. The thermal behavior of the compounds was firstly studied by DSC followed by the investigations of their homo- and copolymerization in solution.

The DSC thermogram of $2\Box 4$, over 200 °C (10 K/min) under nitrogen atmosphere (see Supporting Information Figures S11 \Box S13), showed a melt endotherm with a maximum at 116.4 °C (2), 72.0 °C (3) and 106.8 °C (4). The melting temperature followed the order 2 > 4 > 3 and is associated with melting energies of $\Delta E = \Box 15.9$ (2), $\Box 22.1$ (3) and $\Box 25.9$ kJ/mol (4). No exotherm was observed in the thermograms, indicating that the compounds do not undergo ring-opening reactions when heated at elevated temperature in the absence of initiator. This behavior is similar to that shown by siloxane-briged [*n*]ferrocenophanes, which did not polymerize when heated in the melt at 200 °C [27]. Heating compound **2** to 400 °C showed thermal resistance up to 350 °C, and beyond

that, decomposition of the compound occurred. In addition to the onset at 116.4 $^{\circ}$ C observed in the DSC spectrum of **2**, there is another endothermic peak at 83.7 $^{\circ}$ C, which should probably be assigned to a solid state transition, and thus compound **2** seems to display different polymorphs.

In view of the thermal stability of $2 \Box 4$ in the melt in the absence of an initiator, we decided to perform the reactions in solution with various catalysts (*n*-BuLi, potassium and tetramethylammonium siloxanolate, Purolite CT175). Therefore, compound 2 was treated with 10 mol% of potassium siloxanolate in THF at 100 °C and the reaction was quenched with Me₃SiCl. A color change from blue to green was observed and the material obtained after filtration and evaporation of the solvent was analyzed by mass spectrometry. The EI-MS spectrum of the green residue showed a peak at m/z = 334.1 that can be assigned to the disiloxane-bridged troticene [2]⁺. Other peaks were observed at m/z = 1461.4 and 1721.5 and are assigned to the formation of the oligomers $[5]^+$ and $[6]^+$ that contain one or two troticenyl units (Scheme 2). Unfortunately, the EI-MS spectrometer was calibrated only up to m/z = 2000, so that formation of higher molecular weight oligomers or polymers could not be observed. The same reactions were performed between the larger cycloctroticenylsiloxanes 3 and 4, and KO(SiMe₂O)₁₄K. As observed with compound 2 (vide supra), the color of the mixture turned from blue to green at about 70 °C during heating or after quenching the reaction with Me₃SiCl. The EI-MS spectra of both crude materials displayed peaks of the monomers $[3]^+$ at m/z = 408.0 and $[4]^+$ at m/z = 482.1 together with signals at m/z = 1097.3 and 1245.2, which could not be assigned, and at m/z = 645.2 and 720.2, which correspond to the ringopened products $[7]^+$ and $[8]^+$.



Scheme 2. Reaction of $2\Box 4$ with potassium or ammonium siloxanolate as initiator.

In another approach, compound **2** was polymerized in the presence of ammonium siloxanolate, $Me_4NO(SiMe_2O)_{60}NMe_4$ (10 mol%) as initiator and DMSO as promoter. The reaction was heated at 120 °C and quenched with hexamethyldisiloxane. All volatiles were removed at 140 °C and analysis of the remaining blue residue by mass spectrometry revealed peaks at m/z = 408.0 and 482.1, which can be assigned to the monomers [**3**]⁺ and [**4**]⁺ and indicate a redistribution reaction with expansion of the ring. Interestingly, the ring expands continuously up to eleven repeated SiMe₂O units with formation of the macrocyclic siloxane-bridged troticenophane **9**, from which the molecular ion [**9**]⁺ was detected at m/z = 1075.2. Furthermore, peaks at m/z = 1741.3 and 1911.4 were observed and assigned to the oligo(troticenylsiloxanes) [**10**]⁺ and [**11**]⁺, respectively, in which two or three troticenyl fragments are incorporated in the oligomer chain (Scheme 2). When the polymerization of **2** was attempted using an acidic initiator, Purolite CT-175, a blue residue was also obtained, which was analyzed by mass spectrometry. The EI-MS spectrum showed, together with the peaks of [**3**]⁺ and [**4**]⁺, further expansion of the ring with a peak at m/z = 630.2 that corresponds to the macrocycle [**12**]⁺. Ring-opened products were detected at m/z = 351.1 and 644.2 and assigned to



Scheme 3. Reaction of 2 with Purolite CT-175 as initiator.

A similar redistribution reaction was observed when the polymerizations were carried out using *n*-BuLi as initiator. Indeed, treatment of $2\Box 4$ with *n*-BuLi (526 drops) in toluene or THF at room temperature for 1-24 h followed by addition of Me₃SiCl afforded in the case of 2 and 3 a viscous green oily and for 4 a green solid residue. Analysis of the crude product by mass spectrometry revealed redistribution with formation of oligo(troticenylsiloxanes), ring-opened and ring-expanded troticenophanes. Notably, the EI-MS spectrum of the crude product from 2/n-BuLi showed besides the peak of the molecular ion $[2]^+$ at m/z = 334.0 peaks of the ring-expanded troticenophanes at m/z 408.0 and 482.1. In addition, the ring-opened troticenophane $[20]^+$ and the oligo(troticenylsiloxanes) $[15]^+$ and $[16]^+$ were detected at m/z = 464.2, 1204 and 1538.4, respectively. Similarly, the EI-MS spectrum of the crude product from 3/n-BuLi exhibits signals of the ring-expanded troticenophane $[4]^+$ at m/z = 482.1. The ring-opened troticenophane $[21]^+$ and the oligo(troticenylsiloxanes) $[17]^+$ and $[18]^+$ incorporating two and three troticenyl units were detected at m/z = 538.2, 1163.3 and 1296.3, respectively. Finally, the EI-MS spectrum of the crude product from 4/n-BuLi showed a peak at m/z = 612.2 assigned to the ring-opened troticenophanes $[22]^+$. In contrast, no peak corresponding to ring expansion was observed. The oligotrotic envision $[19]^+$ was detected in the mixture, with the molecular ion appearing at m/z = 758.3 (Scheme 4).



Scheme 4. Redistribution reaction of $2\Box 4$ with *n*BuLi as initiator.

The oligo(troticenylsiloxanes) and other ring-opened or ring-expanded products detected in the homopolymerization demonstrated the possibility of cleaving the Si \Box O bond in 2 \Box 4 with an appropriate initiator. In order to study their behavior in the presence of other monomeric siloxanes, we performed the copolymerization between 2 4 and the strained cyclotrisiloxane (Me₂SiO)₃. Cyclotrisiloxane is known to undergo ROP easily, induced either thermally or by an initiator, with formation of poly(dimethylsiloxane) [3,46]. Thus, the reaction of 2 with cyclotrisiloxane initiated by *n*-BuLi at room temperature gave, after quenching with Me₃SiCl, a viscous green oily residue. The EI-MS spectrum of the crude product showed evidence for ring expansion to 3 with a peak at m/z =408.1. As observed with the homopolymerization, a ring-opened product (m/z = 464.1) that corresponds to $[20]^+$ was detected in the mass spectrum, together with the oligo(siloxanes) $(Me_2SiO)_w^+$ (w = 7, m/z = 518.2; w = 8, m/z = 592.3). However, formation of oligo(troticenylsiloxanes) could not be evidenced by mass spectrometry. The treatment of a mixture of **3** and cyclotrisiloxane with n-BuLi/Me₃SiCl afforded a green solid residue. The EI-MS spectrum of the latter showed peaks at m/z = 482.1 as a result of ring expansion from 3 to 4. The ring-opened products $[20]^+$, $[21]^+$ and $[22]^+$ were detected at m/z = 464.1, 538.1 and 612.2, respectively, together with the mono- or poly(siloxanes) { $Me_2(nBu)Si(OSiMe_2)_vOSiMe_2$ }⁺ (y = 3, m/z = 426.1; y = 4, m/z = 500.1; x = 5, m/z = 574.1; y = 6, m/z = 648.2). In the case of 4 and cyclotrisiloxane, treatment with n-BuLi/Me₃SiCl afforded a viscous green oily residue, for which the EI-MS spectrum exhibited peaks for $[21]^+$ and $[22]^+$ and for the monoand poly(siloxanes) $Me_2(nBu)Si(OSiMe_2)_zOH (z = 1 \Box 7, m/z = 206.1 \Box 652.2)$ (Scheme 5)



Scheme 5. Copolymerization reactions of $2\Box 4$ with cyclotrisiloxane.

4.1. Conclusion

Siloxane-bridged [*n*]troticenophanes ($2\Box 4$) with one to three Si–O–Si units in the ring were synthesized and fully characterized. The dihedral angles δ between the C₅H₄ and the C₇H₆ in **2** and **3** showed that the structures display some degree of strain, which is slightly higher than those found in analogous siloxane-bridged [*n*]ferrocenophanes. Investigation of their thermal behaviour by differential scanning calorimetry (DSC) revealed melting temperatures in the order 2 > 4 > 3 and high resistance (over 200 °C) to ring-opening polymerization (ROP) with decomposition occuring e.g. for **1** around 350 °C. Ring-opening reactions using basic and acidic initiators such as potassium/ammonium siloxanolate or *n*-BuLi and Purolite CT175 led to redistribution reactions with formation of oligo(troticenylsiloxanes) incorporating one to four troticenyl moieties and of ring-opened and ring-expanded products, which were identified by electron ionisation mass spectrometry. Similar cleavage of the Si \Box O bond or ring expansion, and formation of oligo(siloxanes) containing terminal trimethylsilyl or hydroxyl groups were observed during our attemps to copolymerize $2\Box 4$ with hexamethylcyclotrisiloxane and *n*-BuLi as initiator. However, the reactions did not furnish oligo(troticenylsiloxanes). These results demonstrate that ring-opening oligomerization and redistribution processes occur when the siloxane-bridged [*n*]troticenophanes

 $2\Box 4$ are treated with an appropriate initiator using reaction conditions similar to those employed for the polymerization of cyclic siloxanes. Further investigations will focus on the optimization of the polymerization reactions with the goal of detecting, isolating and characterizing high molecular weight polytroticenylsiloxanes.

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Appendice A. Supplementary material

CCDC 944589 and CCDC 944590 contain the supplementary crystallographic data for compounds **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

Appendice B. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem

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Supporting Information

Siloxane-bridged [n]Troticenophanes: Syntheses, Structures and Ring Opening Reactions

Alain C. Tagne Kuate,^a Mihaela Alexandru,^b Matthias Freytag,^a Peter G. Jones,^a Carmen Racles,^b Maria Cazacu,^b and Matthias Tamm^a*

^aInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany

^b "Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41 A, Iasi 700487, Romania

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Figure S1. ORTEP diagram of 4 with thermal displacement parameters drawn at the 50% probability level. Disorder was removed for clarity.





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Figure S13. DSC spectrum of 4.