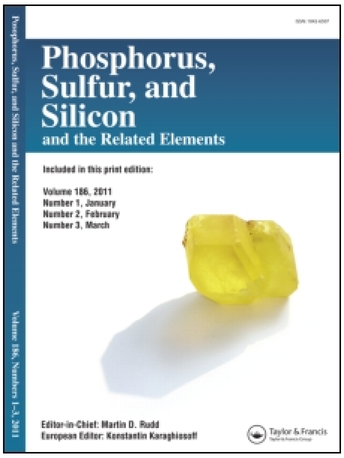

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# Oxidation and Selenization Reactions of a Kinetically Stabilized 1,2-Bisferrocenyldisilene

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# OXIDATION AND SELENIZATION REACTIONS OF A KINETICALLY STABILIZED 1,2-BISFERROCENYLDISILENE

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***The reaction of the first stable (E)-1,2-bisferrocenyldisilene, Tip(Fc)Si=Si(Fc)Tip (Tip = 2,4,6-triisopropylphenyl, Fc = ferrocenyl), with aerobic oxygen afforded the corresponding*** **trans-*****1,3,2,4-dioxadisiletane exclusively, while the reaction of Tip(Fc)Si=Si(Fc)Tip with an excess amount of elemental selenium gave the corresponding*** **trans-*****selenadisilirane in high yield. The structural parameters of the isolated*** **trans-*****1,3,2,4-dioxadisiletane and*** **trans-*****selenadisilirane were revealed by X-ray crystallographic analysis, and the results were compared with those of related compounds.***

**Keywords** 1,2-Bisferrocenyldisilene; 1,3,2,4-dioxadisiletane; disilene; selenadisilirane; X-ray crystallographic analysis

## INTRODUCTION

There has been much interest in the chemistry of doubly bonded organosilicon compounds, especially in that of disilenes.[1] Since the isolation of the first stable disilene, $Mes_2Si=SiMes_2$, by West et al.,[2] a variety of kinetically stabilized disilenes have been synthesized and characterized.[1] In addition, recent attention paid to the elucidation of their reactivity revealed that the cycloaddition reactions of such $\pi$-bond systems of heavier main group elements can be used as convenient methods to obtain novel heterocyclic systems.[3,4] Indeed, $Mes_2Si=SiMes_2$ can be oxidized by atmospheric oxygen giving the corresponding 1,3,2,4-dioxadisiletane derivative,[4] in contrast to most alkenes, which do not react with triplet oxygen ($^3O_2$) under ambient conditions. Furthermore, chalcogenation reactions of disilenes are known to give the corresponding three- or four-membered heterocyclic compounds containing oxygen or chalcogen (S, Se, or Te) atoms.[5] On the other hand, we have recently reported the synthesis and unique properties of the first stable 1,2-bisferrocenyldisilene, (*E*)-Tip(Fc)Si=Si(Fc)Tip (**1**),[6] which is a novel d–$\pi$ system

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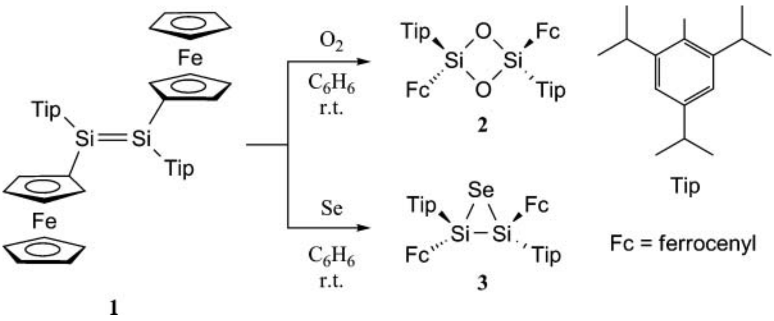
containing an Si=Si double bond and which is a potentially good precursor for novel heterocyclic compounds containing ferrocenyl units. In this sense, it should be important to investigate the reactivity of the Si=Si unit of disilene **1**. In this article, we report the oxidation and selenization reactions of **1** to give the corresponding *trans*-1,3,2,4-dioxadisiletane and *trans*-selenadisilirane derivatives, respectively. The structures of the newly obtained four- and three-membered ring systems were revealed by X-ray crystallographic analysis.

## RESULTS AND DISCUSSIONS

Exposure of the benzene solution of 1,2-bisferrocenyldisilene **1** to air afforded 1,3,2,4-dioxadisiletane **2** as the sole product in 82% isolated yield (Scheme 1). Thus the oxidation reaction of **1** was found to proceed stereospecifically to give **2**. Since the oxidation reactions of many stable disilenes with air oxygen have been reported to give the corresponding 1,3,2,4-dioxadisiletane derivatives usually together with small amount of the corresponding oxadisilirane derivatives,[4,5,7] it should be noted that no byproduct was observed in the case of oxidation reaction of **1** with air oxygen. Of particular note is that the Si=Si moiety of **1** was selectively oxidized with triplet oxygen without suffering the oxidation of the ferrocenyl moiety, although, based on the theoretical calculations, the HOMO of **1** should correspond to the d-orbitals of the Fe atoms.[6] We also examined the reaction of **1** with elemental sulfur in the expectation of obtaining the corresponding 1,3,2,4-thiadisilirane or 1,3,2,4-dithiadisiletane derivative. We isolated indeed two sulfurization products, but their structures have not been determined yet. On the other hand, the selenization reaction of **1** with an excess of elemental selenium afforded selenadisilirane **3** as the sole product in 96% isolated yield. While the selenization reactions of stable disilenes are known to give the corresponding three-, four-, and six-membered heterocycles containing silicon and selenium atoms depending on the bulkiness and/or electronic nature of the substituents on the silicon atoms,[5c,8] compound **1** was found to give the three-membered ring system, selenadisilirane **3**, exclusively. Thus, the reactivity of **1** seems to be predominantly characterized by that of the Si=Si rather than the ferrocenyl unit. In addition, it was found that the reactivity of ferrocenyl-substituted disilene **1** is similar to that of tetramesityldisilene,[5c] which is known to undergo readily a selenization reaction leading to the formation of the corresponding selenadisilirane derivative.



Scheme 1

The structural parameters of **2** and **3** were revealed by X-ray crystallographic analysis. 1,3,2,4-Dioxadisiletane **2** has a center of symmetry in the center of the molecule with a

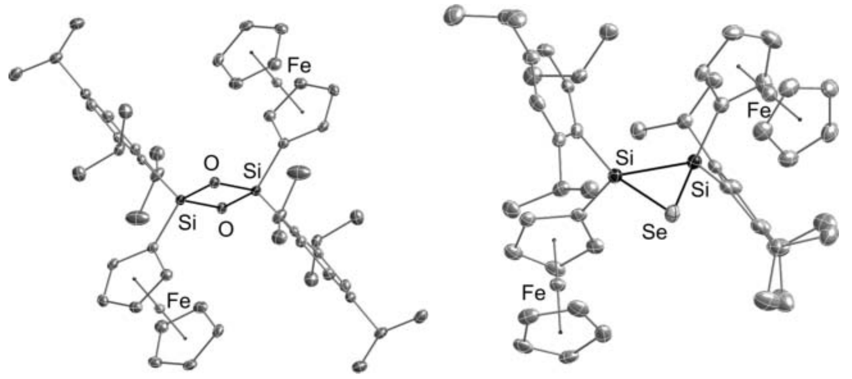


**Figure 1** Molecular structures of 1,3,2,4-dioxadisiletane **2** (left) and selenadisilirane **3** (right) in the crystal; displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

completely planar geometry of the Si–O–Si–O ring skeleton (Figure 1). The Si–O bond lengths are 1.6798(12) and 1.6855(12) Å, which are similar to those of the previously reported tetraaryl-1,3,2,4-dioxadisiletanes,[4,5,7] indicating the less steric and electronic effect of the ferrocenyl groups. A unique short contact [2.4111(9) Å] between the two silicon atoms in the 1,3,2,4-dioxadisiletane ring system was observed for **2** as well as those for the previously reported dioxadisiletanes (for example, the Si—Si distance of $Tip_4Si_2O_2$ is 2.431(2) Å).[5e,9] On the other hand, the selenadisilirane skeleton of **3** was found to form almost an isosceles triangle with two Si–Se [2.3035(8) and 2.3134(9) Å] and one Si–Si [2.2876(12) Å] bonds (Figure 1). The Si–Si bond length in **3** is slightly shorter than that of the previously reported tetramesityl-substituted selenadisilirane **4** [Si–Si: 2.303(2) Å],[5c] indicating almost the same $\pi$-complex character of **3** between the Si=Si moiety and the selenium atom as compared with compound **4**.[5c] In order to obtain more information, the structural optimizations of **2** and **3** were performed at the B3PW91/6–311+G(3d)[6–31G(d) for C,H, DZVP for Fe] level of theory. The optimized structural parameters of **2** (Si–O: 1.683, 1.697 Å, Si—Si: 2.426 Å) and **3** (Si–Si: 2.310 Å, Si–Se: 2.320, 2.321 Å) are both in good agreement with the experimentally observed values. The similarity between the observed $^{29}$Si and $^{77}$Se NMR chemical shifts of **2** ($\delta_{Si} = 2.5$) and **3** ($\delta_{Si} = -56.4$, $\delta_{Se} = -310$) and those calculated at the GIAO-B3PW91/6–311+G(3df)[6–311G(2d,p) for C,H, DZVP for Fe] level of theory [**2** ($\delta_{Si} = 1.4$) and **3** ($\delta_{Si} = -53.4, -53.2$, $\delta_{Se} = -321$)] strongly indicates that the structures of **2** and **3** in solution should be similar to those in the crystalline state. The fact that **2** and **3** were found to have the structural and spectral features similar to those of the previously reported teraaryl-substituted 1,3,2,4-dioxadisiletane and selenadisilirane derivatives suggests that the perturbation by the ferrocenyl groups on the silicon atoms in these small ring systems should not be much different from that of usual aryl groups.

In summary, it was found that the reactions of 1,2-bisferrocenyldisilene **1** with air oxygen and elemental selenium afforded 1,3,2,4-dioxadisiletane **2** and selenadisilirane **3**, respectively, the structures of which were definitively determined by spectroscopic and X-ray crystallographic analyses. Thus, it was demonstrated that the disilene **1** bearing two ferrocenyl moieties exhibits high reactivity of the Si=Si moiety towards oxygen and elemental selenium similar to those of the previously reported tetraaryldisilenes, although

**1** has two ferrocenyl unit as redox-active sites. Further investigations on the properties of **2** and **3** are currently in progress.

## EXPERIMENTAL

All experiments were performed under an argon atmosphere unless otherwise noted. Solvents used for the reactions were purified by The Ultimate Solvent System (Glass Contour Company).[10] Tip(Fc)Si=Si(Fc)Tip (**1**) was prepared according to the reported procedures.[6] $^1$H (300 MHz) and $^{13}$C (75 MHz) spectra were measured in $C_6D_6$ with a JEOL JNM AL-300 spectrometer. The signal due to $C_6D_5H$ (7.15 ppm) was used as an internal standard in $^1$H NMR, and the signal of $C_6D_6$ (128 ppm) was used as internal standard in $^{13}$C NMR. Multiplicity of signals in $^{13}$C NMR spectra was determined by DEPT technique. $^{29}$Si (59 MHz) and $^{77}$Se NMR (76 MHz) spectra were measured in $C_6D_6$ with a JEOL AL-300 spectrometer using signals for $SiMe_4$ (0 ppm) and $Ph_2Se_2$ (480 ppm) as external standards, respectively. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. Gel permeation liquid chromatography (GPLC) was performed on an LC-918 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: toluene). The melting point was determined on a Yanaco micro melting point apparatus and was uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

### 1,3,2,4-Dioxadisiletane 2

A benzene solution (5 mL) of Tip(Fc)Si=Si(Fc)Tip (**1**, 20.0 mg, 24.0 $\mu$mol) was exposed to the air. The color of the solution turned yellow immediately. The solvent was removed from the reaction mixture to afford an orange powder, the $^1$H NMR spectrum of which showed almost quantitative formation of 1,3,2,4-dioxadisiletane **2**. The crude mixture was subjected to GPLC to afford **2** (17.0 mg, 19.7 $\mu$mol, 82%) as orange crystals: mp 265–266°C (sublimation). $^1$H NMR (300 MHz, $C_6D_6$, r.t.): $\delta = 1.23$ (d, $^3J_{HH} = 6.6$ Hz, 12H), 1.38 (d, $^3J_{HH} = 6.6$ Hz, 12H), 1.64 (d, $^3J_{HH} = 6.6$ Hz, 12H), 2.82 (sept, $^3J_{HH} = 6.6$ Hz, 2H), 4.02 (d, $^3J_{HH} = 9.6$ Hz, 4H), 4.03 (sept, $^3J_{HH} = 6.6$ Hz, 4H), 4.10 (s, 10H), 4.11 (d, $^3J_{HH} = 9.6$ Hz, 4H), 7.41 (s, 4H); $^{13}$C NMR (75 MHz, $C_6D_6$, r.t.): $\delta = 24.1$ (q), 25.3 (q), 25.8 (q), 34.6 (d), 34.8 (d), 68.8 (s), 69.0 (d), 71.8 (d), 74.6 (d), 121.4 (d), 128.5 (s), 152.0 (s), 156.4 (s); $^{29}$Si NMR (59 MHz, $C_6D_6$, r.t.): $\delta = 2.50$. Anal. Calcd. for $C_{50}H_{64}FeO_2Si_2$: C, 69.43; H, 7.46%. Found: C, 69.29; H, 7.41%. HRMS (FAB) *m/z*, found: 864.3140 ($[M]^+$), calcd. for $C_{50}H_{64}FeO_2Si_2$ ($[M]^+$): 864.3147.

### Selenadisilirane 3

To a benzene solution (5 mL) of Tip(Fc)Si=Si(Fc)Tip (**1**, 20.0 mg, 24.0 $\mu$mol), elemental selenium (gray selenium, 18.0 mg, 227 $\mu$mol) was added. The color of the solution turned orange immediately. The reaction mixture was filtered through Celite to remove insoluble materials, and the solvent of filtrate was removed. The residue was subjected to GPLC to afford **3** (20.7 mg, 22.7 $\mu$mol, 96%) as red crystals: mp 172–173°C (decomp.). $^1$H NMR (300 MHz, $C_6D_6$, r.t.): $\delta = 1.15$ (d, $^3J_{HH} = 6.6$ Hz, 6H), 1.19 (d, $^3J_{HH} = 6.6$ Hz, 6H), 1.24 (d, $^3J_{HH} = 6.6$ Hz, 6H), 1.25 (d, $^3J_{HH} = 6.6$ Hz, 6H), 1.61 (d, $^3J_{HH} = 6.6$ Hz, 6H), 1.84 (d, $^3J_{HH} = 6.6$ Hz, 6H), 2.83 (sept, $^3J_{HH} = 6.6$ Hz, 2H), 3.69 (sept, $^3J_{HH} = 6.6$ Hz, 2H), 3.75 (m, 2H), 3.86 (m, 2H), 3.93 (m, 2H), 3.98 (m, 2H), 4.20 (s, 10H), 4.81

(sept, ${}^3J_{HH} = 6.6$ Hz, 2H), 7.16 (d, ${}^4J_{HH} = 1.2$ Hz, 2H), 7.34 (d, ${}^4J_{HH} = 1.2$ Hz, 2H); ${}^{13}$C NMR (75 MHz, $C_6D_6$, r.t.): $\delta = 24.0$ (q), 24.1 (q), 24.3 (q), 25.6 (q), 26.1 (q), 26.5 (q), 34.7 (d), 36.4 (d), 37.4 (d), 68.5 (d), 69.1 (s), 70.6 (d), 71.5 (d), 73.3 (d), 77.0 (d), 121.1 (d), 122.7 (d), 127.3 (s), 151.6 (s), 155.5 (s), 157.3 (s); ${}^{29}$Si NMR (59 MHz, $C_6D_6$, r.t.): $\delta = -56.4$ (s with ${}^{77}$Se satellites, ${}^1J_{SeSi} = 77$ Hz); ${}^{77}$Se NMR (76 MHz, $C_6D_6$, r.t.): $\delta = -309.8$ (s with ${}^{29}$Si satellites, ${}^1J_{SiSe} = 77$ Hz). Anal. Calcd. for $C_{57}H_{72}Fe_2SeSi_2$ (**3** · $C_7H_8$): C, 68.19; H, 7.23%. Found: C, 68.40; H, 7.36%. HRMS (FAB) *m/z*, found: 912.2408 ([M]$^+$), calcd for $C_{50}H_{64}Fe_2{}^{80}SeSi_2$ ([M]$^+$): 912.2421.

## X-Ray Structure Determinations

Single crystals of **2** and **3** · $C_7H_8$ suitable for X-ray analysis were obtained by slow recrystallization from hexane (for **2**) and toluene (for **3**) at room temperature. The intensity data were collected on a RIGAKU Saturn70 CCD (system) with VariMax Mo Optic using MoK$\alpha$ radiation ($\lambda = 0.71070$ Å) at $-170$°C to $2\theta_{max} = 51°$. The structure was solved by direct methods (SHELXS-97[11]) and refined by full-matrix least-squares procedures on $F^2$ for all reflections (SHELXL-97[11]). All hydrogen atoms were placed using AFIX instructions. Crystal data for **2** ($C_{50}H_{64}Fe_2O_2Si_2$): M = 864.89, T = 103(2) K, triclinic, *P*–1 (no.2), $a = 10.2128(2)$ Å, $b = 10.5104(3)$ Å, $c = 11.1103(3)$ Å, $\alpha = 94.4274(12)°$, $\beta = 109.8355(12)°$, $\gamma = 94.5322(17)°$, $V = 1111.42(5)$ Å$^3$, Z = 1, $D_{calc} = 1.292$ g cm$^{-3}$, $\mu = 0.745$ mm$^{-1}$, 9863 measured reflections, 4111 independent reflections [$R_{int} = 0.0281$], 259 refined parameters, GOOF = 1.075, $R_1 = 0.0291$ and w$R_2 = 0.0651$ [$I > 2\sigma(I)$], $R_1 = 0.0361$ and w$R_2 = 0.0681$ [for all data], largest diff. peak and hole 0.629 and −0.380 e.Å$^{-3}$. Crystal data for **3** · $C_7H_8$ ($C_{57}H_{72}Fe_2SeSi_2$): M = 1003.99, T = 103(2) K, triclinic, *P*–1 (no.2), $a = 13.0831(3)$ Å, $b = 13.3764(4)$ Å, $c = 17.6020(4)$ Å, $\alpha = 107.3655(10)°$, $\beta = 98.6234(11)°$, $\gamma = 114.8772(18)°$, $V = 2528.61(11)$ Å$^3$, Z = 2, $D_{calc} = 1.319$ g cm$^{-3}$, $\mu = 1.377$ mm$^{-1}$, 22589 measured reflections, 9349 independent reflections [$R_{int} = 0.0519$], 572 refined parameters, GOOF = 1.010, $R_1 = 0.0388$ and w$R_2 = 0.0624$ [$I > 2\sigma(I)$], $R_1 = 0.0758$ and w$R_2 = 0.0682$ [for all data], largest diff. peak and hole 0.966 and –0.556 e.Å$^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 699677 for **2** and CCDC 699678 for **3**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223–336-033; E-mail: deposit@ccdc.cam.ac.uk).

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