

A planar silacyclobutane, 1,1-(*rac*-1,1'-bi-2-naphthoxy)-1-silacyclobutane and its unusual reaction with bis(1,5-cyclooctadiene)platinum(0)

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Abstract

The synthesis, characterization and X-ray crystal structure of 1,1-(*rac*-1,1'-bi-2-naphthoxy)-1-silacyclobutane (**1**) are reported and reveal an unusual planar conformation with a Si-βC distance of 2.302 (5) Å. Reaction of **1** with either stoichiometric or catalytic amounts of bis(1,5-cyclooctadiene)platinum(0) {Pt(cod)₂} gave 1,1'-bi-2-naphthol (BINOL), rather than the expected insertion products or polymer. A mechanism is proposed based on insertion of the Pt(cod) into **1** followed by hydride transfers via the Pt center to the 1,1'-bi-2-naphthoxy group. Anionic ring-opening polymerization of **1** is also reported and gave the poly(carbosilane) (**4**).

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1. Introduction

Organosilicon polymers such as polycarbosilane(s) (PCSs); polysilane(s) (PSs); polysilazane(s) (PSZs); and polycarbosilazanes (PCSZs) have been explored widely as effective precursors to ceramics, which in turn display excellent resistance to extreme thermal and mechanical environments [1]. The synthesis of PCSs has been achieved using two methods; hydrosilylation of unsaturated compounds [2], and ring-opening polymerization (ROP) of sila- [3] and disilacyclobutanes [3a,3b,4]. PCSs derived from this latter protocol are usually of high molecular weight and have been used as precursors to ceramics [1j], resist materials, as oxygen plasma barriers, rubbers [4d] and also as suitable crosslinking chains for other polymers, (e.g., polysiloxanes), to give reinforced materials [3a,3b].

The structures of cyclic carbosilanes greatly affect the likelihood of their undergoing ROP. Thus, the dipolar nature (12%) [5] of the endocyclic Si⁺-C^{δ-} bond, reduced inner valence angles, and the increase in Si-C bond distances all lead to high ring strain within cyclic carbosilanes. This imparts a high degree of unsaturation, and reactivity patterns are similar to those of carbon-carbon double bonds [3a]. Theoretical studies suggest strong Si···β-C transannular π-interactions in the rings wherein the Si···β-C distance is significantly reduced to an optimal distance of 2.35 Å. In order to maintain this Si-β-C interaction, non-planar rings have shown altered dihedral angles, whereas planar rings undergo ring compression [3b]. X-ray crystallographic studies of planar 1,1-di-α-naphthyl-1-silacyclobutane, the only other planar silacyclobutane to date, recorded a Si···β-C distance of 2.334 Å which is in good agreement with the theoretical 2.35 Å distance [3b,6].

Herein, we report the synthesis, characterization and X-ray crystal structure of a second planar silacyclobutane,

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1,1-(*rac*-1,1'-bi-2-naphthoxy)-1-silacyclobutane, and its unusual reactivity towards $\text{Pt}(\text{cod})_2$. Typically cyclic carbosilanes undergo insertion of $\text{Pt}(\text{cod})$ into the strained Si–C bond [3d], followed by polymerization to give polycarbosilanes. In the case of **1** however, no insertion or polymeric products were observed but rather the quantitative formation of *rac*-1,1'-bi-2-naphthol (BINOL). The ability of **1** to form polymer was however confirmed by anionic ROP to give its corresponding poly(carbosilane). The mechanism for the unusual reaction with $\text{Pt}(0)$ is proposed based on studies of the reaction of $\text{Pt}(\text{cod})_2$ with non-spirocyclic *rac*-1,1'-bi-2-naphthoxydimethylsilane (**2**) and other cyclic carbosilanes.

2. Results and discussion

The addition of one equiv. of the dilithio salt of *rac*-1,1'-bi-2-naphthol to an equivalent amount of 1,1-dichloro-1-silacyclobutane in ether at -78°C led to the formation of 1,1-(*rac*-1,1'-bi-2-naphthoxy)-1-silacyclobutane (**1**) as a white solid in 71% yield (Scheme 1).

Silacyclobutane **1**, was fully characterized via ^1H , ^{13}C , ^{29}Si NMR spectroscopy and X-ray crystallographic studies. In the ^1H NMR spectrum, $\text{H}_{2,2\text{A}}$ were observed at δ 1.55–1.60 and H_3 at δ 1.61–1.69. Similarly, the ^{13}C NMR spectrum showed $\text{C}_{2,2\text{A}}$ to resonate at δ 22.3 and C_3 at δ 11.6. The ^{29}Si DEPT NMR spectrum had a signal at δ -4.1 . X-ray crystallography confirmed the structure of **1**, with crystals of *rac*-**1** grown from ether at room temperature. An ORTEP drawing of **1** is shown in Fig. 1, (see Table 1 for crystal data and structure refinement parameters). A key feature of the structure is the planar four-membered ring. Theoretical investigations of analogous systems indicate four-membered silicon heterocycles are usually puckered [3b]. Similarly, X-ray structures reported for heterometallocyclophanes ($\text{M} = \text{Fe}$ or V) [7] show the rings to be puckered. Simpler silacyclobutanes like 1,1-dichloro-1-silacyclobutane [8] and 1,1-dimethyl-1-silacyclobutane [7c] are puckered up to 31.7° and 30° , respectively, as determined by gas-phase electron diffraction studies. However, Ushakov and coworkers have determined the structure of 1,1-di- α -naphthyl-1-silacyclobutane to be planar [6],

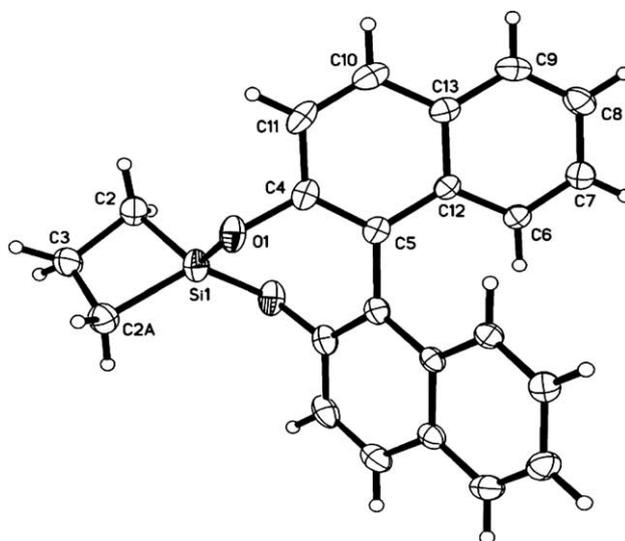
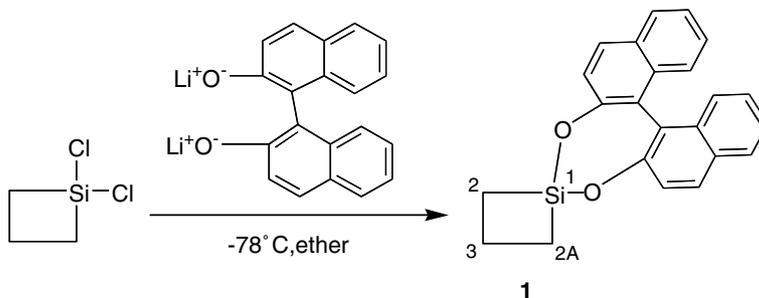


Fig. 1. Molecular structure of **1**, showing the atom numbering scheme and using 20% probability thermal ellipsoids. Bond lengths (Å): Si–O1, 1.646(2), Si–C2, 1.835(3); Si–C3, 2.302(5), O1–C4, 1.397(3), C2–C3, 1.523(4), C4–C5, 1.377(4), C5–C5', 1.490(5). Bond angles ($^\circ$): O1'–Si1–O1, 105.44(14), C4–C5–C5', 120.5(2), O1'–Si1–C2', 119.92(14), Si1–C2', 114.30(13), C2'–Si1–C2, 82.59(19), C4–O1–Si1, 117.64(16), C3–C2–Si1, 86.0(2), C2–C3–C2', 105.5(3), C5–C4–O1, 119.9(3).

and have proposed that the planarity is a consequence of a fixed through space distance between the Si and the β -C of the order of 2.35 Å [3b]. Likewise, Kim and coworkers have performed X-ray crystallographic studies on a series of spiro-siladiatitanacyclobutane complexes, in which the derivative bearing a silacyclobutane motif was planar and the distance between Si... β -C was 2.351(4) Å [9]. For 1,1-di- α -naphthyl-1-silacyclobutane this distance was found to be 2.334 Å [6] and in **1**, we report a similar distance of 2.302(5) Å for Si–C3 and therefore we also suggest the planarity in **1** is due to this transannular interaction. It should be noted however that the barrier between ring conformers is very low in such species [3b].

2.1. Reaction of **1** with $\text{Pt}(0)$ complexes

Silacyclobutanes readily undergo Pt-catalysed ROP to give poly(carbosilane)s. However, attempted Pt catalyzed



Scheme 1. Synthesis of 1,1-(*rac*-1,1'-bi-2-naphthoxy)-1-silacyclobutane (**1**).

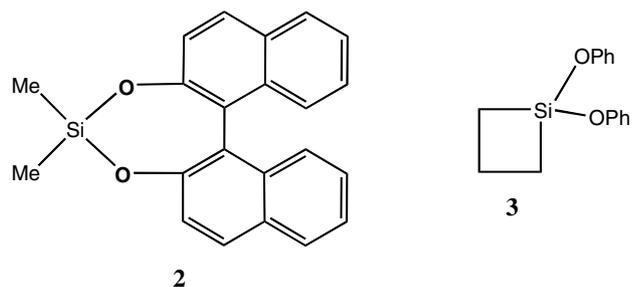
Table 1
Crystal data and structure refinement for **1**

	1
empirical formula	C ₂₃ H ₁₈ O ₂ Si
Formula weight	354.46
Space group	<i>Pbcn</i>
<i>a</i> (Å)	9.5710 (19)
<i>b</i> (Å)	11.134 (2)
<i>c</i> (Å)	16.866 (3)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
<i>V</i> (Å ³)	1797.3 (6)
<i>Z</i>	4
<i>D</i> _{calcd} (Mg/m ³)	1.310
Crystal size (in mm)	0.50 × 0.41 × 0.11
θ Range (°)	3.00–25.00
Absorption coefficient (mm ⁻¹)	0.145
<i>F</i> (000)	744
Data/parameters	1026/122
Goodness-of-fit	1.05
<i>R</i> [<i>I</i> > σ (<i>I</i>)]	0.053
<i>WR</i> ₂ (all data)	0.139

ROP of **1** gave an unusual result. Thus, treatment of **1** with a catalytic amount of Pt(cod)₂ or Karstedt's catalyst (platinum-divinyltetramethyldisiloxane) resulted in no polymerization and partial decomposition to 1,1'-bi-2-naphthol. Treatment with a stoichiometric amount of Pt(cod)₂, with monitoring by ¹H NMR spectroscopy in C₆D₆ showed full conversion of **1** to 1,1'-bi-2-naphthol and 1-5-cyclooctadiene. Other unidentified soluble species with very broad NMR signals ranging from δ 0.9–2.1 were also detected presumably resulting from the carbosilane ring (Scheme 2).

A number of experiments were performed to investigate this unusual reactivity. First, a non-spirocyclic analog of **1**, *rac*-1,1'-bi-2-naphthoxydimethylsilane (**2**), prepared from dimethyldichlorosilane and the dilithio salt of *rac*-1,1'-bi-2-naphthol, was reacted with Pt(cod)₂. Compound **2** was characterized via ¹H, ¹³C and ²⁹Si NMR spectroscopy and has assignments consistent with the proposed structure. After three days of

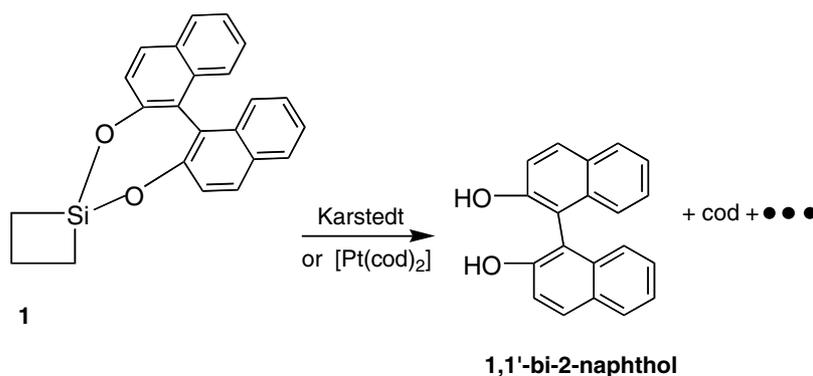
reaction with Pt(cod)₂, no changes were evident in the ¹H NMR spectrum. This result indicates that the carbosilane ring in **1** is required for release of BINOL from **1** in the presence of Pt(0). Second, 1,1-bis(phenoxy)-1-silacyclobutane (**3**) was prepared [10] and reacted with Pt(0). Once again, after 48 h no observable reaction, other than slight decomposition of the Pt(cod)₂, was seen. No phenol, polymeric or insertion products were formed. This result indicates that Pt(0) does not readily cleave the Si-O bonds to form alcohols and that it requires the unique spirocyclic structure of **1** to release BINOL from **1**. Finally, it was shown that the source of the hydroxyl protons in the BINOL product was not the solvent, thus, when the reaction was performed in deuterated solvents only H-containing BINOL was produced quantitatively.



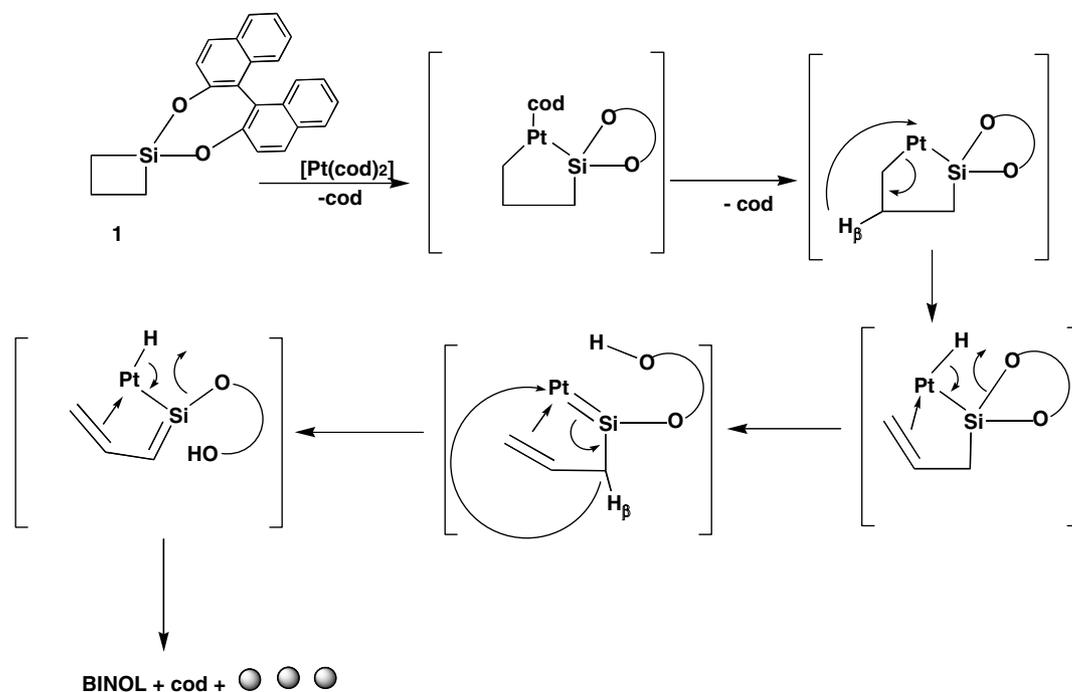
2.2. Mechanistic interpretation

The above difference in reactivity between **1** and **2** towards Pt(cod)₂ must be due to the four membered ring in **1**, whereas the difference in reactivity between **1** and **3** is due to the strained Si-BINOL ring. Thus, we propose the mechanism shown in Scheme 3 for the Pt-catalysed decomposition of **1** to BINOL.

Following loss of one cod ligand the Pt(cod) inserts into the 4-membered ring of **1**. Such insertions are well established for silacyclobutanes [3d] and related cyclic

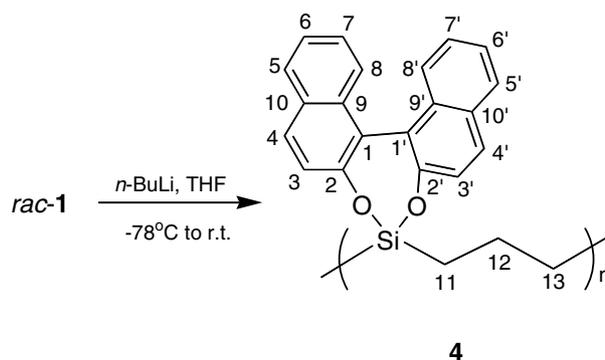


Scheme 2. Decomposition of **1** in the presence of Pt-catalyst.

Scheme 3. Proposed mechanism for Pt-catalysed decomposition of **1**.

silaferrrocenophanes [11]. Obviously, **2** cannot undergo such insertion and we propose that **3** either does not react or undergoes a reversible insertion without loss of phenol or formation of polymer. One possible reason may be that the phenoxy oxygen donor atoms in **3** coordinate to Pt preventing decomposition of the intermediate or polymerization. The binaphthoxy oxygen atoms in **1** are much more constrained and allow the Pt to insert but do not coordinate to the metal.

After insertion of Pt into **1**, loss of the second cod ligand would give a coordinatively unsaturated environment around Pt allowing a β -hydride transfer to the metal. Whitesides and coworkers have documented the decomposition of Pt(II) carbocycles through a similar β -hydride elimination process [12]. Cleavage of one Si–O bond and formation of a hydroxyl group precedes a second β -hydride transfer, this time from the methylene adjacent to silicon. Displacement of 1,1'-bi-2-naphthol from the intermediates would lead to Pt(0) and unidentified products from the residual carbon and silicon containing species. The Pt(0) is most likely colloidal Pt which further catalyses the decomposition of **1**. In other silacyclobutanes [3] and silaferrrocenophanes [13] with Me or Ph groups at silicon Pt-catalysed ROP is observed via decomposition of initial insertion products to colloidal Pt. In contrast, for **1** the driving force for the decomposition to BINOL is the likely relief of ring strain in the Si–BINOL ring. Surprisingly, a comparison of the O–Si–O angle $105.44(14)^\circ$ in **1** with that in a related bis(cyclopentadienyl)yttrium species (108°) [14] shows little difference between these two, ruling out any extra ring strain in **1** that might explain its reactivity. Other mechanisms

Scheme 4. Anionic ROP of **1**.

involving both β -hydride and α -hydride transfers from the carbons of the platinasilacyclobutane intermediate prior to release of BINOL are possible, and that shown in Scheme 3 is offered as only one likely pathway.

2.2.1. Anionic ROP of 1,1-(*rac*-1,1'-bi-2-naphthoxy)-1-silacyclobutane (**1**)

Although *rac*-**1** could not be polymerized via Pt-catalyzed ROP, it was polymerized via anionic ring-opening polymerization. Thus, treatment of *rac*-**1** in THF with a catalytic amount of *n*-BuLi gave polymer **4** as a white powder (50%) (Scheme 4).

Polymer **4** was characterized using ^1H , ^{13}C and ^{29}Si NMR spectroscopy. Protons $\text{H}_{11,13}$ and H_{12} were observed at δ 0.49–0.70 and δ 1.23–1.48, respectively. The ^{13}C NMR spectrum showed C_{12} at δ 16.1, $\text{C}_{11,13}$ at δ 16.9, and shifts for the 1,1'-bi-2-naphthol motif was consistent with the assigned structure. The ^{29}Si

NMR DEPT spectrum shows a single peak at δ 8.3. GPC analysis of polymer **4** showed M_n to be 6800 (PDI = 1.4).

3. Experimental

3.1. Materials

Solvents were dried over Na/benzophenone (THF, diethyl ether), CaH_2 (*n*-hexane), and were freshly distilled prior to use. The solvent used for NMR studies was C_6D_6 as purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). Filtrations used Celite[®] purchased from Fisher Scientific that was preheated and dried before use. *n*-Butyllithium, dichlorodimethylsilane, (*rac*)-1,1'-Bi-2-naphthol were purchased from Acros Organics (NJ) and used as supplied. Karstedt's catalyst (Platinum-divinyltetramethylsiloxane complex; 3–3.5% Pt concentration in vinyl terminated polydimethylsiloxane), and 1,1-dichloro-1-silacyclobutane were purchased from Gelest, Inc. (Tullytown, PA). $\text{Pt}(\text{cod})_2$ was prepared using previously described literature methods [15].

3.2. Equipment

Manipulations of air-sensitive compounds were performed using standard Schlenk techniques under a nitrogen atmosphere. NMR spectra were recorded on Varian VXR-400S (400 MHz) and Varian Unity Inova (500 MHz) NMR Fourier transform spectrometers. Molecular weight distributions were analyzed by gel permeation chromatography using a Waters Associates 2690 Separations Unit. Ultrastaygel columns with a pore size between 500, 10^3 , and 10^5 Å, and a Waters 410 differential refractometer were used. The flow rate of 1.0 mL/min was used, and samples were dissolved in a THF solution. Polystyrene standards purchased from Aldrich were used for calibration.

3.2.1. Preparation of 1,1-(*rac*-1,1'-bi-2-naphthoxy)-1-silacyclobutane (**1**)

A mixture of *rac*-1,1'-bi-2-naphthol (3.675 g, 12.85 mmol) in 50 mL of diethyl ether was treated with 16.06 mL (25.70 mmol) of 1.6 M *n*-BuLi in *n*-hexane at -78 °C. The mixture was allowed to reach room temperature to form the dilithio salt and then recooled to -78 °C and 1,1-dichloro-1-silacyclobutane (1.812 g, 12.85 mmol) in 50 mL diethyl ether added dropwise. After addition the flask was warmed to room temperature and solvents removed in vacuo. Washing with two portions of *n*-hexane (225 mL) and once with diethyl ether (10 mL) at 0 °C, extraction with toluene, filtration through Celite[®], and drying under vacuo afforded *rac*-**1** as a white solid (yield 3.263 g, 71%). Compound **1** is

thermally and air-sensitive and a satisfactory elemental analysis could not be obtained. The compound can be stored for a few days in an inert atmosphere glove box at -30 °C. ^1H NMR: δ 1.55–1.60 (m, 4H, CH_2 (2,2A)), δ 1.61–1.69 (m, 2H, CH_2 (3)), δ 6.88–6.91, 7.09–7.12 (m, 4H, *BINOL*), δ 7.37–7.42, 7.62–7.64 (m, 8H, *BINOL*). ^{13}C { ^1H } NMR: δ 11.6 (C_3), δ 22.3 ($\text{C}_{2,2A}$), δ 150.2 (*BINOL*_{ipso}), 121.9, 124.6, 126.6, 127.5, 128.5, 130.6, 131.1, 134.1 (*BINOL*). ^{29}Si NMR: δ -4.1 .

3.2.2. Preparation of *rac*-1,1'-bi-2-naphthoxydimethylsilane (**2**)

A mixture of *rac*-1,1'-bi-2-naphthol (0.505 g, 1.764 mmol) in 40 mL of diethyl ether was treated with 1.43 mL (3.532 mmol) of 2.47 M *n*-BuLi in *n*-hexane at -78 °C. The mixture was warmed to room temperature and re-cooled to -78 °C after which dichlorodimethylsilane (0.228 g, 1.767 mmol) in 30 mL diethyl ether was added dropwise. The solution was dried in vacuo at room temperature and washed with two portions of *n*-hexane (2×15 mL) and one of diethyl ether (5 mL) at 0 °C. Extraction with toluene, filtration through Celite[®], and drying under vacuo afforded *rac*-**2** as a white solid (yield 0.471g, 78%). ^1H NMR: δ 0.14 (s, 6H, *Me*), δ 6.90 (d, 2H, $\text{H}_{6,6'}$), δ 7.11 (d, 2H, $\text{H}_{5,5'}$), δ 7.32 (d, 2H, $\text{H}_{7,7'}$), $^3J_{\text{H-H}} = 9$ Hz), δ 7.44 (d, 2H, $\text{H}_{4,4'}$), $^3J_{\text{H-H}} = 9$ Hz), δ 7.656 (d, 2H, $\text{H}_{8,8'}$), $^3J_{\text{H-H}} = 8$ Hz), δ 7.663 (d, 2H, $\text{H}_{3,3'}$), $^3J_{\text{H-H}} = 9$ Hz). ^{13}C { ^1H } NMR: δ -3.2 (*Me*), δ 122.0 ($\text{C}_{4,4'}$), δ 122.2 ($\text{C}_{1,1'}$), 124.5 ($\text{C}_{7,7'}$), δ 126.5 ($\text{C}_{6,6'}$), δ 127.5 ($\text{C}_{5,5'}$), δ 128.5 ($\text{C}_{8,8'}$), δ 130.5 ($\text{C}_{3,3'}$), δ 130.9 ($\text{C}_{10,10'}$), δ 134.2 ($\text{C}_{9,9'}$), δ 151.0 ($\text{C}_{2,2'}$). ^{29}Si NMR: δ 12.8.

3.2.3. Preparation of polymer **4**

A solution of *rac*-**1** (0.105 g, 0.297 mmol) in 10 mL THF was treated with a catalytic amount of 1.6 M *n*-BuLi in hexane (0.002 mmol) at -78 °C. The mixture was warmed to room temperature, stirred for 3 h and then dried in vacuo to give a white solid. Dissolution of this solid in a minimum amount of THF (0.7 mL) and precipitation into methanol (35 mL) gave a white precipitate. Washing with methanol (3×10 mL), followed by drying under vacuum overnight gave polymer **4** as a white powder (yield 0.052 g, 50%). $M_n = 6800$; $M_w/M_n = 1.4$. ^1H NMR: δ 0.49–0.70 (br, 4H, $\text{H}_{11,13}$), δ 1.23–1.48 (br, 2H, H_{12}), δ 6.86 (br, 2H, $\text{H}_{6,6'}$), δ 7.01–7.08 (br, 2H, $\text{H}_{5,5'}$), 7.22–7.37 (br, 4H, $\text{H}_{4,4',7,7'}$), δ 7.61 (br, 4H, $\text{H}_{3,3',8,8'}$). ^{13}C { ^1H } NMR: δ 16.1 (C_{12}), δ 16.9 ($\text{C}_{11,13}$), δ 122.1 ($\text{C}_{4,4'}$), δ 121.8 ($\text{C}_{1,1'}$), δ 124.5 ($\text{C}_{7,7'}$), δ 126.6 ($\text{C}_{6,6'}$), δ 127.4 ($\text{C}_{5,5'}$), δ 128.5 ($\text{C}_{8,8'}$), δ 130.4 ($\text{C}_{3,3'}$), δ 130.8 ($\text{C}_{10,10'}$), δ 134.1 ($\text{C}_{9,9'}$), δ 151.2 ($\text{C}_{2,2'}$). ^{29}Si NMR: δ 8.3.

4. X-ray crystal structure determination

Crystals of **1** were mounted on a glass fiber using cyanoacrylate cement. Intensity data were collected on a

Siemens P4 diffractometer at 296 K, using a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The $\theta - 2\theta$ scan technique was applied with variable scan speeds. The intensities of three standard reflections were measured every 97 reflections and corrections were applied. The data were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically by full-matrix least square methods to minimize $\sum w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F) + g(F)^2$. Hydrogen atoms were included in calculated positions. Crystal data, data collection, and least-squares parameters are listed in Table 1. All calculations were performed and graphics created using SHELXTL-97.

Appendix A. Supplementary data

Tables of X-ray Crystallographic data for **1** and ^1H and ^{13}C NMR spectra for **1**, **2**, and **4**. Crystallographic data for **1** have also been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 266057. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK [Fax. (int code) +44(1223)336-033, or Email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorgchem.2005.02.032.

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