

Dimerization of a lattice-framework silanone into the corresponding 1,3-dioxa-2,4-disiletanes

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Abstract

A lattice-framework silanone, a racemate of (4*R*,6*R*)- and (4*S*,6*S*)-2,3,4,6,7,8-hexa-*tert*-butyl-1,5-disilatricyclo[4.2.0.0^{1,4}]octa-2,7-dien-5-one (**4**), was generated by the photoreaction of the corresponding lattice-framework disilene, a racemate of (4*R*,6*R*,4'*R*,6'*R*)- and (4*S*,6*S*,4'*S*,6'*S*)-2,3,4,6,7,8,2',3',4',6',7',8'-dodeca-*tert*-butyl-[5,5']bi{1,5-disilatricyclo[4.2.0.0^{1,4}]octylidene}-2,7,2',7'-tetraene (*dl*-**1**), with mesitronitrile oxide. The silanone **4** was dimerized to produce a mixture of the corresponding *dl*- and *meso*-1,3-dioxa-2,4-disiletane derivatives **2**. DFT calculations suggested that the non-selective dimerization of **4** to **2** is attributed to the irreversibility of the reaction.

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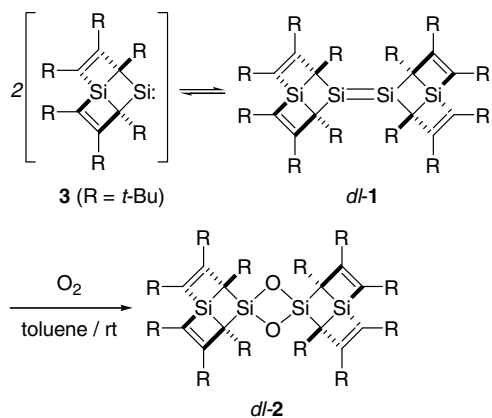
Keywords: Organosilicon compound; 1,3-Dioxa-2,4-disiletane; Silanone; Density functional theory

1. Introduction

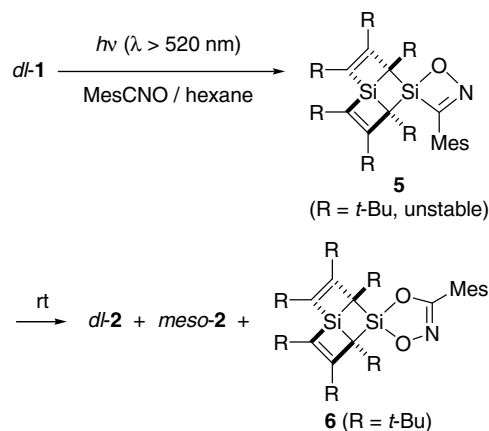
A silicon–oxygen double-bonded species (silanone) has been investigated as one of the most important intermediates in the field of organosilicon chemistry [1–5]. Okazaki and co-workers reported the generation of an overcrowded silanone {Tbt(Mes)Si=O; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = mesityl} by the reaction of a stable silylene-isocyanide complex with nitrile oxides [2]. The silanone was trapped by the nitrile oxides to afford the corresponding 1,3-dioxa-4-aza-2-siloles. It is noteworthy that the dimerization of the silanone gave a mixture of the corresponding (*E*)- and (*Z*)-1,3-dioxa-2,4-disiletanes. This result indicates that the dimerization is not stereoselective.

Very recently, we reported the preparation, structure, and reactions of a unique lattice-framework disilene, a racemate of (4*R*,6*R*,4'*R*,6'*R*)- and (4*S*,6*S*,4'*S*,6'*S*)-2,3,4,6,7,8,2',3',4',6',7',8'-dodeca-*tert*-butyl-[5,5']bi{1,5-disilatricyclo[4.2.0.0^{1,4}]octylidene}-2,7,2',7'-tetraene (*dl*-**1**) [6–9]. As shown in Scheme 1, the reaction of *dl*-**1** with oxygen stereospecifically gave the *dl*-1,3-dioxa-2,4-disiletane derivative **2** [6,9]. Trapping experiments revealed that a thermal equilibrium between *dl*-**1** and the corresponding silylene **3** exists in solution at room temperature [7,9]. Furthermore, photolysis accelerated the dissociation of *dl*-**1** to **3** in solution [7,9]. In this paper, we report the generation of a lattice-framework silanone, a racemate of (4*R*,6*R*)- and (4*S*,6*S*)-2,3,4,6,7,8-hexa-*tert*-butyl-1,5-disilatricyclo[4.2.0.0^{1,4}]octa-2,7-dien-5-one (**4**) by the photoreaction of *dl*-**1** with mesitronitrile oxide (MesCNO), as shown in Scheme 2. The silanone **4** was dimerized to produce a mixture of the corresponding *dl*- and *meso*-**2**. The structure and energetics of **2** and **4** were investigated by DFT

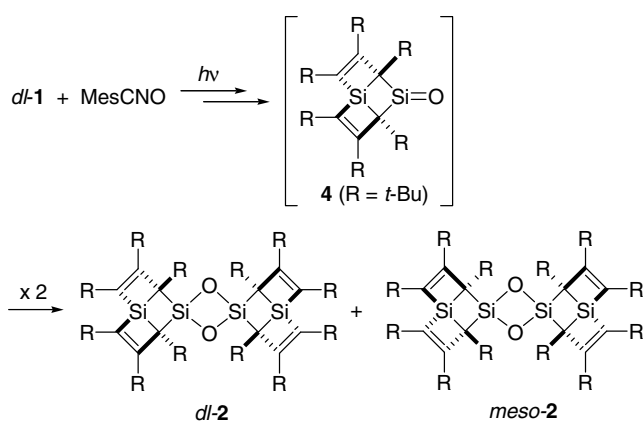
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Scheme 1.



Scheme 3.



Scheme 2.

Table 1
Photoreaction of *dl*-**1** in the presence of mesitronitrile oxide

MesCNO ^a	Yield (%) ^b		
	<i>dl</i> - 2	<i>meso</i> - 2	6
2	29	25	26
30	–	–	77

^a Molar equivalent of mesitronitrile oxide.^b Determined by ¹H NMR spectroscopy.

isolated, a mixture of *dl*-**2** and *meso*-**2** (*dl*:*meso* = 1.2:1) was obtained by GPC. The mixture of *dl*-**2** and *meso*-**2** gave satisfactory elemental analytical data. The identification of *dl*-**2** in the mixture was performed by ¹H, ¹³C, and ²⁹Si NMR spectroscopies. The spectral data of *dl*-**2** were identical to the authentic sample [6,9]. The structure of *meso*-**2** was established by ¹H, ¹³C, and ²⁹Si NMR spectroscopies based on the similarities to that of *dl*-**2**. The ¹H NMR spectrum of the mixture of *dl*-**2** and *meso*-**2** in CDCl₃ showed six kinds of peaks assignable to the *tert*-butyl groups. Three peaks that appeared at 1.22, 1.35, and 1.37 ppm were identical to that of *dl*-**2** and the other three peaks that appeared at 1.25, 1.32, and 1.36 ppm should originate from *meso*-**2**. The ²⁹Si NMR spectrum of the mixture of *dl*-**2** and *meso*-**2** in CDCl₃ showed four kinds of peaks. Two of the four peaks at –54.8 and –2.4 ppm agreed with that of *dl*-**2** and the other two peaks at –48.5 and 0.7 ppm should be derived from *meso*-**2**. The characterization of **5** was performed by only ¹H NMR spectroscopy, because **5** was unstable at room temperature.

In contrast to the above result, the photolysis of a C₆D₆ solution of *dl*-**1** with a 30-fold molar equivalent of mesitronitrile oxide gave only **6** in 77% yield as determined by ¹H NMR spectroscopy.

Okazaki and co-workers reported that the reaction of Tbt(Mes)Si:[NCAr*] (Ar* = 2,4,6-tri-*tert*-butylphenyl) with a 1.1 molar equivalent of mesitronitrile oxide produces the corresponding 1,3-dioxa-4-aza-2-silole derivative and (*E*)- and (*Z*)-1,3-dioxa-2,4-disilanes via the corresponding 1-oxa-2-aza-4-silenes and silanone derivatives [3]. Taking into account this report, the formation of *dl*-**2**,

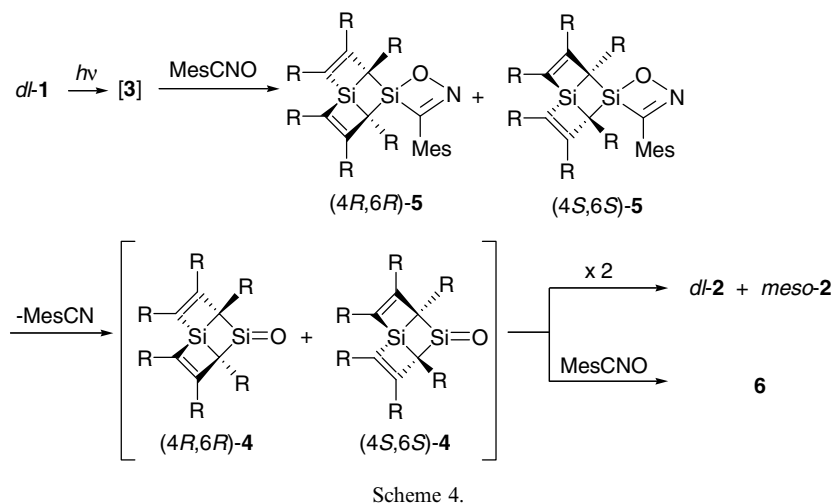
calculations to elucidate the reason for the non-selective dimerization of **4** to **2**.

2. Results and discussion

2.1. Reaction of *dl*-**1** with mesitronitrile oxide

A C₆D₆ solution of *dl*-**1** with a 2-fold molar equivalent of mesitronitrile oxide was irradiated ($\lambda > 520$ nm) until *dl*-**1** was completely consumed. Immediately after the irradiation, a reaction mixture including 1-oxa-2-aza-4-silole **5** was observed in the ¹H NMR spectrum (Scheme 3). The yield of **5** at this time was not determined from the ¹H NMR spectrum, because the signals of the mixture were complicated. After allowing the mixture to stand at room temperature for 3 h, a set of the signals assignable to **5** disappeared. The formation of *dl*-**2**, *meso*-**2**, and 1,3-dioxa-4-aza-2-silole **6** was then observed by ¹H NMR spectroscopy. The ¹H NMR spectrum of the mixture revealed that the yields of *dl*-**2**, *meso*-**2**, and **6** were 29%, 25%, and 26%, respectively, as shown in Table 1.

Compound **6** was isolated by GPC and the structure of **6** was established by mass spectrometry and ¹H, ¹³C, and ²⁹Si NMR spectroscopies. Although *dl*-**2** and *meso*-**2** were not



Scheme 4.

meso-2, and 6 can be reasonably explained by Scheme 4. Thus, the thermally unstable compound 5 was generated by the reaction of 3 with mesitronitrile oxide. The dissociation of 5 gave 4 and mesitronitrile at room temperature. The dimerization of 4 gave both the *dl*- and *meso*-2, and the [2 + 3] cycloaddition of 4 with mesitronitrile oxide produced 6. When *dl*-1 was irradiated with an excess amount of mesitronitrile oxide, the dimerization of 4 to 2 was depressed.

2.2. Theoretical calculations

As described in the experimental section, the photolysis of 1 in the presence of mesitronitrile oxide gave a mixture of the *dl*- and *meso*-isomers of 2. Interesting is the fact that the dimerization of the silanone 4 gave both the *dl*- and *meso*-2, while the dimerization of 3 selectively gave *dl*-1. We carried out DFT calculations to elucidate the reason for the selective dimerization of 3 and the non-selective dimerization of 4. First, the structure and energetics of 2 and 4 were investigated. Also, model compounds 7 and 8, in which all the *tert*-butyl groups in 2 and 4 are replaced by hydrogen atoms, have been calculated in order to evaluate the degree of steric repulsion caused by the bulky substituents (Fig. 1).

The optimized structures of the isomers of 2 and 7 are shown in Fig. 2. The selected geometric parameters and relative stabilities of 2 and 7 are listed in Table 2, together with the experimental values for the X-ray crystallographic structure of *dl*-2 [9]. The optimized structure of *dl*-2 nicely reproduces the solid state structure. The insertion of oxygen atoms between the unsaturated Si=Si bond of *dl*-1 elongates the Si–Si distance in *dl*-2 by 0.245 Å (from 2.274 Å for *dl*-1 to 2.519 Å for *dl*-2), reducing the steric repulsion between the *tert*-butyl groups surrounding the Si₂O₂ ring. The average Si–C–Si–C dihedral angle (0.7°) and Si–Si–Si angle (178.7°) of *dl*-2 indicate that two Si₂C₂ rings in the lattice-framework skeleton are nearly coplanar. For *meso*-2, on the other hand, the average Si–C–Si–C dihedral angle and Si–Si–Si angle are calculated to be 7.3° and 171.3°, respectively, while the Si–Si distance

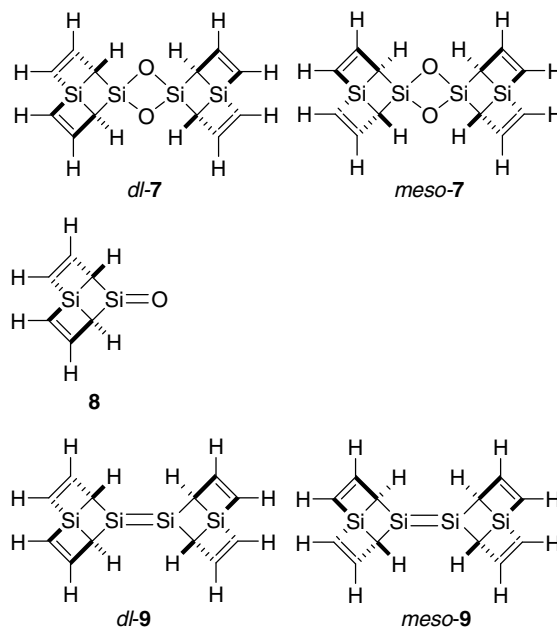


Fig. 1. Calculated model compounds 7–9.

(2.536 Å) in the Si₂O₂ ring is close to that of *dl*-2. The deformed structure of *meso*-2 reflects the large degree of steric repulsion between the *tert*-butyl groups compared to *dl*-2. The difference in geometry between *dl*-2 and *meso*-2 can be associated with their relative stability; *dl*-2 is 42.5 kJ/mol more stable than *meso*-2. This value is smaller than the relative stability between *dl*-1 and *meso*-1 (52.9 kJ/mol) [7] due to the smaller degree of steric repulsion in 2 than that in 1. The optimized structure of *dl*-7 is very close to that of *dl*-2. On the other hand, *meso*-7 has planar Si₂C₂ rings and a highly symmetrical Si₂O₂ ring, unlike *meso*-2 consisting of the distorted four-membered rings. Isomers *dl*-7 and *meso*-7 are energetically almost degenerated, similar to the case of the model disilenes *dl*-9 and *meso*-9 (Fig. 1) [7]. A comparison of the structures and relative stabilities between the isomers of 2 and 7 suggests a large degree of steric repulsion in *meso*-2.

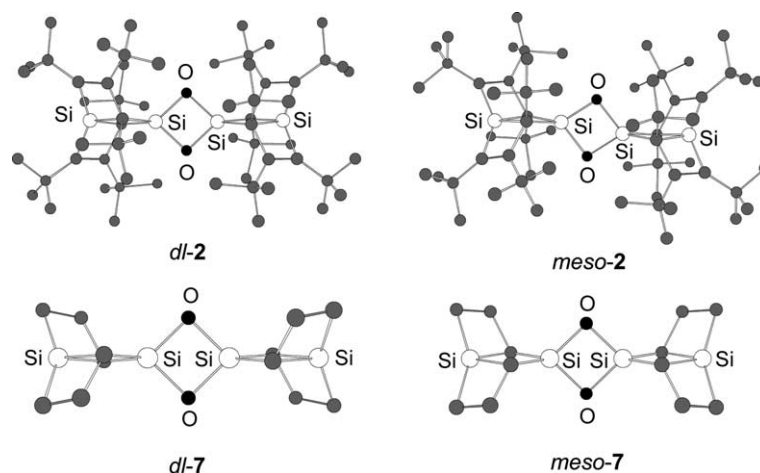
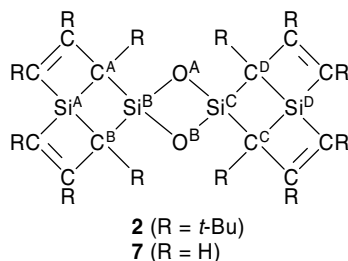


Fig. 2. Optimized structures of the isomers of **2** and **7**. Hydrogen atoms are omitted for clarity.

Table 2

Selected geometric parameters and relative stability of the isomers of compounds **2** and **7**



Compound	<i>dl</i> - 2	<i>meso</i> - 2	<i>dl</i> - 7	<i>meso</i> - 7
<i>Bent length</i> (Å)				
Si ^B –Si ^C	2.519 [2.465] ^a	2.536	2.425	2.425
<i>Bent angle</i> (°)				
Si ^A –Si ^C –O ^A	138.1 [139.6] ^a	145.5	135.5	135.5
Si ^A –Si ^B –O ^B	135.7 [133.7] ^a	128.6	135.5	135.5
Si ^A –Si ^B –Si ^C	178.7 [177.8] ^a	171.3	180	180
<i>Dihedral angle</i> (°)				
C ^A –Si ^B –Si ^C –C ^D	9.4 [8.4] ^a	0.9	7.9	0.1
Si ^A –Si ^B –O ^A –O ^B	178.9 [178.6] ^a	176.7	180	180
ΔE^b (kJ mol ⁻¹)	0	42.5	0	0.1

^a X-ray crystallographic data in Ref. [9].

^b Energy relative to the respective lowest-energy structure (*dl*-**2** for the **2** system and *dl*-**7** for the **7** system).

The energy gap between *dl*-**2** and *meso*-**2** could be large enough to generate only *dl*-**2**, if a thermal equilibrium existed between *dl*-**2** and *meso*-**2**. The dissociation energy of *dl*-**5** for splitting into two molecules of silanone **4** is calculated to be 293.7 kJ/mol. This value is about three times greater than the dissociation energy of *dl*-**1** (92.9 kJ/mol) [7], although it is smaller than 393.0 kJ/mol for *dl*-**7** and 405.3 kJ/mol for 2,2,4,4-tetramethyl-1,3-dioxo-2,4-disilane. Considering the experimental result and the large dissociation energy calculated for **2**, we deduce that a thermal equilibrium between **2** and **4** can be neglected. If the dimerization of silanone **4** proceeds under kinetic control rather than under thermodynamic control, the reason for the non-selective dimerization of **4** can be reasonably understood.

The large dissociation energy of **2** implies that the transition state for the dimerization of **4** appears during the early stage of the reaction process. The transition-state structure should resemble the structure of the reactant, which is close to two molecules of **4**. In the transition-state structure, the steric repulsion caused by the *tert*-butyl groups would be small for both *dl*-**2** and *meso*-**2**. In such a case, the dimerization of (4*R*,6*R*)-**4** and (4*S*,6*S*)-**4** will give a nearly equal amount of *dl*-**2** [(4*R*,6*R*,4'*R*,6'*R*)-**2** and (4*S*,6*S*,4'*S*,6'*S*)-**2**] and *meso*-**2** [(4*R*,6*R*,4'*S*,6'*S*)-**2**], because the large dissociation energy of **2** implies that the thermal equilibrium between **2** and **4** can be neglected at room temperature.

3. Conclusion

In summary, a lattice-framework silanone, (4*R*,6*R*)- and (4*S*,6*S*)-2,3,4,6,7,8-hexa-*tert*-butyl-1,5-disilatricyclo[4.2.0.0^{1,4}] octa-2,7-dien-5-one (**4**), was generated by the photoreaction of the lattice-framework disilene, (4*R*,6*R*,4'*R*,6'*R*)- and (4*S*,6*S*,4'*S*,6'*S*)-2,3,4,6,7,8,2',3',4',6',7',8'-dodeca-*tert*-butyl-[5,5']bi[1,5-disilatricyclo[4.2.0.0^{1,4}]octylidene]-2,7,2',7'-tetraene (*dl*-**1**), with mesitronitrile oxide. The intermediate **4** was dimerized to produce a mixture of the corresponding *dl*- and *meso*-1,3-dioxo-2,4-disilane derivatives **2**. Based on the DFT calculations, the reason for the non-selective dimerization of **4** to *dl*- and *meso*-**2** can be explained by the irreversibility of the dimerization, which stems from the very large dissociation energy of **2**.

4. Experimental

4.1. General methods

The ¹H, ¹³C, and ²⁹Si NMR spectra were recorded using a Varian INOVA 300 FT-NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. The mass spectra were recorded using Shimadzu GCMS-QP5050A and Hitachi M-2500 mass spectrometers. Gel permeation chromatography (GPC) was conducted using a LC908 recycling

high-pressure liquid chromatograph (Japan Analytical Instruments Co., Ltd.) with JAIGEL-1H (20 × 600 mm) and JAIGEL-2H (20 × 600 mm) columns and toluene as the eluent.

4.2. Materials

Toluene and CDCl₃ were commercially available and used as supplied. Hexane and C₆D₆ were freshly distilled from potassium. Disilene *dl*-1 [6,9] and mesitonitrile oxide [12] were prepared according to the reported procedures.

4.3. Reaction of *dl*-1 with mesitonitrile oxide

- (a) A C₆D₆ (0.6 mL) solution of disilene *dl*-1 (1.24 mg, 1.31×10^{-6} mol) and mesitonitrile oxide (0.46 mg, 2.9×10^{-6} mol) was irradiated ($\lambda > 520$ nm) for 18 min at room temperature under an argon atmosphere. Immediately after the irradiation, a set of signals assignable to 1-oxa-2-aza-4-silole **5** in the reaction mixture was observed by ¹H NMR spectroscopy. After standing at room temperature for 3 h, the ¹H NMR spectrum of the reaction mixture showed the formation of *dl*-2, *meso*-2, and 1,3-dioxa-4-aza-2-silole **6** in 29, 25, and 26% yields, respectively.
- (b) A hexane (15 mL) solution of *dl*-1 (31 mg, 3.3×10^{-5} mol) and mesitonitrile oxide (11 mg, 6.8×10^{-5} mol) was irradiated ($\lambda > 500$ nm) for 33 min at room temperature under an argon atmosphere. The vacuum evaporation of the solvent resulted in a solid. Separation of the residue using a recycling GPC (toluene as an eluent) gave **6** (10.5 mg, 1.62×10^{-6} mol, 9.8%) and a mixture of *dl*- and *meso*-2 (11.2 mg, 1.19×10^{-5} mol, 36%). The ratio of *dl*-2 to *meso*-2 (*dl*-2:*meso*-2 = 1.2:1) was determined by the ¹H NMR results.
- (c) A C₆D₆ (0.6 mL) solution of *dl*-1 (0.706 mg, 7.5×10^{-7} mol) and mesitonitrile oxide (4.0 mg, 2.5×10^{-5} mol) was irradiated ($\lambda > 500$ nm) for 20 min at room temperature under argon atmosphere. After standing at room temperature for 5 h, the ¹H NMR spectrum of the reaction mixture showed the formation of **6** in 77% yield.

6: Colorless crystal; mp 182.5–184.5 °C; ¹H NMR (C₆D₆, δ) 1.31 (s, 9H), 1.32 (s, 9H), 1.34 (s, 9H), 1.35 (s, 9H), 1.45 (s, 9H), 1.51 (s, 9H), 2.03 (s, 3H), 2.52 (s, 6H), 6.68 (s, 2H); ¹³C NMR (C₆D₆, δ) 20.92 (CH₃), 21.02 (CH₃), 32.94 (CH₃), 33.08 (CH₃), 33.53 (CH₃), 33.62 (CH₃), 34.47 (C), 34.49 (C), 34.70 (CH₃), 34.95 (CH₃), 35.72 (C), 36.19 (C), 38.58 (C), 38.60 (C), 126.16 (C), 128.90 (CH), 138.06 (C), 139.42 (C), 162.09 (C), 165.70 (C), 165.76 (C), 165.96 (C), 166.92 (C); ²⁹Si NMR (C₆D₆, δ) -47.3 (SiC₄), 5.6 (SiO₂); MS (70 eV) *m/z* (%) 648 (M⁺, 20), 235 (19), 208 (29), 207 (100). Anal. Calc. for C₄₀H₆₅NO₂Si₂: C, 74.13; H, 10.11; N 2.07. Found: C, 74.00; H, 10.30; N 2.16%.

dl-2: ¹H NMR (CDCl₃, δ) 1.22 (s, 36H), 1.35 (s, 36H), 1.37 (s, 36H); ¹³C NMR (CDCl₃, δ) 33.66 (CH₃), 34.07 (CH₃), 35.08 (CH₃), 35.46 (C), 36.21 (C), 37.77 (C), 66.92 (C), 166.31 (C), 167.72 (C); ²⁹Si NMR (CDCl₃, δ) -54.8 (SiC₄), -2.4 (Si₂O₂).

meso-2: ¹H NMR (CDCl₃, δ) 1.25 (s, 36H), 1.32 (s, 36H), 1.36 (s, 36H); ¹³C NMR (CDCl₃, δ) 33.69 (CH₃), 33.79 (CH₃), 35.28 (C), 35.39 (CH₃), 35.61 (C), 37.77 (C), 66.55 (C), 163.09 (C), 167.85 (C); ²⁹Si NMR (CDCl₃, δ) -48.5 (SiC₄), 0.7 (Si₂O₂).

A mixture of *dl*-2 and *meso*-2: Anal. Calc. for C₆₀H₁₀₈O₂Si₄: C, 74.00; H, 11.18. Found: C, 74.18; H, 11.38%.

5: ¹H NMR (C₆D₆, δ) 1.07 (s, 9H), 1.26 (s, 9H), 1.34 (s, 9H), 1.36 (s, 9H), 1.54 (s, 9H), 1.61 (s, 9H), 2.08 (s, 3H), 2.62 (s, 6H), 6.75 (s, 2H).

4.4. Theoretical calculations

All calculations were carried out using the GAUSSIAN 98 program [10]. The optimized structures of **2** were computed with the B3LYP hybrid functional [11,12]. The 3-21G(d) basis sets were used for the C and H atoms in the *tert*-butyl groups. The 6-31G(d) basis sets were used for the other atoms. For **7** and 2,2,4,4-tetramethyl-1,3-dioxa-2,4-disilane, all calculations were performed at the B3LYP/6-311 + G(d,p) level.

Appendix A. Supplementary data

Copies of this information can be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.12.009.

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