J. Am. Chem. Soc. **2001,** *123,* 1676−1682

A Mechanistic Study of Reactions of Stable Disilenes with Haloalkanes

Mitsuo Kira,* Tai Ishima, Takeaki Iwamoto, and Masaaki Ichinohe

Contribution from the Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

Received July 28, 2000. Revised Manuscript Received November 30, 2000

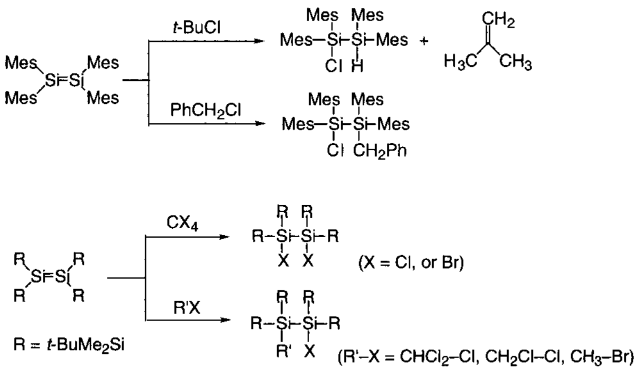
Abstract: Mechanisms of the reactions of three tetrakis(trialkylsilyl)disilenes and a tetraaryldisilene with various haloalkanes such as carbon tetrachloride, chloroform, dichloromethane, which gave the corresponding 1-alkyl-2-chlorodisilanes and/or 1,2-dichlorodisilanes, were investigated in detail. As evidenced by an ESR observation of an intermediate radical, these reactions were quite unusual, forming neutral radical pairs from two closed shell molecules at the first step; no similar reactions have been observed between alkenes and haloalkanes. Low oxidation potentials of these disilenes, large negative activation entropies, and solvent effects for the rates are in good accord with the direct halogen abstraction of disilenes from haloalkanes instead of single-electron transfer at the rate-determining first step. The structure−reactivity relationship of the reactions and the Hammond postulate suggest that the transition state structures for the first step are similar to those for the halogen abstraction by silyl radicals, but more product-like.

Introduction

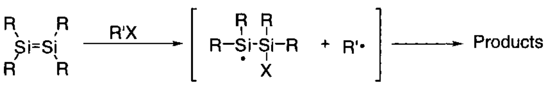
Since the isolation of tetramesityldisilene as the first stable disilene in 1981,[1] there have been reported a number of distinctive reactions of stable disilenes with various reagents such as hydroxylic compounds (water, alcohols, and phenols) and carbon−carbon multiply bonded compounds (alkenes, alkynes, and 1,3-dienes) giving various types of adducts.[2] Whereas the mechanisms of these reactions have not been investigated yet in detail, the reaction modes and reactivity of disilenes appear to be remarkably different from those of alkenes. Typically, in contrast to C═C double bonds, Si═Si double bonds react with water and various alcohols very smoothly without catalysts to give the corresponding adducts, but the mechanistic details of the reactions including the origin of the diverse stereochemical outcome are still under active discussion.[3,4]

Recently, West et al.[5] and our group[6] have found that disilenes react rather unusually with various haloalkanes giving several types of products as shown in Scheme 1. The formation of these products is apparently suggestive of the radical nature of the reactions. These reactions are rationalized if a pair of the corresponding halodisilanyl radical and alkyl radical is formed in the first step (Scheme 2); in the second step, various types of products will be formed via recombination, disproportionation of the radical pair in the cage, or abstraction of the second halogen by the halodisilanyl radical out of the cage.

Scheme 1



Scheme 2



These reactions are quite unusual because *a neutral radical pair is formed from two neutral closed shell molecules*;[7] no similar reactions have been observed between alkenes and haloalkanes. Elucidation of the mechanisms of these reactions may contribute to understanding the characteristics of double

---

(1) West, R.; Fink, M. J.; Michl, J. *Science (Washington)* **1981**, *214*, 1343.

(2) For reviews on disilenes, see: (a) West, R. *Pure Appl. Chem.* **1984**, *56*, 163. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (c) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (d) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Part 2, Chapter 17. (e) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (f) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125. (g) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (h) Kira, M.; Iwamoto, T. *J. Organomet. Chem.* **2000**, *610*, 236.

(3) Sakurai, H. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley: New York, 1998; Vol. 2, Part 1, Chapter 15.

(4) (a) Apeloig, Y.; Nakash, M. *J. Am. Chem. Soc.* **1996**, *118*, 9798. (b) Apeloig, Y.; Nakash, M. *Organometallics* **1998**, *17*, 1260. (c) Apeloig, Y.; Nakash, M. *Organometallics* **1998**, *17*, 2307. See also: Takahashi, M.; Veszprémi, T.; Hajgató, B.; Kira, M. *Organometallics* **2000**, *19*, 4660.

(5) Fanta, A. D.; Belzner, J.; Powell, D. R.; West, R. *Organometallics* **1993**, *12*, 2177.

(6) Iwamoto, T.; Sakurai, H.; Kira, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2741.

(7) As a rather exceptional case, reactions of a dioxirane with olefins etc. have been proposed to proceed via a similar radical pair formation,[8] while a concerted mechanism is claimed as an alternative mechanism.[9]

10.1021/ja002798s CCC: $20.00

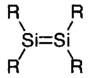
Table 1. Reactions of Various Disilenes with Haloalkanes in Hexane[a]

disilene	R′X	yields (%)[b] 2	yields (%)[b] 3
1a (R = *i*-Pr_2MeSi)	CCl_4	83 (**2a**)	0
	$CHCl_3$	26 (**2a**)	70 (**3a**)
	CH_2Cl_2	0	93 (**3a′**)
	$PhCH_2Cl$	0	51 (**3a″**)
1b (R = *t*-$BuMe_2Si$)[c]	CCl_4	83 (**2b**)	0
	$CHCl_3$	0	78 (**3b**)
	CH_2Cl_2	0	85 (**3b′**)
1c (R = *i*-Pr_3Si)	CCl_4	70 (**2c**)	0
	$CHCl_3$	62 (**2c**)	0
	t-BuBr	81 (**2c′**)	0
1d (R = Tip)	CCl_4	84 (**2d**)	0
	$CHCl_3$	94 (**2d**)	0
	CH_2Cl_2	85 (**2d**)	0

[a] See Experimental Section for detailed reaction conditions. [b] Determined by NMR. [c] Reference 6.

bonds of group-14 elements. In this paper, we discuss the detailed mechanisms of the reactions of several stable disilenes (**1a**−**d**) with various haloalkanes.

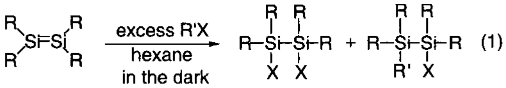
Chart 1



1a; R = *i*-Pr_2MeSi
1b; R = *t*-$BuMe_2Si$
1c; R = *i*-Pr_3Si
1d; R = 2,4,6-triisopropylphenyl (Tip)

Results and Discussion

A. Overall Profile of Reaction. 1. Product Study. Tetrasilyldisilenes **1a**−**c**[11] and a tetraaryldisilene **1d**[12] reacted with various haloalkanes in the dark to give the corresponding dihalodisilanes **2** and 1-alkyl-2-halodisilanes **3** in high yields (eq 1), while the reaction rates and product distribution depended



1 2 3 (1)

strongly on the types of disilenes and haloalkanes as shown in Table 1. The reactions of sterically very bulky disilenes **1c** and **1d** gave only the corresponding 1,2-dihalodisilanes **2c** (or **2c′**) and **2d** irrespective of the structure of haloalkanes. The reactions of less bulky disilene **1a** with dichloromethane and benzyl chloride gave only the simple addition products **3a′** and **3a″**, while the reaction of **1a** with chloroform produced a mixture of **2a** and **3a**. Carbon tetrachloride was the most reactive among investigated haloalkanes toward these disilenes to afford only the corresponding 1,2-dichlorodisilanes. These results suggest that the two types of products are produced via the two competitive reactions from the radical pair shown in Scheme 2.

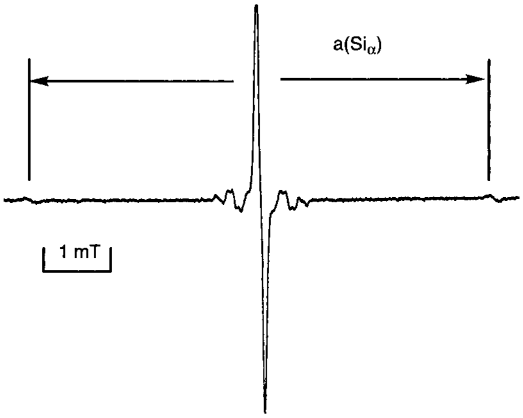


Figure 1. An ESR spectrum of disilanyl radical **4c** observed during the reaction of **1c** with *tert*-butyl chloride in benzene-d_6 at room temperature.

2. ESR Spectra of Intermediates. If the reaction of a disilene with a haloalkane proceeds via the corresponding 2-halodisilanyl radical and alkyl radical, the 2-halodisilanyl radical as a key intermediate might be observed by ESR. During the reaction of **1c** with excess *tert*-butyl chloride in benzene-d_6 at room temperature (eq 2), an intense singlet ESR signal with several satellites due to ^{29}Si nuclei was observed (Figure 1).

(2)

4c (R = *i*-Pr_3Si)

The ESR spectrum is assignable to the corresponding oligosilanyl radical **4c** on the basis of the *g* value and splitting pattern of the satellite signals: $g = 2.0054$, $a(Si_\alpha) = 5.73$ mT, and hfs values of five satellites with 1.03, 0.73, 0.59, 0.46, and 0.27 mT due to other ^{29}Si and ^{13}C nuclei. The *g* and $a(Si_\alpha)$ values for **4c** are similar to those of tris(trialkylsilyl)silyl radicals:[13] $a(Si_\alpha) = 5.56$ and 5.71mT, $g = 2.0061$ and 2.0055 for $(i\text{-}Pr_3Si)_3Si^\bullet$ [13b] and $(t\text{-}BuMe_2Si)_3Si^\bullet$,[13c] respectively. The reaction of **1c** with *tert*-butyl chloride was very slow and only 10% of **1c** were consumed after 1 month at room temperature; the ESR signal intensity continued slowly to increase for more than half a year. Disilanyl radical **4c** was exceptionally long-lived, probably because **4c** is well protected sterically to cause neither the chlorine abstraction from *tert*-butyl chloride nor recombination with *tert*-butyl radical. Isobutene and isobutane were detected in the reaction mixture by NMR, indicative of the formation of *tert*-butyl radicals during the reaction.

In contrast, disilenes **1a** and **1b** react with *tert*-butyl chloride rather smoothly to show no ESR signals due to silyl radicals during the reactions. The major products were **2a** and **2b**, but several other products involving ene-addition products of isobutene with the disilenes were also formed.[14] Very weak ESR signals were detected but unidentified during the reaction of **1d** with *tert*-butyl chloride, although the reaction was very slow similar to the corresponding reaction of **1c**; the major product

---

(8) (a) Bravo, A.; Fontana, F.; Fronza, G.; Minisci, F. *Tetrahedron Lett.* **1995**, *38*, 6945. (b) Bravo, A.; Fontana, F.; Fronza, G.; Minisci, F.; Zhao, L. *J. Org. Chem.* **1998**, *63*, 254.

(9) Adam, W.; Curci, R.; D'Accolti, L.; Dinoi, A.; Fusco, C.; Gasparrini, F.; Kluge, R.; Paredes, R.; Schulz, M.; Smerz, A. K.; Veloza, L. A.; Weinkötz, S.; Winde, R. *Chem. Eur. J.* **1997**, *3*, 105.

(10) Dixon, C. E.; Hughes, D. W.; Bains, K. *J. Am. Chem. Soc.* **1998**, *120*, 11049.

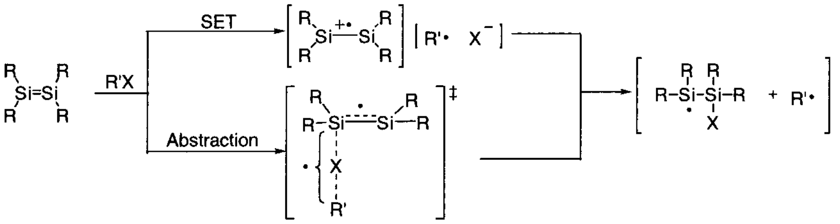
(11) Kira, M.; Maruyama, T.; Kabuto, C.; Ebata, K.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1489.

(12) Watanabe, H.; Takeuchi, K.; Fukata, N.; Kato, M.; Goto, M.; Nagai, Y. *Chem. Lett.* **1987**, 1341.

(13) (a) Kyushin, S.; Sakurai, H.; Betsuyaku, T.; Matsumoto, H. *Organometallics* **1997**, *16*, 5386. (b) Kyushin, S.; Sakurai, H.; Matsumoto, H. *Chem. Lett.* **1998**, 107. (c) Kira, M.; Obata, T.; Kon, I.; Hashimoto, H.; Ichinohe, M.; Sakurai, H.; Kyushin, S.; Matsumoto, H. *Chem. Lett.* **1998**, 1097. (d) Cooper, J.; Hudson, A.; Jackson, R. A. *Mol. Phys.* **1972**, *23*, 209.

(14) The ene-addition reactions of disilenes **1b** are reported to occur very easily via the six-membered cyclic transition states.[6]

Scheme 3



was again dichlorodisilane **2d**. The intermediate silyl radicals formed from disilenes **1a**, **1b**, and **1d** with *tert*-butyl chloride should be more reactive than **4c** due to less severe steric bulkiness of the substituents for **1a** and **1b**, and due to possible homolytic aromatic addition of silyl radicals[15] for **1d**.

B. The First Step: Single-Electron Transfer or Halogen Abstraction. As shown in Scheme 3, the first step may proceed either through (1) the single-electron transfer (SET) from disilene to haloalkane followed by the coupling of the disilene cation radicals and chloride anion or through (2) the direct halogen abstraction of disilene from haloalkane, where the disilene is supposed to serve as a biradical.

1. Cyclic Voltammetry of Disilenes. To distinguish the above two possible mechanisms, the assessment of the SET mechanism using the Marcus theory[17] will be effective. For this purpose, oxidation (E_{ox}) as well as reduction potentials (E_{red}) of various disilenes have been investigated in THF by cyclic voltammetry by using a conventional three-electrode cell design; an AgCl-coated silver wire, a glassy carbon rod, and a platinum metal wire were used as a working electrode, a reference electrode, and a counter electrode, respectively. It was confirmed by ^{1}H NMR spectroscopy that disilenes **1a** and **1d** did not react for several hours with supporting electrolyte [Bu$_4$N][PF$_6$] in THF-d_8. Since both reduction and oxidation of these disilenes were irreversible, the peak potentials were compared in Table 2.

Table 2. Peak Potentials of Various Disilenes in THF[a]

disilene	$E_{\mathrm{p,Ox}}$ (V)	$E_{\mathrm{p,Red}}$ (V)
1a	+0.88	−1.82, −2.41
1c	+0.70	−1.70, −2.56
1d	+0.56, +1.32	−2.66
$Mes_2Si{=}SiMes_2$	+0.44 (+0.38)[b]	−2.12 (−2.12)[b]

[a] Conditions: Potentials in V vs ferrocene/ferrocenium (+0.61 V), supporting electrolyte 0.1 M [NBu$_4$][PF$_6$], reference electrode Ag/Ag$^+$, at ambient temperatures in THF at 0.2 V/s. [b] The data in parentheses are taken from ref 18a.

The oxidation potentials of the investigated tetraaryldisilenes and tetrasilyldisilenes were in the range of +0.4 to +0.9 V. The relatively high oxidation potentials of these disilenes eliminate the possible SET mechanism for the initial reactions of disilenes with haloalkanes. According to the Marcus theory,[17] the second-order rate constant (k) for an SET reaction is estimated by using the following eqs 3 and 4, where Z, λ, C, and ΔG are the frequency factor, reorganization energy, Coulomb energy, and free energy difference, respectively.

$$\Delta G/(\mathrm{kcal{\bullet}mol^{-1}}) = 23.06(E_{\mathrm{ox}} - E_{\mathrm{red}})/\mathrm{V} + C \qquad (3)$$

$$k = Z\exp\left\{-\frac{\lambda}{4RT}\left(1+\frac{\Delta G}{\lambda}\right)^2\right\} \qquad (4)$$

The ΔG value for the SET reaction between **1c** and chloroform is estimated to be larger than 34 kcal·mol^{-1}, because E_{ox} of **1c** and E_{red} of chloroform are +0.70 and <−1.0 V,[18b] respectively; the Coulomb energy is estimated to be −5 kcal·mol^{-1} by assuming the interatomic distance of 10 Å. The rate constant k is suggested to be $<10^{-14}$ M^{-1}·s^{-1}, if we assume that the λ value is ca. 50 kcal·mol^{-1} according to the evaluation by Eberson[19] for reduction of haloalkanes, and the Z value is ca. 10^{11} M^{-1}·s^{-1}. As shown in the next section, k is measured to be 1.2×10^{-2} M^{-1}·s^{-1} for the reaction of **1c** with chloroform at 298 K. The observed k is 10^{12} times larger than the above estimated k, and hence incompatible with the SET process between **1c** and chloroform. Since disilenes **1a**−**d** react with those haloalkanes which have even lower E_{red} than chloroform, the reaction mechanisms should not involve the initial SET process.

Meanwhile, interesting substituent effects on both oxidation and reduction potentials of disilene were observed. The oxidation potentials of tetrasilyldisilenes **1a** and **1c** were 0.14−0.44 V higher than those of tetramesityldisilene and **1d**, and the first reduction potentials of tetrasilyldisilenes **1a** and **1c** were ca. 0.3−0.9 V lower than those of tetraaryldisilenes. The results suggest that both HOMO and LUMO of tetrasilyldisilenes are significantly lower in energy than those of tetraaryldisilenes as shown in Figure 2; tetrasilyldisilenes are more electron-accepting and less electron-donating than tetraaryldisilenes. Significant differences in the various reactions of tetrasilyldisilenes from those of tetraaryldisilenes may be explained by the major electronic effects of the substituents, while the steric effects should also be taken into account; for example, tetrasilyldisilenes **1a** and **1b** react with 2,3-dimethylbutadiene to produce the corresponding Diels−Alder adducts, while no [4+2] addition of tetramesityldisilene to 1,3-butadienes has been reported.[6] The more electron-accepting tetrasilyldisilenes **1a** and **1c** afforded

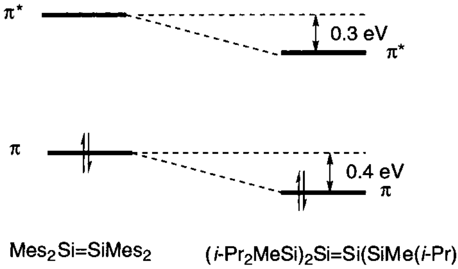


Figure 2. Schematic representation of the relative energy levels of the frontier orbitals of tetrasilyldisilenes and tetraaryldisilenes.

---

(15) For reviews of silyl radicals, see: (a) Sakurai, H. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley & Son: New York, 1973; Vol. II. (b) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229.

(16) Recently, Bains et al. have found the reactions of stable disilenes with ketones to proceed via biradical adducts, while the detailed discussion on the transition states for the step was not given: Dixon, C. E.; Hughes, D. W.; Bains, K. *J. Am. Chem. Soc.* **1998**, *120*, 11049.

(17) (a) Marcus, R. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. *J. Chem. Phys.* **1965**, *43*, 679. (c) Marcus, R. *J. Phys. Chem.* **1968**, *72*, 891.

(18) (a) Shepherd, B. D.; West, R. *Chem. Lett.* **1988**, 183. (b) $E_{\mathrm{ox,p}}$(chloroform) = −1.67 V (SCE) in a dioxane-water (75/25) mixture: Mann, C. K.; Barnes, K. K. *Electrochmical Reactions in the Nonaqueous Systems*; Marcel Dekker Inc: New York 1970.

(19) Eberson, L. *Acta Chem. Scand.* **1982**, *B36*, 533.

Table 3. Rate Constants of the Reactions of Disilenes with Chloroform at 303 K in Various Solvents

	10^4k ($M^{-1}{\cdot}s^{-1}$)		
solvent	**1c**	**1d**	E_T (kcal·mol^{-1})[a]
hexane	160	1.6	30.9
toluene	210	0.82	33.9
benzene	200	2.2	34.5
THF	110	*b*	37.4
chlorobenzene	330	8.0[c]	37.5
dichloromethane	*d*	4.9[c]	41.1

[a] Data were taken from ref 23. [b] A complex mixture of products was formed. [c] Reactions of **1d** with these solvents were assumed to be too slow to affect the rate constants. [d] Not determined.

the second reduction potentials at around −1.8 and −2.5 V, while **1d** and tetramesityldisilene showed only one reduction peak at >−2.5 V. The results coincide with the fact that tetrasilyldisilenes **1a** and **1b** are reduced by lithium metal in THF to give the corresponding dianions,[20] while a similar lithium reduction of **1d** is known to give the corresponding disilenyllithium via the Si−Ar bond cleavage.[21]

2. Kinetic Order, Rates, Activation Parameters, and Solvent Effects. The reactions of disilenes with haloalkanes in hexane were followed by UV spectroscopy, using the absorbance at the $\pi\pi^*$band maxima of the disilenes. When the initial concentrations of a disilene and haloalkane were ca. 10^{-6} and 10^{-3} M, pseudo-first-order kinetics was observed (eq 5). Several kinetic runs showed that the apparent first-order rate constants (k_{obs}) were proportional to the concentrations of the haloalkane (eq 6); the second-order rate constants k were determined as

$$-\frac{d[\mathbf{1a}]}{dt} = k_{obs}[\mathbf{1a}] \quad (5)$$

$$k_{obs} = k[CHCl_3] \quad (6)$$

the slope. The reaction was thus characterized as obeying an overall second-order rate law, first order in disilene and first order in haloalkane. All the reactions investigated here showed similar kinetics, indicating that the rate-determining step of these reactions is the first step to form radical pairs.

Typically, k's for the reactions of **1c** and **1d** with chloroform were thus determined to be (1.58 ± 0.005) × 10^{-2} and (1.62 ± 0.06) × 10^{-4} $M^{-1}{\cdot}s^{-1}$, respectively, in hexane at 303 K. From the temperature dependence of k, the activation parameters were determined as $\Delta H^\ddagger = 7.0 \pm 0.1$ kcal·mol^{-1} and $\Delta S^\ddagger = -43.9 \pm 0.05$ cal·mol^{-1}·K^{-1} for **1c** and $\Delta H^\ddagger = 7.4 \pm 0.1$ kcal·mol^{-1} and $\Delta S^\ddagger = -43.1 \pm 0.07$ cal·mol^{-1}·K^{-1} for **1d**. The very large negative activation entropies of these reactions support the bimolecular chlorine abstraction mechanism for the first step of the reactions; large negative activation entropies around −40 cal·mol^{-1}·K^{-1} have also been observed for the reactions of tetramesityldisilene with phenols.[4c] The SET mechanism is again eliminated because typical SET reactions should show relatively small and even positive activation entropy.[22]

As shown in Table 3, while rates for disilene **1c** are much larger than those for disilene **1d**, these rate constants were not significantly solvent dependent. Polar solvents slightly accelerated the reactions but the extent is smaller than that expected for the SET reactions. All the features of the reactions, i.e., relatively low oxidation potentials of these disilenes, large negative activation entropies, and solvent effects for the rates, are incompatible with the SET reactions at the rate-determining initial step.

Table 4. Comparison of Second-Order Rate Constants of Halogen Abstractions of Disilenes (at 303 K in hexane) and Silyl Radicals (at 300 K) from Various Haloalkanes

	k ($M^{-1}{\cdot}s^{-1}$)			
haloalkane	**1c**	**1d**	$Et_3Si^{\bullet}$ [a]	$(Me_3Si)_3Si^{\bullet}$ [b]
CCl_4		1.7×10^{-1}	4.3×10^9	1.7×10^8
$CHCl_3$	1.6×10^{-2}	1.6×10^{-4}	2.5×10^8	6.8×10^6
CH_2Cl_2	5.2×10^{-5}	1.4×10^{-7}	7.1×10^7	
Cl_3CCCl_3		2.6×10^{-3}	4.1×10^9	
$Cl_2CHCHCl_2$		2.0×10^{-3}	2.2×10^8	
$PhCH_2Cl$	1.4×10^{-3}	1.6×10^{-6}	2.0×10^7	4.6×10^6
t-BuCl	7.4×10^{-7}		2.5×10^6	4.0×10^5
t-BuBr	8.8×10^{-3}		1.1×10^9	1.2×10^8
i-PrBr	2.2×10^{-4}			4.6×10^7
$CH_3(CH_2)_4Br$	1.0×10^{-5}		5.4×10^8	2.0×10^7
PhBr	1.7×10^{-7}		1.1×10^8	4.6×10^6

[a] Reference 24b. In di-*tert*-butylperoxide−triethylsilane. [b] Reference 24d. In hexadecane.

The reactions of disilenes with haloalkanes are judged to proceed via the rate-determining halogen abstraction of disilenes, where the disilenes serve as biradicals. Since the role of group-14 element unsaturated bonds as biradicals is rather exceptional, we have investigated further in detail the structure−reactivity relationship of the reactions to elucidate the transition state structures.

C. Transition-State Structure for the First Step. 1. Disilenes vs Silyl Radicals. To determine the electronic and steric requirement for the first-step reactions, the second-order rate constants were compared with those for the halogen abstraction by silyl radicals.[24−26] In Table 4, the rate constants for the halogen abstractions of disilenes **1c** and **1d** are shown together with those reported for silyl radicals.

The absolute rates for disilenes are 10^8−10^{14} times slower than the corresponding reactions for silyl radicals. These differences are understood on the basis of the reaction enthalpies (ΔH_0). The reactions of silyl radicals are well-known to be exothermic by more than 30 kcal·mol^{-1}, irrespective of chlorine or bromine abstraction.[27] On the other hand, the reactions of the disilenes with haloalkanes will be less exothermic (ΔH_0 = −5 to −15 kcal·mol^{-1}), because a Si−Si π bond is cleaved during the reactions.[30] The higher reactivity of tetrasilyldisilenes

---

(20) Iwamoto, T.; Yin, T.; Maruyama, T.; Kabuto, C.; Kira, M. To be submitted for publication. See also: *10th International Symposium on Organosilicon Chemistry*; Poznán, Poland, 1993; Abstracts, p 263.

(21) (a) Scott, J. P.; Batchller, A.; Masamune, S. *J. Organomet. Chem.* **1989**, *367*, 39. (b) Weidenbruch, M.; Willms, S.; Saak, W.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2503.

(22) Typically, the activation entropy for the electron transfer from anthracene anion to butyl bromide was reported to be +5 cal·mol^{-1}·K^{-1}: Lexa, D.; Sáveant, J.-M.; Su, K.-B.; Wang, D.-L. *J. Am. Chem. Soc.* **1988**, *110*, 7617.

(23) Kosower, E. M.; Mohammad, M. *J. Am. Chem. Soc.* **1968**, *90*, 3271.

(24) (a) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C.; Woynar, H. *J. Am. Chem. Soc.* **1981**, *103*, 3231. (b) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123. (c) Lusztyk, J.; Maillard, B.; Ingold, K. U. *J. Org. Chem.* **1986**, *51*, 2457. (d) Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1989**, *54*, 2492. (e) Ito, O.; Hoteiya, K.; Watanabe, A.; Matsuda, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 962. (f) Sluggett, G. W.; Leigh, W. J. *Organometallics* **1992**, *11*, 3731.

(25) Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343.

(26) (a) Tamblyn, W. H.; Vogler, E. A.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 3912. (b) Blackburn, E. V.; Tannner, D. D. *J. Am. Chem. Soc.* **1980**, *102*, 692.

(27) For this discussion, bond dissociation energies (BDE) of Si−Cl, Si−Br, C−Cl, and C−Br were taken to be 113, 96, 80, and 64 kcal·mol^{-1}.[28] The BDE values depend significantly on the substituents. For further detailed discussion in this paper, the BDE values of C−Cl are taken to be 83.6, 82.8, 79.2, and 70.3 kcal·mol^{-1} for CH_3−Cl, $ClCH_2$−Cl, Cl_2CH−Cl, and Cl_3C−Cl, respectively.[29]

(28) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(29) Weissman, M.; Benson, S. W. *J. Phys. Chem.* **1983**, *87*, 243.

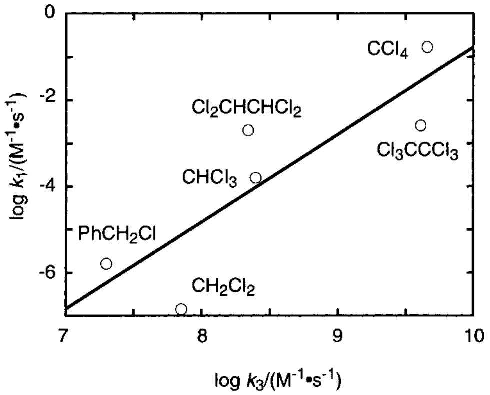


Figure 3. A log–log plot of the rate constants of the chlorine abstraction between disilene **1d** (k_1) and triethylsilyl radical (k_3).

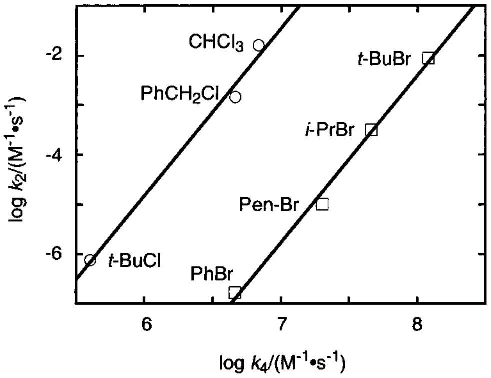


Figure 4. A log–log plot of the rate constants for the reactions of disilene **1c** (k_2) vs (Me$_3$Si)$_3$Si$^•$ (k_4).

than tetraarydisilenes may be attributed to the smaller π-bond energy for the former.

Despite the significant difference of the reaction enthalpies between disilenes and silyl radicals, the structure–reactivity relationships of these reactions are rather parallel to each other. As shown in Figure 3, logarithms of rate constants for the reactions of **1d** with various haloalkanes correlated roughly linearly with those for triethylsilyl radical, with a correlation coefficient of 0.854. The reason for the rather poor correlation may be ascribed in part to the significant difference in the electronic and steric effects of the substituents at the radical centers between **1d** and triethylsilyl radical.

A plot of log *k* for the reactions of chloro- and bromoalkanes with **1c** against those with tris(trialkylsilyl)silyl radical gave two different linear lines for chloro- and bromoalkanes with almost the same slope as shown in Figure 4; the slopes and correlation coefficients were 3.37 ($r = 0.994$) and 3.36 ($r = 0.996$) for chloro- and bromoalkanes, respectively. For halogen abstraction of silyl radicals, it is well-recognized that the reaction with *tert*-butyl chloride is much slower than the reaction with *tert*-butyl bromide, while the reaction enthalpies are almost the same; ΔH_0-(*t*-BuX) $= -30.7$ and -29.7 kcal•mol^{-1}, for X = Cl and Br, respectively, but k[*t*-BuBr]/k[*t*-BuCl] $= 4.4 \times 10^2$ and 3.0×10^2 for Et$_3$Si$^•$ and (Me$_3$Si)$_3$Si$^•$, respectively. The reason for the rate difference is usually ascribed to the stabilization of the transition states by polar effects, which is larger for bromine abstraction than that for chlorine abstraction.[24b] For disilene **1c**, the reactivity difference between *t*-BuCl and *t*-BuBr was observed to be much larger in extent in accord with the reactivity–selectivity principle; k[*t*-BuBr]/k[*t*-BuCl] $= 1.2 \times 10^4$ at 303 K.

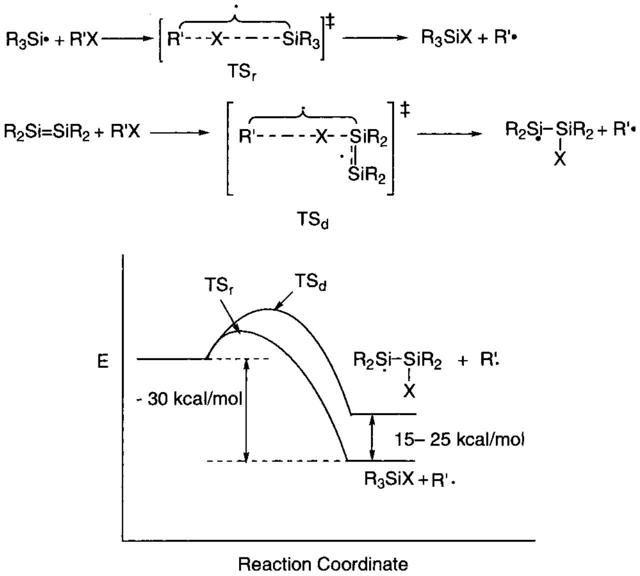


Figure 5. Comparison of the reaction profile of the halogen abstraction of a silyl radical with that of a disilene.

The fact that the reactivities of disilenes toward various haloalkanes are parallel to those of silyl radicals with larger selectivity for the former suggests the similarity of the transition states between these two types of halogen abstractions. Since, like other atom abstraction reactions, the transition states for halogen abstraction by a silyl radical are considered to have a linear arrangement of (halide carbon)–halogen–silicon atoms, similar linear transition states will be applicable to the corresponding reactions of disilenes as shown in Figure 5. According to the Hammond postulate,[33] the transition state for a silyl radical should be early and reagent-like. On the other hand, the transition state for a disilene should be later, where the carbon–halogen bond cleavage is significantly developed.

2. Hammett-Type Relationship. Chatgilialoglu and Ingold[34] have investigated the substituent effects on the rate for chlorine abstraction of triethylsilyl radical from benzyl chlorides, and found a linear plot of log$k$ vs σ_p with ρ of +0.64, indicative of significant polar effects, i.e., significant development of negative charge on the benzylic carbon in the transition state for this reaction. In radical reactions, however, spin delocalization effects due to substituents may also be important. On this basis, Jiang et al. have recently proposed a two-parameter relationship for radical reactions using various combinations of polar and spin delocalization substituent constants.[35] Substituent effects on the rates for the bromine abstraction of tris(trimethylsilyl)silyl radical from substituted benzyl bromide (eq 7) were thus

---

[30] The π bond energies of disilenes may be estimated roughly from the rotational barrier around the Si=Si bonds, which are reported to be ca. 25 and 15 kcal•mol^{-1} for several 1,2-diaryldisilenes[31] and a tetrasilyldisilene,[32] respectively. Since the barrier for a tetrasilyldisilene is lowered by the effective σ–π conjugation at the transition state, the barrier of 15 kcal•mol^{-1} for tetrasilyldisilenes should be taken as the lower limit of the π bond energy.

[31] (a) Michalczyk, M. J.; West, R.; Michl, J. *Organometallics* **1985**, *4*, 826. (b) Shephered, B. D.; Powell, D. R.; West, R. *Organometallics* **1989**, *8*, 2664. (c) Batcheller, S. A.; Tsumuraya, T.; Tempkin, O.; Davis, W. M.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 9394. See also ref 1 g.

[32] Kira, M.; Ohya, S.; Iwamoto, T.; Ichinohe, M.; Kabuto, C. *Organometallics* **2000**, *19*, 1817.

[33] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

[34] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Org. Chem.* **1987**, *52*, 928.

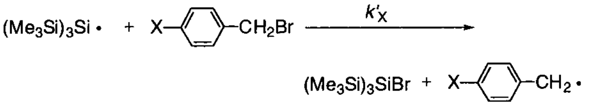
[35] (a) Jiang, X. K.; Ji, G. Z.; Xie, J. R. Y. *Tetrahedron* **1997**, *53*, 8479. (b) Jiang, X. K. *Acc. Chem. Res.* **1997**, *30*, 283. (c) Jiang, X. K.; Ji, G. Z. *J. Org. Chem.* **1992**, *57*, 6051.

Table 5. Second-Order Rate Constants for the Reaction of Disilene **1c** with Substituted Benzyl Chlorides and Substituent Constants at 303 K in Hexane

X	10^3k_X ($M^{-1}\cdot s^{-1}$)	σ_p[a]	σ_{JJ}[b]
t-Bu	1.7	−0.20	0.26
Me	1.2	−0.17	0.15
H	1.4	0	0
F	1.5	0.06	−0.02
Cl	7.7	0.23	0.22
CF_3	4.1	0.54	−0.01
CN	13.0	0.66	0.42

[a] Reference 36. [b] Reference 35.

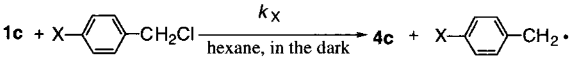
expressed by eq 8,[36] typically, using σ_p for polar substituent constants and $\sigma_{JJ}^\bullet$ for spin delocalization constants.



(7)

$$\log(k_X/k_H) = 0.31\sigma_p + 0.27\sigma_{JJ} \quad (r = 0.977) \tag{8}$$

To elucidate further in detail the electronic nature of the transition state for the reactions of disilenes with haloalkanes, we investigated the substituent effects on the reaction rate of disilene **1c** with benzyl chlorides (eq 9). The rate constants for various benzyl chlorides are shown in Table 5 together with pertinent substituent constants. A dual parameter correlation using σ_p and $\sigma_{JJ}^\bullet$ constants (eq 10) was clearly better than the single parameter correlation.

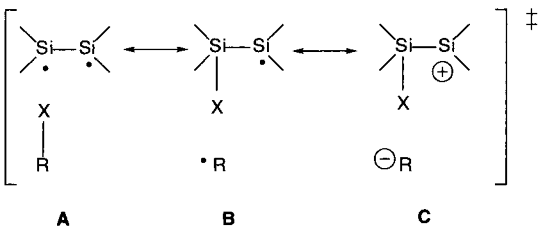


(9)

$$\log(k_X/k_H) = 0.89\sigma_p + 1.12\sigma_{JJ} \quad (r = 0.947) \tag{10}$$

Substituent effects on these two reactions are parallel, while the ρ values for the reaction of eq 9 are 3−4 times larger than those for the reaction of eq 8, in accord with the reactivity−selectivity principle. The ratio of polar and spin effects, ρ_p/ρ_{JJ}, for the reactions of **1c** (eq 9) was 0.79, which was a little smaller than the 1.09 ratio for the reactions of $(Me_3Si)_3Si^\bullet$ (eq 7).[35] As shown in Chart 2, the resonance structures A−C will contribute to the transition states for both two-halogen-abstraction reactions. The comparison of the ρ_p/ρ_{JJ} values suggests that the relative importance of spin structure A to the polar structure C in the reaction of **1c** is a little larger than that in the reactions of $(Me_3Si)_3Si^\bullet$.

Chart 2



D. Concluding Remarks. The origin of the biradical character of disilenes can be discussed based on several grounds. Teramae has shown theoretically that disilene has weak but significant singlet biradical character as a result of the existence of the UHF instability; the percent biradical character of parent disilene was calculated to be 13% for the CASSCF/6-31G** structure.[37] This biradical character may be related to the π bond energy, because the smaller the energy required to break the π bond is, the more favorable the biradical formation. Since the π bond energies for disilenes (25 kcal·mol^{-1}) are much smaller than for the usual alkenes (65 kcal·mol^{-1}), disilenes should have larger biradical character. The reason for the small π bond energies of disilenes would be attributed to the large positive singlet−triplet energy differences of the component silylenes [$\sum\Delta E_{ST}$; $\Delta E_{ST} = E(\text{triplet}) - E(\text{singlet})$] on the basis of CGMT theory.[38,39] The extension of the above discussion to alkenes suggests that those alkenes that are composed of singlet carbenes may work as biradicals in their reactions. Actually, tetrafluoroethylene, whose π bond energy is significantly smaller than those of the normal alkenes in relation to the large ΔE_{ST} of difluorocarbene,[38,40] has been known to work as a biradical in its reactions with 1,3-dienes.[41]

Experimental Section

General Methods. ESR spectra were recorded on a Bruker ESP-300E spectrometer (9.5-GHz frequency, 3300-G magnetic field, and field modulation at 100 kHz) and were calibrated with perylene anion radical in DME. ^1H NMR (300 MHz) spectra were obtained on a Bruker AC-300 FT spectrometer. ^{13}C and ^{29}Si NMR spectra were collected on the machine at 75.5 and 59.6 MHz, respectively. Chemical shifts are based on the resonances of the deuterated solvents. Mass spectra and high-resolution mass spectra were obtained on a JEOL JMS 600W mass spectrometer. Electronic spectra were recorded on a Milton-Roy SP3000 spectrometer. All solvents were dried and degassed over a potassium mirror in vacuo prior to use.

Electrochemistry. Voltammetric experiments were performed with a Hokuto Denko Model HA-501 Potentiostat with a HA-104 Function Generator in a glovebox (VAC MO-40-M). A conventional three-electrode cell design was used, the experimental reference electrode being an AgCl-coated silver wire. Potentials in this paper are referenced, however, to the ferrocene/ferrocenium couple whose potential was fixed to +0.61 V in THF.[18a] The working electrode was a Pt wire polished by a standard method.

Materials. Tetrakis(2,4,6-triisopropylphenyl)disilene (**1d**),[12] tetramesityldisilene,[42] and three tetrakis(trialkylsilyl)disilenes (**1a**−**c**)[11] were prepared accoring to the literature.

Reactions of Disilenes with Haloalkanes. All the yields of products **2** and **3** were determined NMR spectroscopically after the complete consumption of the disilenes.

The reactions of **1a**−**d** with carbon tetrachloride gave the corresponding 1,2-dichlorodisilanes **2a**−**d**. In a typical procedure, to a Schlenk tube (50 mL) containing **1d** (30 mg, 3.45×10^{-5} mol) was introduced a mixture of CCl_4 (2.0 mL) and hexane (2.0 mL) through a vacuum line at −50 °C. With increasing temperatures to room temperature, the mixture turned from yellow to colorless rapidly. After completion of the reaction, a constant amount of 1,3,5-trimethylbenzene was added to the reaction mixture as an internal standard. The ^1H NMR analysis showed formation of the corresponding 1,2-dichlorodisilane **2d** in 84% yield. Pure **2d** was obtained after removal of solvent and recrystallization. **2d**: colorless crystals; mp 245 °C; ^1H NMR ($CDCl_3$) δ −0.07 (d, J = 6.7 Hz, 6 H), −0.06 (d, J = 6.7 Hz, 6 H), 0.11 (d, J

---

(36) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(37) (a) Teramae, H. *J. Am. Chem. Soc.* **1987**, *109*, 4140. (b) Teramae, H.; Maxika, J. Private communication. Whereas the author has proposed the biradical character as the origin of the trans-bent geometry of disilene, the biradical nature may be taken as a consequence of the CGMT theory.[38,39]

(38) Carter, E. A.; Goddard, W. A., III *J. Phys. Chem.* **1986**, *90*, 998. Carter, E. A.; Goddard, W. A., III *J. Am. Chem. Soc.* **1988**, *110*, 4077.

(39) (a) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303. (b) Malrieu, J.-P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916. (c) Trinquir, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130.

(40) Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282.

(41) (a) Bartlett, P. D. *Science* **1968**, *159*, 833. (b) Bartlett, P. D.; Mallet, J. J.-B. *J. Am. Chem. Soc.* **1976**, *98*, 143.

(42) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793.

= 6.7 Hz, 6 H), 1.07−1.20 (m, 42H), 1.31 (d, $J = 6.7$ Hz, 6 H), 1.36 (d, $J = 6.7$ Hz, 6 H), 2.68 (sept, $J = 6.7$ Hz, 2 H), 2.78 (sept, $J = 6.7$ Hz, 2 H), 2.92 (sept, $J = 6.7$ Hz, 2 H), 3.21 (sept, $J = 6.7$ Hz, 2 H), 3.29 (sept, $J = 6.7$ Hz, 2 H), 3.55 (sept, $J = 6.7$ Hz, 2 H), 6.74 (s, 4 H), 6.80 (s, 2 H), 7.06 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.5, 23.0, 23.1, 23.7, 23.96, 23.99, 24.1, 25.0, 25.4, 25.5, 26.8, 29.5, 33.7, 33.9, 34.2, 34.4, 36.5, 37.5, 122.7, 123.5, 124.3, 124.4, 130.1, 136.9, 150.2, 150.9, 152.8, 154.7, 155.8, 155.9; ^{29}Si NMR ($CDCl_3$) δ −4.45; MS (EI, 14 eV) *m*/*z* (%) 938 (0.5, M^+), 903 (0.3, $M^+ - 35$), 735 (1.8, $M^+ - 203$), 469 (100). Anal. Calcd for $C_{60}H_{92}Si_2Cl_2$: C, 76.63; H, 9.86. Found: C, 76.13; H, 9.95.

2a: 83%; colorless oil; ^{1}H NMR (C_6D_6) δ 0.42 (s, 12 H), 1.19 (d, $J = 7.2$ Hz, 24 H), 1.23 (d, $J = 7.2$ Hz, 24 H), 1.52 (sept, $J = 7.5$ Hz, 8 H); ^{13}C NMR (C_6D_6) δ −6.0 ($SiCH_3$), 15.2, 15.4 (Si*C*H(CH_3)$_2$), 19.8, 20.1, 20.3, 20.5 (SiCH(*C*H$_3$)$_2$); ^{29}Si NMR (C_6D_6) δ 3.9 (SiCl), 9.4 (SiMe(*i*-Pr)$_2$); MS (EI, 14 eV) *m*/*z* (%) 642 (1.7, M^+), 627 (47, $M^+ -$ 15), 607 (100, $M^+ - 35$), 599 (52, $M^+ - 43$), 513 (9.9, $M^+ - 119$).

2c: 70%; colorless crystals; mp 170 °C; ^{1}H NMR (C_6D_6) δ 1.35 (d, $J = 6.7$ Hz, 36 H), 1.37 (d, $J = 6.7$ Hz, 36 H), 1.77 (sept, $J = 6.7$ Hz, 12 H); ^{13}C NMR (C_6D_6) δ 16.4 (Si*C*H(CH_3)$_2$), 22.0, 22.2 (SiCH(*C*H$_3$)$_2$); ^{29}Si NMR (C_6D_6) δ 11.9 (Si(*i*-Pr)$_3$), 21.3 (SiCl); MS (EI, 14 eV) *m*/*z* (%) 711 (16, $M^+ - 43$ (*i*-Pr)), 562 (100, $M^+ - 192$), 377 (53). Anal. Calcd for $C_{36}H_{84}Si_6Cl_2$: C, 57.15; H, 11.19. Found: C, 57.11;, H, 11.06.

2c′: 81%; a colorless oil; ^{1}H NMR (C_6D_6) δ 1.37 (d, $J = 7.5$ Hz, 36 H), 1.38 (d, $J = 7.5$ Hz, 36 H), 1.84 (sept, $J = 7.5$ Hz, 12 H); ^{13}C NMR (C_6D_6) δ 16.8 (Si*C*H(CH_3)$_2$), 22.2, 22.4 (SiCH(*C*H$_3$)$_2$); ^{29}Si NMR (C_6D_6) δ 5.2 (SiBr), 12.2 (Si(*i*-Pr)$_3$).

Typical procedures for the reactions of disilenes **1b** with chloroform and dichloromethane are presented in ref 6. A similar reaction of **1a** with chloroform gave an adduct **3a** (70%) in addition to **2a** (26%). **3a**: colorless oil; ^{1}H NMR (C_6D_6) δ 0.42 (s, 6 H), 0.48 (s, 6 H), 1.13−1.28 (m, 48 H), 1.54 (sept, $J = 6.8$ Hz, 4 H), 1.56 (sept, $J = 6.8$ Hz, 4 H), 6.18 (s, 1 H); ^{13}C NMR (C_6D_6) δ −5.0, −3.8 ($SiCH_3$), 15.2, 15.4, 15.5, 15.6 (Si*C*H(CH_3)$_2$), 20.0, 20.2, 20.57, 20.62, 20.70, 20.77 (SiCH(*C*H$_3$)$_2$), 65.1 ($SiCHCl_2$); ^{29}Si NMR (C_6D_6) δ 18.8 ($SiCHCl_2$), 2.9, 3.8 (SiMe(*i*-Pr)$_2$), 5.4 (SiCl); MS (EI, 14 eV) 675 (22, $M^+ - 15$), 655 (74, $M^+ - 35$), 647 (16, $M^+ - 57$), 607 (10, $M^+ - 83$), 73 (100).

Product of reaction of **1a** with dichloromethane. **3a′**: 93%; a colorless oil; ^{1}H NMR (C_6D_6) δ 0.39 (s, 6 H), 0.42 (s, 6 H), 1.15−1.28 (m, 48 H), 1.47 (sept, $J = 6.8$ Hz, 4 H), 1.48 (sept, $J = 6.8$ Hz, 4 H), 3.68 (s, 2 H); ^{13}C NMR (C_6D_6) δ −5.5, −4.3 ($SiCH_3$), 15.42, 15.48, 15.7, 15.8 (Si*C*H(CH_3)$_2$), 20.1, 20.3, 20.5, 20.65, 20.69, 20.8 (SiCH(*C*H$_3$)$_2$), 31.4 (CH_2Cl); ^{29}Si NMR (C_6D_6) δ −46.5 ($SiCH_2Cl$), 2.8 (SiMe(*i*-Pr)$_2$), 4.1 (SiMe(*i*-Pr)$_2$), 5.9 (SiCl); MS (EI, 14 eV) 656 (1.8, M^+), 623 (100), 613 (59, $M^+ - 43$).

Adduct of **1a** with benzyl chloride (**3a″**): 51%; a colorless oil; ^{1}H NMR (C_6D_6) δ 0.36 (s, 6 H), 0.43 (s, 6 H), 1.07−1.40 (m, 52 H), 1.52 (sept, $J = 6.7$ Hz, 4 H), 3.13 (s, 2 H), 7.00 (m, 2 H), 7.12 (m, 1 H), 7.40 (d, $J = 7.4$ Hz, 2 H); ^{13}C NMR (C_6D_6) δ −5.2, −4.4 ($SiCH_3$), 15.1, 15.3, 15.6, 15.7 (Si*C*H(CH_3)$_2$), 20.03, 20.09, 20.26, 20.29, 20.53, 20.60, 20.64, 20.68 (SiCH(*C*H$_3$)$_2$), 22.5 (Si*C*H$_2$Ph), 125.0, 128.3, 129.8, 142.3; ^{29}Si NMR (C_6D_6) δ 49.0 ($SiCH_2Ph$), 2.3, 3.3 (SiMe(*i*-Pr)$_2$), 10.1 (SiCl); MS (EI, 14 eV) 683 (4, $M^+ -$ Me), 663 (13, $M^+ -$ Cl), 656 (6, $M^+ -$ (*i*-Pr)), 607 (6, $M^+ -$ (CH_2Ph)), 59 (100).

Reaction of 1c with *tert*-Butyl Chloride Monitored by ESR. In a glass tube (5 mm ϕ) containing **1c** (10 mg, 1.46×10^{-5} mol) were introduced degassed *tert*-butyl chloride (1.5 μL, 1.38×10^{-5} mol) and benzene-d_6 (0.5 mL) by distillation through a vaccum line. The tube was sealed and left to react at room temperature in the dark and then the ESR spectra were measured. The NMR spectroscopy revealed that only 10% of **1c** was consumed after reaction for 1 month. In addition to a small amount of **2c**, equal amounts of isobutene and isobutane were detected by the NMR. Signal intensities of the ESR spectra increased slowly for 6 months.

Acknowledgment. This work was supported by the Ministry of Education, Science, Sports, and Culture of Japan (Grant-in-Aids for Scientific Research (A) No. 08404042, Scientific Research (B) No.11440185, and Scientific Research on Priority Areas (A), “The Chemistry of Inter-element Linkage” (No. 09239101)).

Supporting Information Available: Cyclic voltagrams of **1a**−**d** and tetramesityldisilene in THF and plots of ln *A* vs *t* for the reaction of **1d** with chloroform in hexane and the dependence of the pseudo-first-order rates for the reaction of **1d** with chloroform in hexane on concentrations of chloroform and temperatures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA002798S