

# Novel fluoride ion mediated synthesis of unsymmetrical siloxanes under phase transfer catalysis conditions

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## Abstract

Unsymmetrical siloxanes have been prepared from silanols or hydrosilanes using phase transfer catalytic (PTC) systems  $\text{Me}_3\text{SiN}_3$ –CsF–18-crown-6–toluene or  $\text{Me}_3\text{SiN}_3$ –CsF–18-crown-6– $\text{H}_2\text{O}$ –toluene, correspondingly. The target unsymmetrical siloxanes were prepared in yields up to 100%. Quantum chemical calculation of mechanism of unsymmetrical siloxanes formation has been performed.

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*Keywords:* Fluoride ion; Unsymmetrical siloxanes; Phase transfer catalysis

## 1. Introduction

Siloxanes [1,2] are of interest as potential materials with specific properties [3–6] and biologically active compounds [7]. Unsymmetrical disiloxanes were usually obtained in the reaction of corresponding silanol with chlorosilane–pyridine [8,9], Na–chlorosilane [9–11], chlorosilane–NaOH–EtOH [12], aminosilane [8,13,14], alkoxysilane [15–23], acyloxysilane [24] or silanol–HCl–dioxane [25]. Hydrosilanes and silanols were converted to unsymmetrical siloxanes in the presence of zinc and cadmium halides–DMF [26–29], rhodium complex catalysts [30–32], Pd–C [33] or dibutyltin diacetate, dilaurate or di(2-ethyl)hexanoate [34]. Unsymmetrical siloxanes were also obtained in the reaction of chlorosilanes in presence of symmetric siloxane– $\text{FeCl}_3$  [35], symmetric siloxane under elevated pressure at 300 °C [36] or chlorosilane–PhH– $\text{H}_2\text{O}$  [37], and by oxidation of hydrosilanes with bis(trimethylsilyl)peroxide [38]. However, the yields and selectivity in the synthesis of unsymmetrical siloxanes usually not high.

Fluoride ion as activator of silicon bonds is widely used in silylation reactions [39–42]. Recently O-silylation of alcohols and phenols by  $\text{Me}_3\text{SiN}_3$  in the presence of  $\text{Bu}_4\text{NBr}$  [43] and carboxylic acids in the system  $\text{Me}_3\text{SiN}_3$ –CsF–18-crown-6 [44] was described. The aim of this work was to examine the phase transfer catalytic (PTC) system  $\text{Me}_3\text{SiN}_3$ –CsF–18-crown-6–toluene containing water (or without it) for the synthesis of unsymmetrical siloxanes from silanols and hydrosilanes.

## 2. Results and discussion

We have found that reaction of hydrosilanes ( $\text{R}'\text{R}''\text{R}'''\text{SiH}$ ) with azidotrimethylsilane in the system CsF–18-crown-6– $\text{H}_2\text{O}$ –toluene readily proceeds at 50 °C to afford unsymmetrical siloxanes ( $\text{R}'\text{R}''\text{R}'''\text{SiOSiMe}_3$ ) as main products, along with a small amount of corresponding symmetrical siloxanes ( $\text{R}'\text{R}''\text{R}'''\text{SiOSiR}'\text{R}''$ ). Formation of disiloxane  $\text{Me}_3\text{SiOSiMe}_3$  was not detected (GC–MS data).

The influence of amount of CsF and water in the reaction of dimethylphenylsilane (**2**) with azidotrimethylsilane (Table 1) was studied. It was found that one equivalent of CsF and water was optimal amount of reagents for the selective synthesis of unsymmetrical

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Table 1  
Products of PTC reaction of dimethylphenylsilane (**2**) with azidotrimethylsilane at 50 °C during 20 h

| CsF (equivalent) | Me <sub>3</sub> SiN <sub>3</sub> (equivalent) | H <sub>2</sub> O (equivalent) | Relative content after reaction completion (%) (GC data) |  |   |
|------------------|---|-------------------------------|--|--|---|
|                  |   |                               | PhMe <sub>2</sub> SiH                                    | PhMe <sub>2</sub> SiOSiMe <sub>3</sub> | PhMe <sub>2</sub> SiOSiMe <sub>2</sub> Ph |
| 1                | 3   | 1                             | 0  | 90                                     | 10  |
| 0.5              | 3   | 1                             | 3  | 71                                     | 26  |
| 0.2              | 3   | 1                             | 8  | 82                                     | 10  |
| 1                | 3   | 0.2                           | 59   | 40                                     | 1   |
| 1                | 3   | 2                             | 0  | 61                                     | 39  |
| 0                | 3   | 1                             | 100  | 0                                      | 0   |
| 1                | 2   | 1                             | 0  | 74                                     | 26  |
| 1                | 4   | 1                             | 0 <sup>a</sup>   | 41                                     | 22  |

<sup>a</sup> 37% of PhMe<sub>2</sub>SiN<sub>3</sub>.

pentamethylphenyldisiloxane (**7**) (selectivity 90%, preparative yield 70%). In the absence of cesium fluoride the formation of siloxane **7** was not observed.

The selectivity of pentamethylphenyldisiloxane (**7**) synthesis was influenced also by amount of azidotrimethylsilane. Thus, interaction of hydrosilane with three equivalents of Me<sub>3</sub>SiN<sub>3</sub> leads to desired disiloxane **7** in 90% selectivity. In the presence of two equivalents of azide the selectivity of disiloxane **7** formation was lower. Interestingly, that reaction of PhMe<sub>2</sub>SiH with large excess of azidotrimethylsilane (four equivalents) in the system (above mentioned) leads to formation of three products: PhMe<sub>2</sub>SiOSiMe<sub>3</sub> (41%), PhMe<sub>2</sub>SiOSiMe<sub>2</sub>Ph (22%) and PhMe<sub>2</sub>SiN<sub>3</sub> (37%) (GC–MS data). We supposed that the formation of azidodimethylphenylsilane [45,46] occurs from corresponding hydrosilane (PhMe<sub>2</sub>SiH) and Me<sub>3</sub>SiN<sub>3</sub> by fluoride ion mediated transfer of azido group.

The catalytic system Me<sub>3</sub>SiN<sub>3</sub>–solid CsF–18-crown-6 (molar ratio hydrosilane:Me<sub>3</sub>SiN<sub>3</sub>:CsF:18-crown-6 = 1:3:0.1:0.1) as the most active was used in the synthesis of unsymmetric siloxanes **6–9** from hydrosilanes **1** to **4** (Scheme 1). The siloxanes **6–9** were obtained in 45–70% yields (Table 2). This method was used also in the synthesis of trisiloxane **9** (yield 33%) from diphenylsilane (**4**) and six equivalents of Me<sub>3</sub>SiN<sub>3</sub>. Unfortunately, the yields of corresponding siloxanes **7** and **8** were not high due to sterical hindrance.

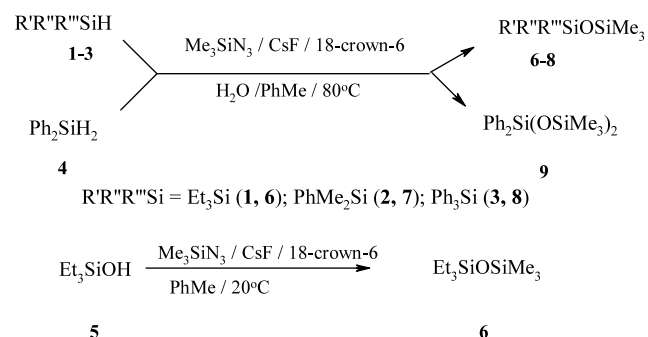


Table 2  
Synthesis of siloxanes **6–9** from hydrosilanes and Me<sub>3</sub>SiN<sub>3</sub> in the system CsF–18-crown-6–H<sub>2</sub>O–PhMe

| Hydrosilane | Reaction time (h) | Product               | Yield (%) |
|-------------|-------------------|-----------------------|-----------|
| <b>1</b>    | 19                | <b>6</b> [8,35,37]    | 70        |
| <b>2</b>    | 20                | <b>7</b> [38,47]      | 63        |
| <b>3</b>    | 25                | <b>8</b> [9,10,15,25] | 45        |
| <b>4</b>    | 20                | <b>9</b> [48,49]      | 33        |

The reaction of triethylsilanol (**5**) with azidotrimethylsilane in the PTC system CsF–18-crown-6–toluene (molar ratio **5**:Me<sub>3</sub>SiN<sub>3</sub>:CsF:18-crown-6 = 1:1:0.05:0.05) at room temperature led to 1,1,1-triethyl-3,3,3-trimethyldisiloxane (**6**) in quantitative yield during 30 min. Silylation of silanol **5** in the absence of fluoride ion source also occurred at room temperature. However, in this case only about 60% yield of desired product **6** was obtained during 12 h.

Quantum chemical calculations of mechanism of unsymmetrical siloxanes formation in the PTC system was carried out. Selected distances in Å are shown in figures.

We suppose that at the first step of the reaction with water the following complex with crown ether and cesium fluoride is formed [HO<sup>−</sup>–2(18-crown-6)Cs<sup>+</sup>–F<sup>−</sup>–H<sup>+</sup>]. Thus, dissociated water molecule has been transported into organic phase.

The starting state of proton and hydroxyl anion interaction with hydrosilane molecule is shown in Fig. 1. The distance between hydrosilane negative charged hydrogen (−0.232 e) and proton is 2.53 Å. The distance between silicon atom of this molecule and hydroxyl anion is 5.50 Å. At the beginning of the process the proton approaches to negatively charged hydrogen. Then cleavage of silicon–hydrogen bond proceeds with formation of hydrogen molecule. The next step is addition of hydroxyl anion to positively charged silicon and formation of silanol molecule. Final state is shown in the Fig. 2. The heat of reaction is −378.1 kcal mol<sup>−1</sup>.

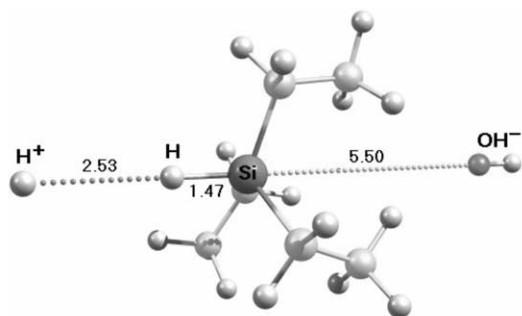


Fig. 1. The initial state of silanol formation.

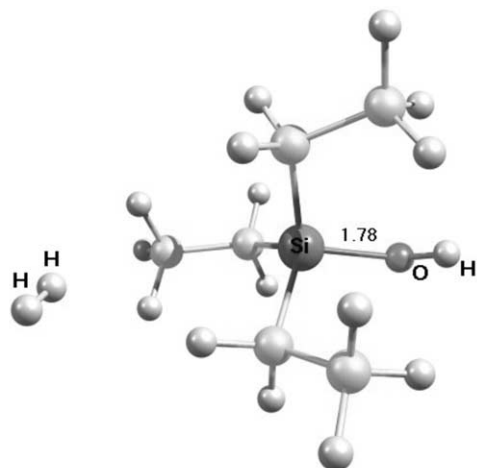


Fig. 2. The formation of hydrogen and silanol molecules.

The calculations show that the silanol formation reaction proceeds spontaneously without an activation barrier.

The Figs. 3 and 4 show the following process: the interaction between silanol and fluoride ion. At first the distance between fluoride anion and positively charged hydrogen atom (+0.211 e) in hydroxyl group is 3.85 Å (Fig. 3). Formation of HF molecule and silanol anion occurred (Fig. 4) as the result of this interaction. The negative charge is located on the oxygen atom (−0.937 e) in silanol anion. The heat of reaction is equal  $-81.5 \text{ kcal mol}^{-1}$ .

The next reaction step is interaction between silanol anion and azidotrimethylsilane (Figs. 5 and 6). At the

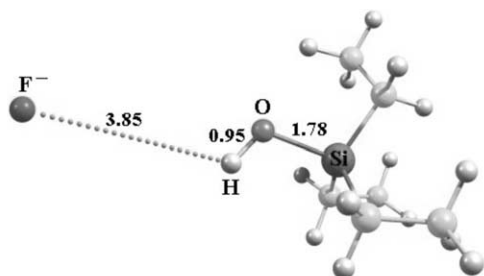


Fig. 3. The fluoride ion attack to silanol hydroxyl group.

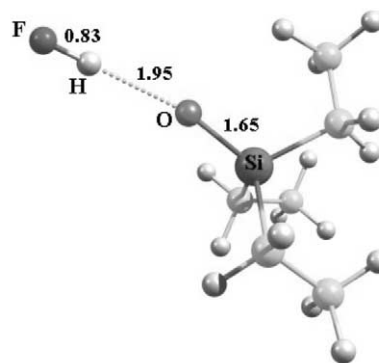


Fig. 4. The silanol anion formation.

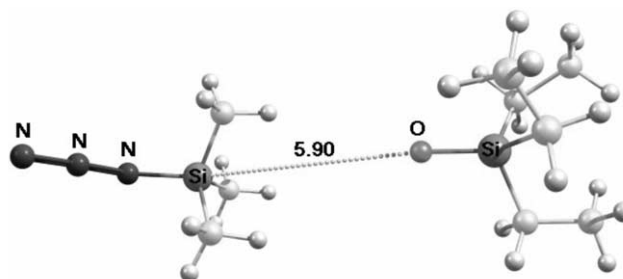


Fig. 5. The initial state of azidotrimethylsilane attack to silanol anion.

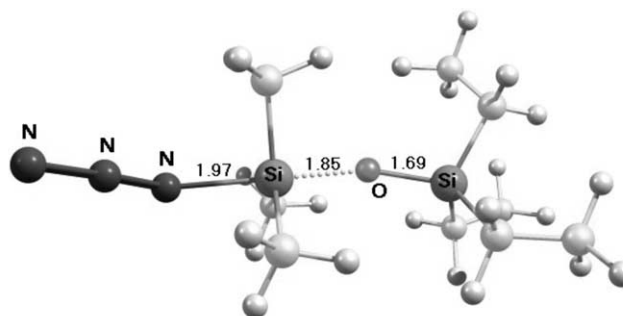


Fig. 6. Azidotrimethylsilane and silanol anion complex formation.

beginning (Fig. 5) the distance between silicon atom in azidotrimethylsilane and oxygen atom is 5.90 Å. Then the formation of complex of azidotrimethylsilane with silanol anion occurred (Fig. 6). Stabilization energy of this complex is  $-35.7 \text{ kcal mol}^{-1}$ . Bond between silicon in azidotrimethylsilane and bridge type oxygen atom is weak because its order is only 0.473. Then negatively charged complex reacted with proton (Fig. 7) from 2(18-crown-6) $\text{Cs}^+ - \text{F}^- - \text{H}^+$  species. During the reaction addition of proton to nitrogen, which is bonded with silicon atom, proceeds. The result of this process is cleavage of Si–N bond, and formation of  $\text{HN}_3$  and unsymmetrical disiloxane (Fig. 8). The heat of reaction is  $-290.3 \text{ kcal mol}^{-1}$ .

The quantum-chemical calculations of the unsymmetrical siloxanes synthesis allows to propose the reaction mechanism described in Fig. 9.

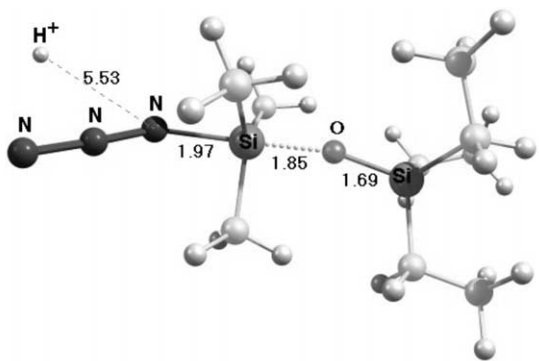


Fig. 7. The interaction of negatively charged complex and proton.

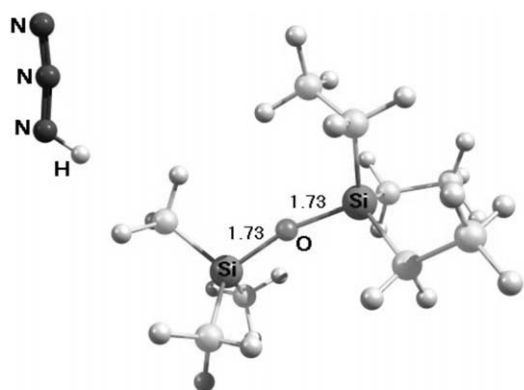


Fig. 8. The unsymmetrical siloxane formation.

### 3. Materials and methods

#### 3.1. Instrumental

MS spectra were registered on a GC–MS HP 6890 (70 eV) apparatus. GC analysis was performed on a Chrom-5 instrument equipped with a flame-ionization detector using a glass column packed with 5% OV-101/Chromosorb W-HP (80–100 mesh) (1.2 m × 3 mm). Azidotrimethylsilane, hydrosilanes, 18-crown-6 (Acros) were used without additional purification. Toluene was distilled over metallic sodium.

#### 3.2. General procedure of dimethylphenylsilane reaction with azidotrimethylsilane under PTC conditions

Dimethylphenylsilane (0.155 ml, 1 mmol) was added to the mixture of freshly calcinated CsF (for amount see Table 1), azidotrimethylsilane (0.397 ml, 3 mmol), water (for amount see Table 1) and 18-crown-6 (0.026 g, 0.1 mmol) in 1.5 ml of dry toluene under argon atmosphere. Reaction was carried out at 50 °C temperature (GC

control—180–250 °C) for 20 h. The products were identified by MS spectra. The results see in Table 1.

#### 3.3. General procedure of hydrosilane reaction with azidotrimethylsilane under PTC conditions

Hydrosilane 1–3 (1 mmol) was added to the mixture of freshly calcinated CsF (0.152 g, 1 mmol), azidotrimethylsilane (0.397 ml, 3 mmol or 0.796 ml, 6 mmol for synthesis of trisiloxane 9), water (0.018 ml, 1 mmol) and 18-crown-6 (0.026 g, 0.1 mmol) in 1.5 ml of dry toluene under argon atmosphere. Reaction was carried out at 70 °C temperature (GC control—180–250 °C) for 20 h. The products were purified by column chromatography (eluent hexane:ethyl acetate in different mixtures). The products were identified by spectroscopic data. The results see in Table 2. The formation of HN<sub>3</sub> (b.p. 36 °C, Caution: explosive on heating) as side product of silylation occurred.

#### 3.4. Synthesis of 1,1,1-triethyl-3,3,3-trimethyldisiloxane (6) from triethylsilanol (5) under PTC conditions

Triethylsilanol (5) (0.306 ml, 2 mmol) was added to the mixture of freshly calcinated CsF (0.0152 g, 0.1 mmol), azidotrimethylsilane (0.264 ml, 2 mmol) and 18-crown-6 (0.026 g, 0.1 mmol) in 1.5 ml of dry toluene under argon atmosphere. Reaction was carried out at 20 °C (GC control—150 °C) for 0.5 h. Yield 100% (GC–MS data).

#### 3.5. Theoretical calculations

All calculations were carried out using the semiempirical AM1 [50] method as implemented in MOPAC 6 [51]. All structures were fully optimized using the eigenvector following routine under the more rigorous criteria of the keyword PRECISE. Starting states of molecular systems (Figs. 1, 3, 5 and 7) preceding optimization were selected without constraints and with sufficient distances between reacting particles. The frequencies analysis has shown that all optimum structures present the minimum points on the potential energy surface. The heat of reactions was calculated as a difference between the heat of the final system formation and the sum of heat of formation of reagents. All studied reactions proceed spontaneously (barrierless). To obtain the data on the change in geometry during the optimization process, calculations were performed using keyword FLEPO. Post processing animation was carried out with JMOL [52] program. Computer design of the reaction system was realized by means of the CHEMCRAFT software package [53].

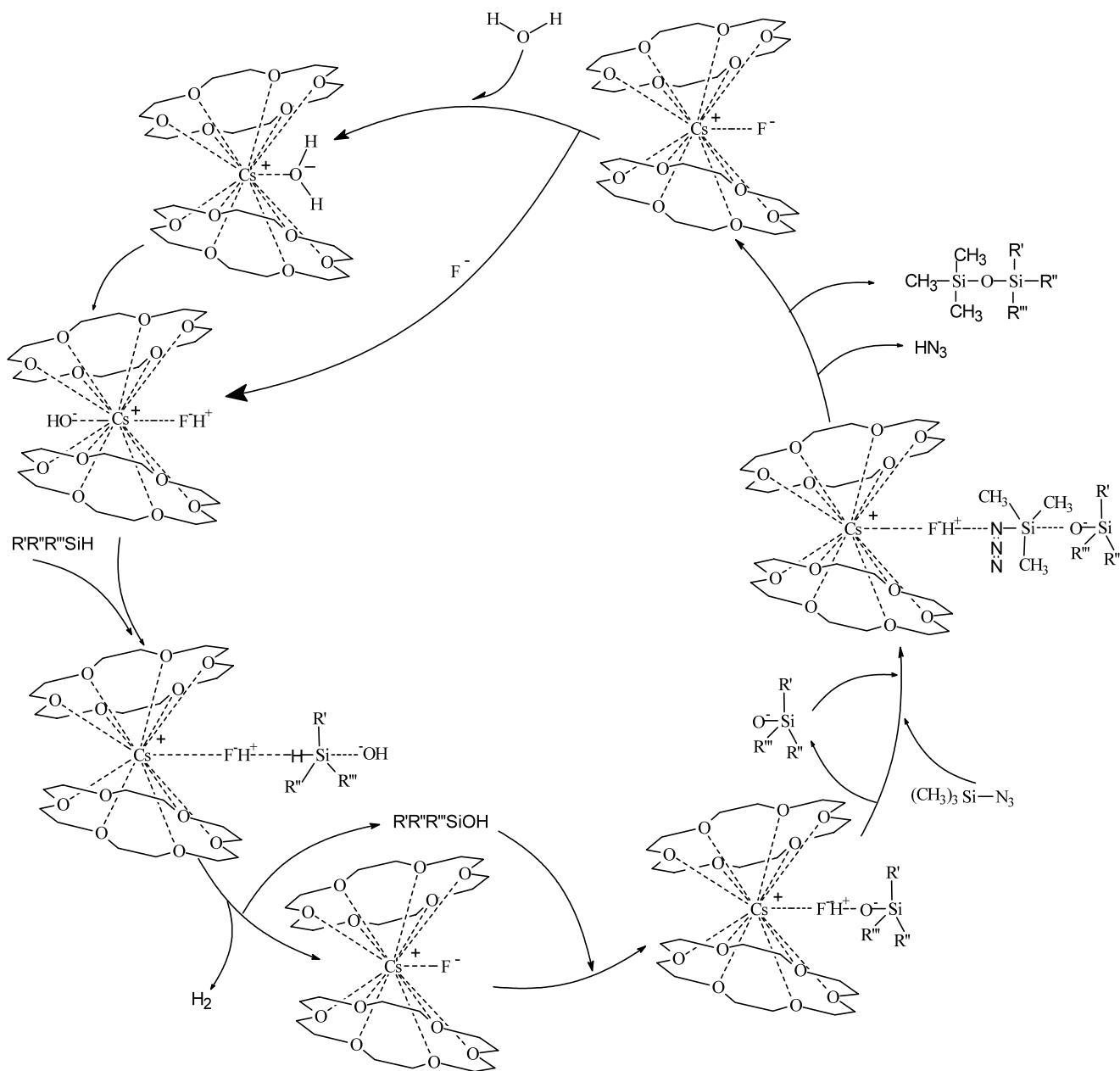


Fig. 9. Mechanism of unsymmetrical siloxanes formation.

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