

Note

## Preparation and reactivity of polyfunctional six- and eight-membered cyclic silicates

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### Abstract

Six- and eight-membered cyclic silicates with reactive Si–H or Si-vinyl functional groups have been prepared: hexakis(dimethylsiloxy)cyclotrisiloxane (**I**), hexakis(vinyl-dimethylsiloxy)cyclotrisiloxane (**II**), octakis(dimethylsiloxy)cyclotetrasiloxane (**III**) and octakis(vinyl-dimethylsiloxy)cyclotetrasiloxane (**IV**). Reaction of pseudo wollastonite ( $\text{Ca}_3\text{Si}_3\text{O}_9$ ) with dimethylchlorosilane or vinyl-dimethylchlorosilane gives **I** and **II**, respectively. **IV** has been prepared similarly by reaction of octakis[chloro calcium oxy]cyclotetrasilicate [ $\text{Ca}_8\text{Si}_4\text{O}_{12}\text{Cl}_8$ ] with vinyl-dimethylchlorosilane. On the other hand, acid catalyzed siloxane exchange between tetramethyldisiloxane and octakis(trimethylsiloxy)cyclotetrasiloxane (**V**) gave **III**. Cyclic silicates (**I–VI**) are surprisingly resistant to acid catalyzed ring opening polymerization. In addition, **II**, **IV**, **V** and hexakis(trimethylsiloxy)cyclotrisiloxanes (**VI**) are resistant to phosphazene  $\text{P}_4$ -*t*-Bu superbase catalyzed ring opening polymerization.

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### 1. Introduction

Tetrakis(dimethylsiloxy)silane and tetrakis(vinyl-dimethylsiloxy)silane are examples of well known commercially available tetra-functional silicates. On the other hand, analogous polyfunctional six- and eight-membered cyclic silicates are not known. There is considerable interest in highly branched materials. Such reactive cyclic silicates might serve as the focal point for the preparation of dendrimers or star polymers.

Both six- and eight-membered polyfunctional cyclic silicates were prepared from wollastonite, an inexpensive linear calcium silicate mineral. Heating wollastonite to 750–800 °C in the presence of calcium chloride dihydrate leads to formation of octakis[chloro calcium oxy]cyclotetrasilicate [ $\text{Ca}_8\text{Si}_4\text{O}_{12}\text{Cl}_8$ ] an eight-membered cyclic

silicate [1]. On the other hand, heating wollastonite to ~1300 °C gives pseudo wollastonite ( $\text{Ca}_3\text{Si}_3\text{O}_9$ ), a six-membered calcium silicate [2,3]. These reactions may be analogous to the well known thermal reversion reaction which converts linear polydimethylsilicone (PDMS) into cyclic oligomers such as octamethylcyclotetrasiloxane ( $\text{D}_4$ ) and hexamethylcyclotrisiloxane ( $\text{D}_3$ ) [4] (see Fig. 1).

Hexakis(trimethylsiloxy)cyclotrisiloxanes (**VI**) has been prepared by reaction of  $\text{Ca}_3\text{Si}_3\text{O}_9$  with trimethylchlorosilane in a mixture of acetone and water [2]. Likewise, we have prepared octakis(trimethylsiloxy)cyclotetrasiloxane (**V**) by reaction of  $\text{Ca}_8\text{Si}_4\text{O}_{12}\text{Cl}_8$  with trimethylchlorosilane.

Trimethylsiloxy groups bonded to silicon are stable under many reaction conditions. On the other hand, Si–OR, Si–H and Si-vinyl are reactive. Compounds which contain Si–OR bonds are reactive in nucleophilic displacement reactions and toward hydrolysis in hydroxylic solvents. On the other hand, Si–H and Si-vinyl groups are stable towards neutral hydroxylic solvents

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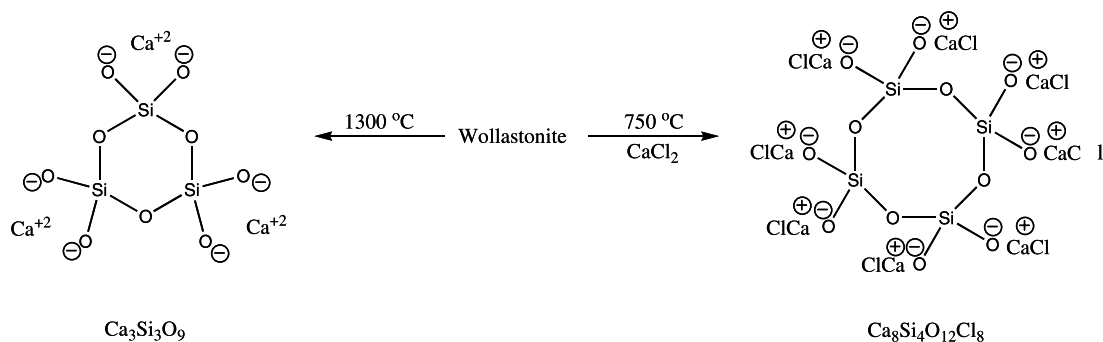


Fig. 1. Conversion of wollastonite to  $\text{Ca}_3\text{Si}_3\text{O}_9$  and to  $\text{Ca}_8\text{Si}_4\text{O}_{12}\text{Cl}_8$ .

but easily undergo platinum catalyzed hydrosilylation reactions. In this regard, octakis(ethoxy)cyclotetrasiloxane has been prepared by reaction of ethanol/HCl with  $\text{Ca}_8\text{Si}_4\text{O}_{12}\text{Cl}_8$ . However, a similar reaction of  $\text{Ca}_3\text{Si}_3\text{O}_9$  with propanol has been reported not to give the expected hexakis(propanoxy)cyclotrisiloxane rather an alicyclic silicate, octakis(propanoxy)trisiloxane, was isolated. Apparently ring opening of the six-membered silicate ring occurs under these reaction conditions [5].

## 2. Results and discussion

Cyclic silicates substituted with Si—H or Si-vinyl groups have **not** been previously reported. Herein, we report the preparation, albeit in low yield (9%), of hexakis(dimethylsiloxy)cyclotrisiloxanes (**I**) by reaction of dimethylchlorosilane with  $\text{Ca}_3\text{Si}_3\text{O}_9$ . We have synthesized hexakis(vinyl dimethylsiloxy)cyclotrisiloxane (**II**), in a similar manner, by reaction of vinyl dimethylchlorosilane with  $\text{Ca}_3\text{Si}_3\text{O}_9$  in 14% yield (see Fig. 2).

Octakis(vinyl dimethylsiloxy)cyclotetrasiloxane (**IV**) has been prepared similarly by reaction of  $\text{Ca}_8\text{Si}_4\text{O}_{12}\text{Cl}_8$  with vinyl dimethylchlorosilane in 30% yield (see Fig. 3).

On the other hand, attempts to prepare octakis(dimethylsiloxy)cyclotetrasiloxane in a similar manner by reaction of  $\text{Ca}_8\text{Si}_4\text{O}_{12}\text{Cl}_8$  with dimethylchlorosilane failed.

An unexpected observation lead us to a successful synthetic route to **III**. Octamethylcyclotetrasiloxane ( $\text{D}_4$ ) and hexamethylcyclotrisiloxane ( $\text{D}_3$ ) both undergo rapid acid catalyzed ring opening polymerization (ROP). In fact, acid catalyzed ROP of  $\text{D}_4$  in the presence of hexamethyldisiloxane, an end-capping reagent, is an industrial method used to prepare  $\alpha, \omega$ -bis-trimethylsiloxy PDMS which has a controlled most probable molecular weight distribution ( $M_w/M_n = 2$ ) [6]. Similarly, acid catalyzed ROP of  $\text{D}_4$  in the presence of tetramethyldisiloxane provides easy access to  $\alpha, \omega$ -dihydrido-PDMS with  $M_w/M_n = 2$  [7]. Nevertheless, attempts to carry out similar acid catalyzed polymerization of either **VI** or **V** in the presence of a small

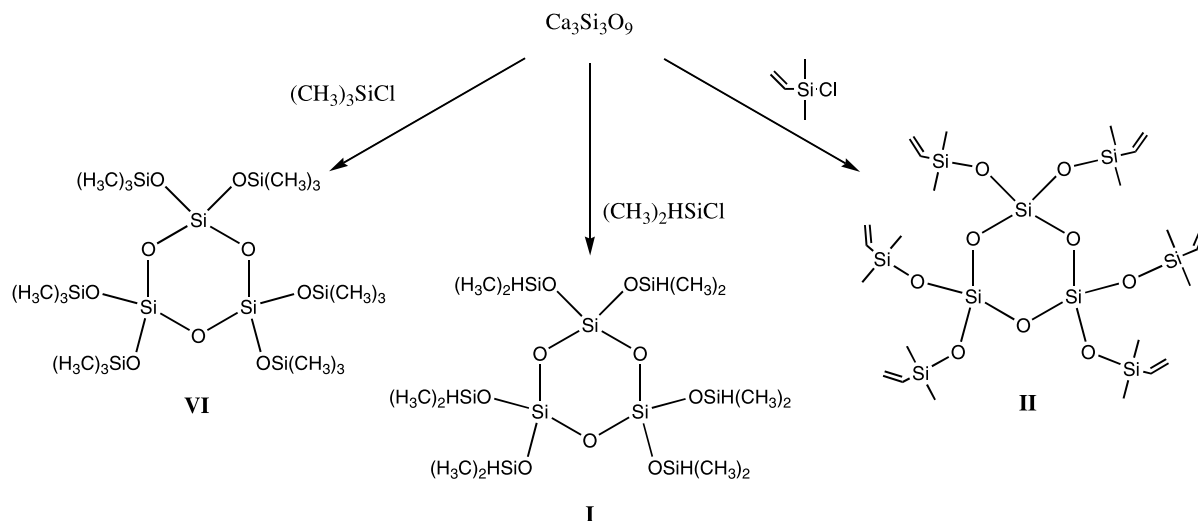


Fig. 2. Conversion of  $\text{Ca}_3\text{Si}_3\text{O}_9$  to **I**, **II** and **VI**.

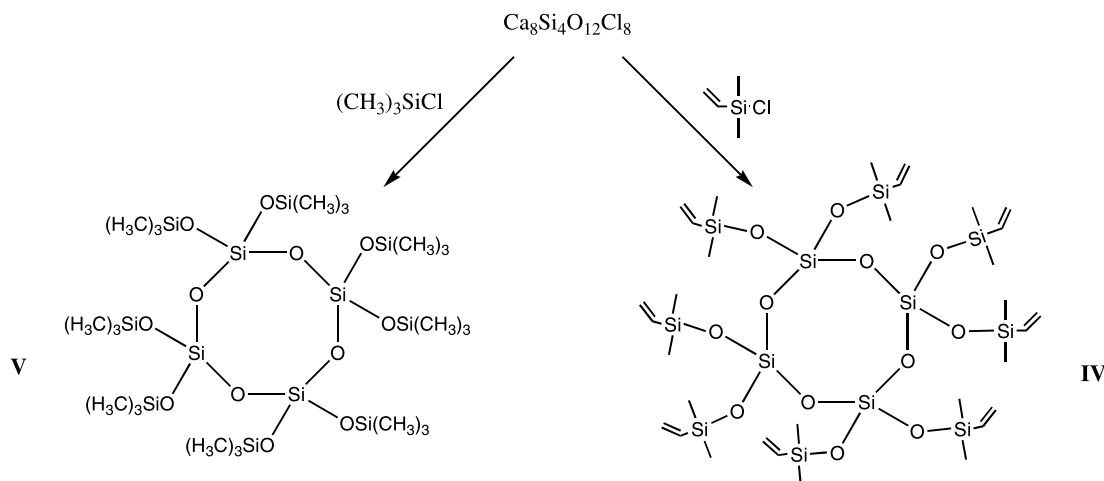


Fig. 3. Conversion of  $\text{Ca}_8\text{Si}_4\text{O}_{12}\text{Cl}_8$  to **IV** and **V**.

amounts of hexamethyldisiloxane and triflic acid gave only recovered starting materials.

On the other hand, when polymerization of **V** was carried out in the presence of a small amount of tetramethyldisiloxane with triflic acid as catalyst, pentamethyldisiloxane, hexamethyldisiloxane and heptakis(trimethylsilyloxy)dimethylsiloxycyclotetrasiloxane were identified by GC/MS. Apparently, while **V** does not undergo acid catalyzed polymerization, it does undergo acid catalyzed siloxane exchange. Such acid catalyzed exchange is well known for disiloxanes [8]. For example, heating hexamethyldisiloxane and tetramethyldisiloxane in the presence of a catalytic amount of triflic acid leads to equilibrium mixture of hexamethyldisiloxane, pentamethyldisiloxane and tetramethyldisiloxane. We have prepared **III** by a similar triflic acid catalyzed exchange reactions of **V** with a large excess of tetramethyldisiloxane (see Fig. 4).

Both  $\text{D}_3$  and  $\text{D}_4$  also undergo base catalyzed ROP to yield PDMS. In such anionic ring opening polymerizations,  $\text{D}_3$  is much more reactive than  $\text{D}_4$  [6]. Lithium silanolates are effect catalysts for ROP of  $\text{D}_3$  in THF at low temperature.  $\text{D}_4$ , on the other hand, will undergo ROP catalyzed by strong bases at moderate tempera-

tures. Recently, the phosphazene superbase  $\text{P}_4$ -*t*-Bu has been shown to be a particularly effective for ROP of  $\text{D}_4$  systems [9–13]. This difference in reactivity has been attributed to ring strain of the  $\text{D}_3$  ring.

Despite the increased reactivity of cyclotrisiloxanes, neither cyclic six-membered silicate: **VI**, nor **II** undergo ROP catalyzed by  $\text{P}_4$ -*t*-Bu. Similarly, neither eight-membered cyclic silicates: **V** nor **IV**, undergo ROP catalyzed by  $\text{P}_4$ -*t*-Bu superbase. Similar experiments were not carried out either with **I** or with **IV** since the Si–H bonds of these are not stable under basic conditions in the presence of even small amounts of adventitious moisture.

On the other hand, the Si–H and Si–vinyl bonds of these cyclic silicates are reactive under platinum catalyzed hydrosilylation conditions. This provides a method to introduce these interesting units into more complicated molecules. The chemistry of octavinylsilsesquioxane  $(\text{CH}_2=\text{CH})_8[\text{SiO}_{3/2}]_8$  [14] may provide suggestions which can be applied to **IV** while the chemistry of octahydridosilsesquioxane  $[\text{HSiO}_{3/2}]_8$  [15] and  $[\text{H}(\text{CH}_3)_2\text{SiOSiO}_{3/2}]_8$  [16] may provide concepts which can provide inspiration in developing the chemistry of **III**. Clearly, the results reported here suggest

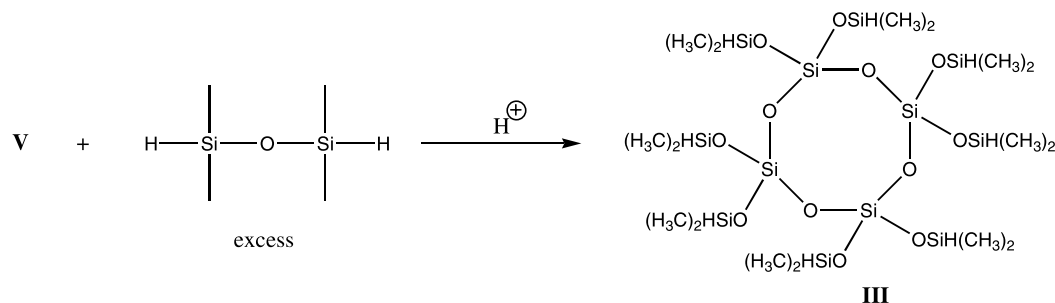


Fig. 4. Acid catalyzed equilibration of **V** with tetramethyldisiloxane to give **III**.

that these cyclic silicates are stable to both acidic and basic conditions. This is quite different from that observed for D<sub>3</sub> and D<sub>4</sub>.

### 3. Experimental

<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR were obtained on a Bruker AMX-500 spectrometer. Five percent w/v C<sub>6</sub>D<sub>6</sub> solutions were used to obtain <sup>1</sup>H NMR spectra. Fifty percent w/v C<sub>6</sub>D<sub>6</sub> solutions were used to obtain <sup>13</sup>C and <sup>29</sup>Si NMR spectra. <sup>13</sup>C NMR spectra were obtained with broad band proton decoupling. <sup>29</sup>Si NMR were run using a NO-NOE pulse sequence with a pulse delay of 60 sec. <sup>1</sup>H and <sup>13</sup>C NMR spectra were internally referenced to residual C<sub>6</sub>H<sub>6</sub>. <sup>29</sup>Si NMR spectra were externally referenced to TMS. IR spectra of neat films on AgCl plates were recorded on a Perkin–Elmer Spectrum 2000 FT-IR spectrometer.

All reactions were run in flame dried flasks equipped with a Teflon covered magnetic stir bar under nitrogen. D<sub>4</sub>, D<sub>3</sub>, vinyl dimethylchlorosilane, dimethylchlorosilane, wollastonite were purchased from Gelest (Tullytown, PA).

High resolution mass spectra were run at the University of California at Riverside Mass Spectroscopy Facility on a VG-76070 EHF instrument. Exact masses were determined by peak matching against known masses of perfluorokerosene. Ammonia was employed as the chemical ionization agent.

#### 3.1. Pseudo wollastonite (Ca<sub>3</sub>Si<sub>3</sub>O<sub>9</sub>)

Wollastonite (250 g, 0.71 mol) was placed in a graphite crucible (3" × 5" × 2") and was heated at 1300 °C for 4 h in a Carbolite RHF 14/35 silicon carbide furnace to give a white chalk like material [2].

#### 3.2. Octakis(trimethylsiloxy)cyclotetrasiloxane (V)

Wollastonite (4 g, 34 mmol) and CaCl<sub>2</sub> · 2H<sub>2</sub>O (10.1 g, 68 mmol) were thoroughly ground together in a mortar and pestle. This mixture was then placed in a carbon boat which was inserted into a quartz tube. The quartz tube and its contents were heated to 775 °C for 17 h in a tube furnace while nitrogen gas was passed through the tube. After cooling to room temperature, 10.4 g of Ca<sub>8</sub>Si<sub>4</sub>O<sub>12</sub>Cl<sub>8</sub>, a hygroscopic white solid was obtained. This was ground to a fine powder in a mortar and pestle under nitrogen. The powder (4.4 g, 4.8 mmol) was placed in a 250 mL round bottom flask equipped with a reflux condenser. Trimethylchlorosilane (5 g, 46 mmol) and acetone (100 mL) were added. The mixture was refluxed for 24 h. The solution was then filtered and the volatiles were removed by evaporation under reduced pressure. The residue was passed through a silica

gel column with hexane as the eluting solvent. The hexane was removed by evaporation under reduced pressure to yield 1.2 g, 32% yield of white crystals mp 170 °C. <sup>1</sup>H NMR δ: 0.12 (s). <sup>13</sup>C NMR δ: 1.56. <sup>29</sup>Si NMR δ: 10.23 (s, 2Si), -108.1 (s, 1Si). IR ν: 2959, 2901, 1941, 1418, 1251, 1060, 841, 755, 603 cm<sup>-1</sup>. The spectral properties of this material were in complete agreement with those previously reported [17].

#### 3.3. Octakis(vinyl dimethylsiloxy)cyclotetrasiloxane (IV)

Ca<sub>8</sub>Si<sub>4</sub>O<sub>12</sub>Cl<sub>8</sub>, a white powder (3.9 g, 4.3 mmol) and dry acetone (100 mL) were reacted with vinyl dimethylchlorosilane (5.2 g, 43 mmol) as above. White crystals, mp 160 °C, 1.3 g, 30% yield were obtained. <sup>1</sup>H NMR δ: 0.18 (s, 48 H), 5.75 (dd, 8 H, J = 20 and 4 Hz), 5.92 (dd, 8 H, J = 15 and 4 Hz), 6.13 (dd, 8 H, J = 20 and 15 Hz). <sup>13</sup>C NMR δ: 0.24, 132.1, 138.9. <sup>29</sup>Si NMR δ: -1.5 (s, 16Si), -108.6 (s, 8Si). IR ν: 3185, 3054, 3015, 2961, 1913, 1597 (C=C), 1065, 771 cm<sup>-1</sup>. Chemical ionization HRMS calcd for C<sub>32</sub>H<sub>72</sub>O<sub>12</sub>Si<sub>12</sub>Na: 1007.2147, found [MNa]<sup>+</sup>: 1007.2182.

#### 3.4. Octakis(dimethylsiloxy)cyclotetrasiloxane (III)

V (1.0 g, 1.1 mmol) and tetramethyldisiloxane (11.8 g, 88.0 mmol) were placed in 25 mL round bottom flask equipped with a reflux condenser and a Teflon-covered magnetic stir bar. Triflic acid (10 μL) was added. The reaction was stirred for overnight at reflux. The mixture was allowed to cool to room temperature and 0.5 g MgCO<sub>3</sub> and 5 mL CH<sub>2</sub>Cl<sub>2</sub> were added. The solution was stirred for 0.5 h, filtered and the volatiles were removed by evaporation under reduced pressure. A clear colorless waxy solid, 0.70 g, 80% yield was obtained. <sup>1</sup>H NMR δ: 0.23 (d, 48 H, J = 2.5 Hz), 4.73 (septet, 8 H, J = 3.0 Hz). <sup>13</sup>C NMR δ: 0.24. <sup>29</sup>Si NMR δ: -3.64 (d, 8Si, J = 4.5 Hz), -107.16 (s, 4Si). IR ν: 2964, 2905, 2139 (Si–H), 1422, 1255, 1072, 902, 837, 767, 631, 545 cm<sup>-1</sup>.

#### 3.5. Hexakis(trimethylsiloxy)cyclotrisiloxanes (VI)

This compound was prepared in 30% yield by reaction of Ca<sub>3</sub>Si<sub>3</sub>O<sub>9</sub> with trimethylchlorosilane in acetone following the literature methods. <sup>29</sup>Si NMR δ: 10.9 (6Si), -99.8 (3Si) [17].

#### 3.6. Hexakis(vinyl dimethylsiloxy)cyclotrisiloxane (II)

Ca<sub>3</sub>Si<sub>3</sub>O<sub>9</sub> (17.0 g, 49 mmol) was dissolved in a mixture of dry acetone (56.4 mL) and *t*-butanol (0.74 mL). Vinyl dimethylchlorosilane (24.0 mL, 176 mmol) was added. The mixture was refluxed for 12 h. Volatiles were removed by evaporation under vacuum. The residue was distilled at 141–143 °C/0.6 mm. A clear liquid, 4.4 g, 13.6% yield, was obtained. <sup>1</sup>H NMR δ: 0.24 (s, 36 H),

5.84 (dd, 6 H,  $J = 20.0$  and  $3.8$  Hz), 5.99 (dd, 6 H,  $J = 14.7$  and  $3.7$  Hz), 6.18 (dd, 6 H,  $J = 20.2$  and  $14.9$  Hz).  $^{13}\text{C}$  NMR  $\delta$ : 0.28, 132.77, 138.81.  $^{29}\text{Si}$  NMR  $\delta$ :  $-3.9$  (s, 6Si),  $-103.7$  (s, 3Si). IR  $\nu$ : 3048, 3013, 2956, 2900, 1598, 1410, 1273, 1253, 1122, 1045, 1002, 954, 837, 783  $\text{cm}^{-1}$ . Elemental Anal. Calc. for  $\text{C}_{24}\text{H}_{54}\text{O}_9\text{Si}_9$ : C, 39.98; H, 7.36. Found: C, 39.86; H, 7.24%.

### 3.7. Hexakis(dimethylsiloxy)cyclotrisiloxane (I)

$\text{Ca}_3\text{Si}_3\text{O}_9$  (30.0 g, 86 mmol) was dissolved in a mixture of dry acetone (56.4 mL) and *t*-butanol (0.74 mL). Dimethylchlorosilane (34 mL, 308 mmol) was added. The mixture was refluxed for 12 h. Volatiles were removed by evaporation under vacuum. The residue was distilled through a 15 cm vacuum jacketed Vigreux column. A fraction bp 82–83 °C/0.05 mm, 4.4 g, 8.8% yield was obtained.  $^1\text{H}$  NMR  $\delta$ : 0.22 (s, 36 H), 4.72 (s, 6 H).  $^{13}\text{C}$  NMR  $\delta$ : 0.390.  $^{29}\text{Si}$  NMR  $\delta$ :  $-8.4$  (s, 6 Si),  $-105.2$  (s, 3Si). IR  $\nu$ : Si–H at 2137  $\text{cm}^{-1}$ . High resolution mass spectrum calculated for  $[\text{C}_{12}\text{H}_{41}\text{O}_9\text{Si}_9]^+$ , (M-1) $^+$ : 581.0674, observed 581.0706.

## 4. Summary

Direct synthetic routes, albeit in low yields, to six- and eight-membered cyclic silicates completely substituted with reactive Si–H or Si-vinyl groups have been developed. The silicate ring structure of these is quite resistant to both strong acid and strong base catalyzed ring opening. On the other hand, acid catalyzed siloxane exchange of substituent silyl groups is observed. This has been used to prepare certain derivatives, e.g. **III**.

These may be useful as focal points for the synthesis six- and/or eight-branched star polymers or dendrimers.

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