

# The electrochemistry of tetramesityldisilene, $\text{Mes}_2\text{Si}=\text{SiMes}_2$

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The outcome of the controlled potential oxidation and reduction of a disilene, tetramesityldisilene (TMDS), indicates that the main silicon containing products involve only one silicon atom and have the general structure  $\text{Mes}_2\text{SiX(Y)}$ , X and Y being H, OH or F.

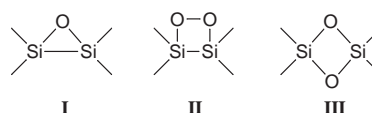
A great deal of progress has been made in disilene chemistry since the isolation of the first stable disilene in 1981.<sup>1</sup> Advances in the chemistry of stable (and marginally stable) disilenes are described in a recent review,<sup>2</sup> and several other reviews covering Si=Si double bonds have been published.<sup>3–6</sup> The disilenes are far more reactive than their alkene counterparts. Even though the stable disilenes are sterically hindered, they are remarkably reactive toward many electrophilic and nucleophilic reagents, providing a complex and elaborate chemistry of the Si=Si double bond.<sup>2–6</sup>

Information in the literature on the electrochemical behavior of disilenes is very limited. To the best of our knowledge, the only published work related to cyclic voltammetry measurements.<sup>7</sup> All tetraaryl- and dialkyldiaryl-disilenes investigated exhibited one irreversible oxidation wave and one irreversible reduction wave. The oxidation potentials were similar (0.4–0.5 V vs. SCE), indicating that the highest occupied molecular orbital (HOMO) of each species lies at approximately the same energy level. However, their reduction potentials were found to be dependent on the substitution pattern, –2.0 to –2.2 V for tetraaryldisilenes and about –2.6 V (vs. SCE) for dialkyldiaryldisilenes. These results indicate that the lowest unoccupied molecular orbital (LUMO) of tetraaryldisilenes is lower in energy than the LUMO of dialkyldiaryldisilenes.

The present communication reports for the first time results of the controlled potential electrolysis of a disilene. Tetramesityldisilene,  $\text{Me}_2\text{Si}=\text{SiMe}_2$  (TMDS) was studied by both anodic oxidation and cathodic reduction. The products obtained upon electrochemical oxidation of TMDS in MeCN using  $\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte are shown in Fig. 1. Interestingly, all of the detected products contain only one silicon atom. It seems that the anodic process involves the cleavage of both the  $\pi$  and  $\sigma$  bonds. This behavior is remarkably different from what has been observed by chemical oxidation.

For example, reactions of disilenes with the single-oxygen transfer agents  $\text{N}_2\text{O}$  or azoxybenzene<sup>8</sup> give three-membered

rings of type **I**. Disilenes react with oxygen<sup>8,9</sup> of the air to give compounds **I** and/or 1,2-disiladioxetanes **II**; the latter undergo rearrangement to cyclodisiloxanes **III** in a subsequent step.<sup>10</sup>



Upon comparing the results described in Table 1, column A (in THF) with those in column B (in MeCN), in both cases, the same six products were formed (**1–6**), but the ratio of products which contain fluorine atoms (**1–3**) to those without fluorine atoms (**4–6**) is higher in MeCN. When the electrolyte was changed from  $\text{Bu}_4\text{NPF}_6\text{-MeCN}$  (column B) to  $\text{Et}_4\text{NBF}_4\text{-MeCN}$  (column C), only five products were obtained (**1–5**), the fluorinated ones becoming even more predominant. In  $\text{Bu}_4\text{NClO}_4\text{-MeCN}$  solution (column D), the reaction became more selective to yield three products only, **4–6**. Upon changing the Pt anode material (column C) to glassy carbon (column E), leaving all other conditions the same, the reaction became somewhat less selective and yielded more non-fluorinated products at the expense of the fluorinated ones. Evidently, the preferred products in THF or in the presence of  $\text{ClO}_4^-$  are **5** and **6**, whereas **3** is favored in the presence of  $\text{BF}_4^-$ . The above results indicate that solvent, electrolyte and anode material all play a role in the product outcome upon electrochemical oxidation of tetramesityldisilene.

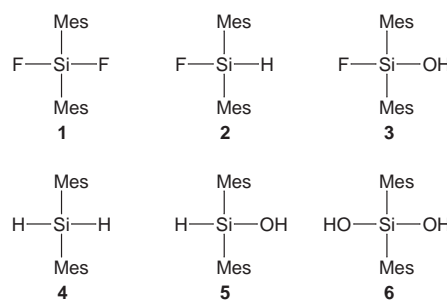
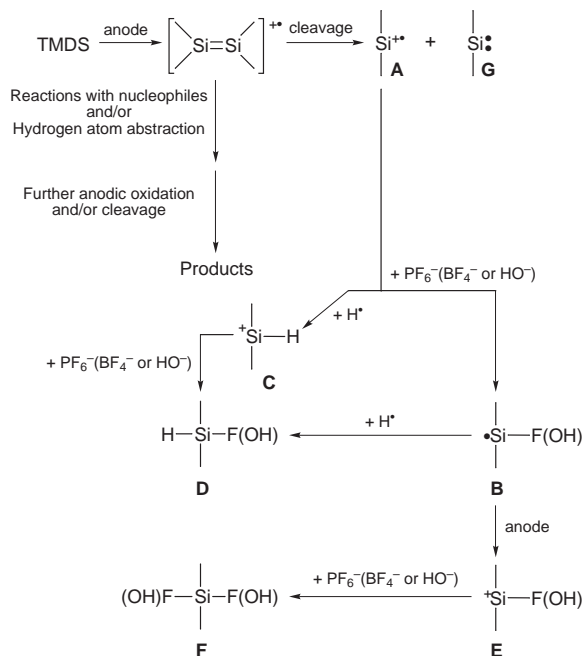


Fig. 1 Molecular structures of products obtained by anodic oxidation of TMDS.

Table 1 Product distribution from electrochemical oxidation of TMDS<sup>11</sup>

Product	Yield (%) <sup>a</sup>					Mass spectrum (EI) ( <i>m/z</i> )
	A	B	C	D	E	
<b>1</b>	5	21	27	—	11	304( $\text{M}^+$ ), 289(100%), 184, 120
<b>2</b>	6	26	11	—	13	286( $\text{M}^+$ ), 271, 166, 120(100%)
<b>3</b>	15	17	40	—	36	302( $\text{M}^+$ ), 287, 182, 120(100%)
<b>4</b>	13	17	5	13	11	268( $\text{M}^+$ ), 253, 148(100%), 120
<b>5</b>	25	13	15	26	19	284( $\text{M}^+$ ), 269, 164, 120(100%)
<b>6</b>	36	6	—	52	10	300( $\text{M}^+$ ), 285, 180(100%), 120

<sup>a</sup> Yields reported are relative and estimated by GLC. A, Electrolyte solution  $0.1 \text{ mol l}^{-1} \text{ Bu}_4\text{NPF}_6\text{-THF}$ ; working electrode: Pt. B, Electrolyte solution:  $0.1 \text{ mol l}^{-1} \text{ Bu}_4\text{NPF}_6\text{-MeCN}$ ; working electrode: Pt. C, Electrolyte solution:  $0.1 \text{ mol l}^{-1} \text{ Et}_4\text{NBF}_4\text{-MeCN}$ ; working electrode: Pt. D, Electrolyte solution:  $0.1 \text{ mol l}^{-1} \text{ Bu}_4\text{NClO}_4\text{-MeCN}$ ; working electrode: Pt. E, Electrolyte solution:  $0.1 \text{ mol l}^{-1} \text{ Et}_4\text{NBF}_4\text{-MeCN}$ ; working electrode: glassy carbon.



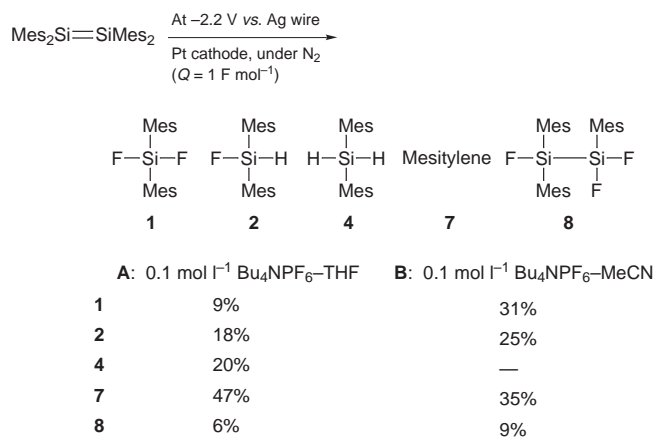
**Scheme 1** Mechanism for the electrochemical oxidation of TMDS.

A plausible mechanism which accounts for the formation of all products in the electrochemical oxidation process is outlined in the over simplified Scheme 1. The initially formed unstable radical cation from TMDS is a highly reactive species and could undergo a number of different reactions, *i.e.* reactions with nucleophiles, abstraction of hydrogen atoms, cleavage, *etc.* For example, the direct cleavage may lead to a radical cation **A** and silylene **G**. The radical cation **A** may undergo an attack by  $\text{PF}_6^-$  ( $\text{BF}_4^-$  or  $\text{HO}^-$ ) anion to form the radical **B**, or abstract a hydrogen atom (from solvent or electrolyte) to generate a silylenium cation **C**, followed by a chemical reaction with a nucleophile to yield **D** (products **2** and **5**). Intermediate **B** could undergo further anodic oxidation to the cation **E**, or abstract a hydrogen atom from its surroundings to generate **D**. Cation **E** may react with  $\text{PF}_6^-$  ( $\text{BF}_4^-$  or  $\text{HO}^-$ ) anion to form **F** (products **1**, **3** and **6**). It is noteworthy that the formation of some of the products outlined in Fig. 1, as well as **4**, could also originate from silylene **G**.

Results of the controlled potential electrochemical reduction<sup>12</sup> of TMDS in both THF and acetonitrile are shown in Scheme 2. A major product found was mesitylene. As in the anodic process, the silicon products (except for compound **8**) contain only one silicon atom, probably due to fragmentation of the initial electrochemically generated anion radical. The same four products (**1**, **2**, **7** and **8**) were obtained both in THF and MeCN. However, an additional product, **4**, was detected in THF.

Surprisingly, some of the products (**1**, **2** and **4**) observed by the electrochemical reduction process are identical to those obtained by the anodic oxidation. Therefore, it is reasonable to suggest that these products could stem from the same intermediate, which might be generated in both types of reactions. Attempts to trap such intermediate and characterize its nature are underway.

The electrochemical reduction of TMDS in MeCN– $\text{Bu}_4\text{NClO}_4$  (0.1 mol  $\text{l}^{-1}$ ) solution was also attempted. The GLC chromatogram indicated the formation of a very complex mixture of products (> 20 peaks!), which has yet to be analysed, among which  $\text{Mes}_2\text{SiH}_2$  and  $\text{Mes}_2\text{Si(H)(OH)}$  could be detected.



**Scheme 2** Results of cathodic reduction of TMDS.

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- All experiments were carried out in a drybox ( $[\text{H}_2\text{O}] < 1 \text{ ppm}$ ;  $[\text{O}_2] < 1 \text{ ppm}$ ), employing controlled potential electrolysis (on Pt) in an 'H' type two-compartment cell and pulsing from 0 to 0.5 V (vs. Ag wire) every 0.5 s. Typically, the working compartment contained 0.1–0.2 mmol of disilene dissolved in 25 ml solution. Electricity consumption is ca. 1 F  $\text{mol}^{-1}$ . Solvents MeCN and THF were distilled over  $\text{P}_2\text{O}_5$  and benzophenone/Na, respectively. All electrolytes were dried under vacuum (ca. 30 mmHg) at 105 °C for 48 h. HRMS results for MH<sup>+</sup>: Found (calc. for M): **1**: 305.1547 (305.1547 for  $\text{C}_{18}\text{H}_{23}\text{F}_2\text{Si}$ ); **2**: 287.1620 (287.1640 for  $\text{C}_{18}\text{H}_{24}\text{FSi}$ ); **3**: 303.1590 (303.1595 for  $\text{C}_{18}\text{H}_{24}\text{FOSi}$ ); **4**: 269.1733 (269.1745 for  $\text{C}_{18}\text{H}_{25}\text{Si}$ ); **5**: 285.1500 (285.1694 for  $\text{C}_{18}\text{H}_{25}\text{OSi}$ ); **6**: 301.1420 (301.1643 for  $\text{C}_{18}\text{H}_{25}\text{O}_2\text{Si}$ ); **7**: 120.0910 (120.0948 for  $\text{C}_9\text{H}_{12}$ ); **8**: 470.2155 (470.2120 for  $\text{C}_{27}\text{H}_{33}\text{F}_3\text{Si}_2$ ).
- The chemical reduction of sterically congested disilenes by alkali metals has not been studied. Formation of disilene anion radicals is reported to result from reductions of the corresponding dichlorodisilenes by alkali metals,<sup>13</sup> but to the best of our knowledge there is no report on the nature of products obtained by reaction/decomposition of this type of anion radical.
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