



# Siloxane-bridged [n]troticenophanes: Syntheses, structures and ring-opening reactions

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## ABSTRACT

Salt elimination reactions between dilithiotroticene  $[(\eta^7-C_7H_6Li)Ti(\eta^5-C_5H_4Li)] \cdot pmdta$  (**1**) ( $pmdta = N,N',N'',N'''$ -pentamethyldiethylenetriamine) and siloxane dichlorides  $ClMe_2Si-(OSiMe_2)_m-Cl$  ( $m = 1-3$ ) at low temperature allowed the synthesis and isolation of the siloxane-bridged [n]troticenophanes  $[(\eta^7-C_7H_6)Ti(\eta^5-C_5H_4)](OSiMe_2)_m(SiMe_2)$  (**2**,  $m = 1$ ; **3**,  $m = 2$ ; **4**,  $m = 3$ ) as blue crystalline solids in moderate yield. The compounds were characterized by  $^1H$ ,  $^{13}C$  and  $^{29}Si$  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**;  $4.9/3.7^\circ$  for **3**) and distortion ( $\delta = 176.2^\circ$  for **2**;  $174.3/176.3^\circ$  for **3**) angles between the two rings. The structure of **4** was severely disordered. Compounds **2-4** 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 **2-4** with basic initiators such as potassium siloxanolate, ammonium siloxanolate or *n*-BuLi and analysis of the product distribution by electron ionization mass spectrometry revealed the formation of oligotroticenyloxanes incorporating one or more troticeny units, ring-opened troticenes and ring-expanded troticenophanes  $[(\eta^7-C_7H_6)Ti(\eta^5-C_5H_4)](OSiMe_2)_r(SiMe_2)$  ( $r > m$ ). Similar cleavage and extension of the ring were observed by treatment of **2-4** with the acidic initiator Purolite CT-175, and ring-opened troticenes having mixed terminal -OH and -SiMe<sub>3</sub> groups were detected. Attempts to copolymerize **2-4** and cyclotrisiloxane with *n*-BuLi afforded essentially the monomeric and polymeric siloxanes  $[Me_2SiO]_w$  ( $w = 7, 8$ ),  $Me_2(nBu)Si[OSiMe_2]_yOSiMe_2$  ( $y = 3-6$ ) and  $Me_2(n-Bu)Si[OSiMe_2]_zOH$  ( $z = 1-7$ ), together with the ring-opened and ring-expanded products mentioned above.

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## 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 [1–6].

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 silicon atom is replaced by a main group element (B, Sn, S, P, As) [7–11] or by a transition metal (Ti, Zr, Ni, Co) [11–14], have been synthesized and structurally characterized, but very few have been the subjects of polymerization studies. The boracyclotrisiloxane  $(PhBO)(Ph_2SiO)_2$  was reported to undergo ring–ring transformation reactions at elevated temperature in the presence of  $K[OSiMe_3]$  [7], and the polystannasiloxane  $[(tBuSnO)(Ph_2SiO)_2]_n$  was generated in the solid state by condensation of  $[Ph_2(OH)Si]_2O$  with  $tBu_2SnCl_2$  [8c].

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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 [15–22]. Relevant examples are the homo- and copolymers  $(\text{Me}_3\text{SiO})(\text{MeSi}(\text{CH}_2\text{CH}_2\text{Fc})\text{O})_n(\text{SiMe}_3)$  (**I**,  $n \sim 35$ ) and  $(\text{Me}_3\text{SiO})(\text{MeSiFcO})_n(\text{Me}_3\text{SiO})_m(\text{SiMe}_3)$  (**II**,  $n = 30\text{--}35\%$ ,  $m = 65\text{--}70\%$ , Fc = ferrocene), containing pendant ferrocenyl moieties, which were synthesized by hydrosilylation of ferrocenylvinylsilane with polysiloxanes containing terminal Si–H bonds [23]. The linear polyferrocenylsiloxanes **III–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**) [24–26]. ROP of siloxane-bridged  $[n]$ ferrocenophanes (**VI**) (**Chart 2**) was also attempted, but instead of polymerization, redistribution and skeletal cleavage reactions occurred [27].

Compounds of type **VI** are known for more than five decades [28–30] and belong to the family of the related *ansa*-ferrocenes  $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)](\text{ER}_x)_n$  (**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,  $\text{Fe}(\eta^5\text{-inden-1-yl-SiMe}_2)_2\text{O}$ , which was reported to copolymerize with octamethylcyclotetrasiloxane to afford a green material [32]. Other non-iron *ansa* complexes, for instance group 4 (Ti, Zr, Hf) [33–37] 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–Cp) sandwich complexes or on their incorporation into the chains of polymeric siloxanes. The only related work involving siloxanes and Cht–Cp sandwich units is the synthesis and structural elucidation of the disiloxane-bridged bitrovacene  $[(\eta^7\text{-C}_7\text{H}_7)\text{V}(\eta^5\text{-C}_5\text{H}_4)]_2(\text{Me}_2\text{SiO-SiMe}_2)$ , which aimed at studying the intermetallic communication between the two paramagnetic groups across the Si–O–Si bridge [39].

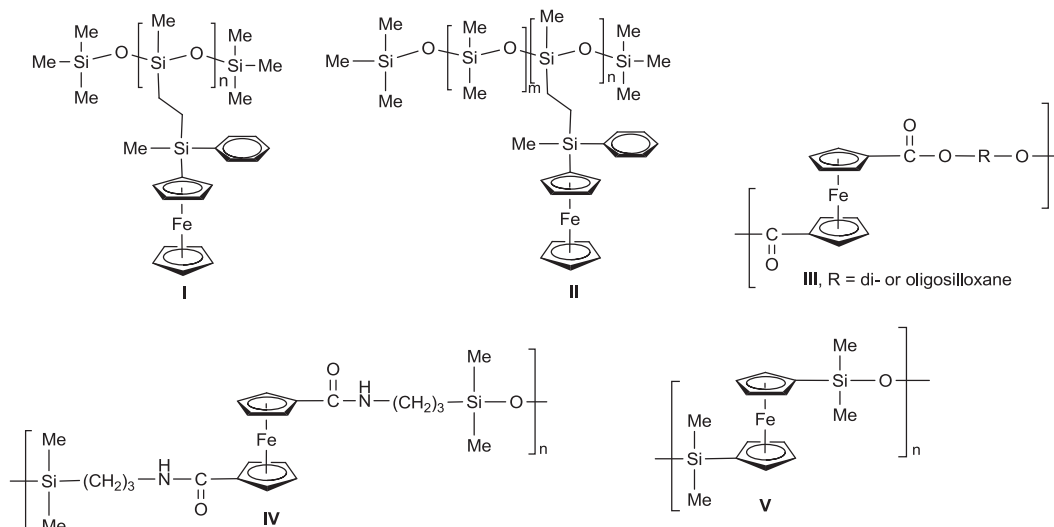
In the course of a systematic study of the functionalization of  $[(\eta^7\text{-C}_7\text{H}_7)\text{M}(\eta^5\text{-C}_5\text{H}_5)]$  ( $\text{M} = \text{Ti}$ , trovicene;  $\text{V}$ ; trovacene,  $\text{Cr}$ , trochrocene), we and other research groups recently reported the first examples of the *ansa*-Cht–Cp complexes  $[(\eta^7\text{-C}_7\text{H}_6)\text{M}(\eta^5\text{-C}_5\text{H}_4)](\text{ER}_x)_n$  (**VIII**,

**Chart 2**) with phosphorus, boron, silicon, germanium and tin in the bridge. These complexes were obtained by selective lithiation of trovicene, 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  $\text{Cl}_2(\text{ER}_x)_n$  reagent [40–42]. For the sila-, germa- and stanna[1]trovicenophanes, 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(trovicenylsilane), poly(trovicenylgermane) and poly(trovicenylstannane), respectively [41b,h]. Furthermore, poly(trovicenylstannane) of moderate molecular weight ( $M_w = 14113 \text{ g mol}^{-1}$ ) [41b] was synthesized by living anionic ROP of stanna[1]trovicenophane with *n*-BuLi as initiator, while transition-metal-catalyzed ROP of sila[1]trovicenophane and sila[1]trochrocenophane was achieved by reaction with Pt<sup>0</sup> at elevated temperature to give low-molecular-weight polymers ( $M_w = 1301$  and  $6400 \text{ g mol}^{-1}$ , respectively) [41f,42e]. In a continuation of our work on the ROP of *ansa*-trovicenes, we have synthesized and structurally characterized siloxane-bridged  $[n]$ trovicenophanes (**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 GloveBox 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 ( $\delta$ ) 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 analyzer. 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



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

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