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Reactions of Tetramesityldisilene with Acid Chlorides and Ketenes

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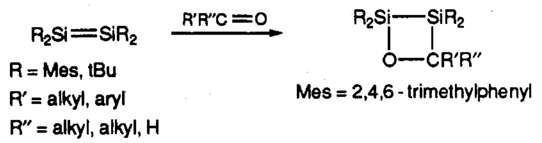
Tetramesityldisilene (1) reacts with dimethylketene and diphenylketene by [2+2] cycloaddition to the carbonyl group to give 3-methylidene-1,2-disilaoxetanes, **4b** and **4c**. Acetyl and dimethylacetyl chlorides react with 1 with elimination of HCl to give similar products, **4a** and **4b**, along with 1,1,2,2-tetramesityl-1-chlorodisilane (**3**). Nonenolizable acid chlorides react variously with 1: Heptafluorobutyryl chloride gives the [2+2] cycloaddition product, **11**; trimethylacetyl chloride undergoes a slow reaction to give **3** and *iso*-butene; 3,4,5-trimethoxybenzoyl chloride produces 25% of a [2+4] cycloaddition product, **14**. The X-ray crystal structure of **4b** was determined: triclinic, $P1$, $Z = 2$, with cell dimensions $a = 10.442(2)$ Å, $b = 11.123(2)$ Å, $c = 16.124(3)$ Å, $\alpha = 78.06(3)°$, $\beta = 87.93(3)°$, and $\gamma = 72.94(3)°$.

Introduction

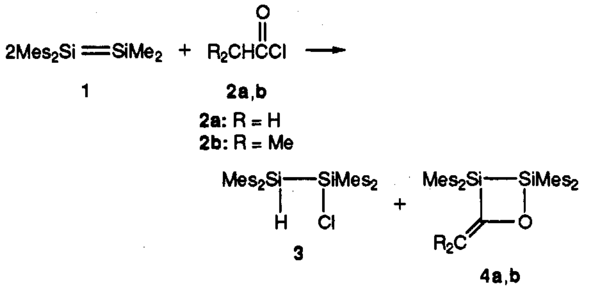
It has previously been demonstrated that stable disilenes react with ketones and aldehydes by [2+2] cycloaddition to form 2,3-disilaoxetanes (eq 1).[1,2] The reaction appears to be quite general, and the products do not exhibit the thermal instability of similar 2-silaoxetanes formed by analogous reactions of carbonyl compounds with silenes.[3] Additionally, it is also known that tetramesityldisilene (1) reacts with benzyl chloride by 1,2-addition of the C–Cl bond to the Si=Si double bond.[4] Thus the manner in which disilenes behave towards acid chloride is of interest. In this paper we report the reactions of 1 with various acid chlorides, both enolizable and nonenolizable, as well as with two ketenes.



(1)

Reactions of Tetramesityldisilene with Enolizable Acid Chlorides

When an excess of acetyl chloride (**2a**) was added to 1 at room temperature, the characteristic yellow color of the disilene disappeared after 2 h. Analysis of the reaction mixture by ^{1}H NMR revealed that two products were present in a 1:1 ratio. The products were identified as **3**,[5] the result of HCl addition across the Si=Si double bond, and **4a**, the formal [2+2] cycloadduct of dimethylketene and 1 (eq 2). A similar reaction was also observed with dimethylacetyl chloride (**2b**) and 1, leading to **3** and **4b**.



(2)

Both compounds **4a** and **4b** were colorless air-stable solids that were unchanged in refluxing benzene. The ^{1}H NMR for both compounds showed only two nonequivalent mesityl groups, indicating that a plane of symmetry was present. The ^{29}Si NMR shifts for the silicon nuclei bound to the oxygen were nearly identical and in the same area as for other 2,3-disilaoxetanes formed from tetramesityldisilene.[1] The other ^{29}Si resonance for each compound was shifted upfield from that for the ^{29}Si bonded to the ring carbon in other known 2,3-disilaoxetanes. Such shifts are common when comparing a ^{29}Si nucleus attached to an sp^3 center and an sp^2 center.[6]

Two pathways can be envisaged to explain the results of these experiments (Scheme I). In pathway a, the first step is addition of the carbonyl group of **2a,b** to disilene 1, forming a disilaoxetane intermediate. This pathway assumes that the carbonyl bond is sufficiently polar to allow it to react with 1 in preference to the C–Cl bond. The second step requires the disilene to assist in the dehydrohalogenation of the disilaoxetane intermediate. Pathway b requires the disilene to formally extract HCl from **2a,b** to form a ketene which in turn can cycloadd to another molecule of 1 to form **4a,b**.

To determine if pathway a was feasible, the reaction of 1 with a tertiary halide, *tert*-butyl chloride, was investigated. After 3 d at room temperature no reaction was observed. The mixture was then heated to 60 °C for 10 d. After this time only two products were seen by ^{1}H NMR, **3** and *iso*-butene (**5**) (eq 3). These results demonstrate that abstraction of Cl by 1 from a reactive tertiary alkyl halide can occur but under conditions substantially more vigorous than those used with acetyl chloride and 1.

As a test of pathway b in Scheme I the reaction of 1 with two ketenes was examined. Diphenylketene (**6c**),[19] syn-

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[1] Fanta, A. D.; DeYoung, D. J.; Belzner, J.; West, R. *Organometallics* **1991**, *10*, 3466.

[2] For reviews on disilene chemistry, see: Raabe, G.; Michl, J. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1015. West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201.

[3] Barton, T. J. *Pure Appl. Chem.* **1980**, *52*, 615.

[4] McKillop, K.; West, R. Unpublished result.

[5] Fink, M. J.; DeYoung, D. J.; West, R. *J. Am. Chem. Soc.* **1983**, *105*, 1071.

[6] Marsmann, H. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin and New York, 1981; Vol. 17, p 153.

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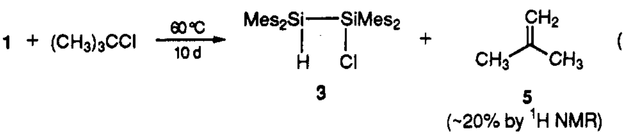
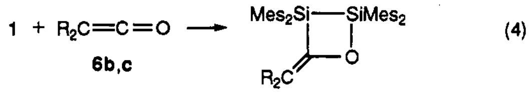


(~20% by ^{1}H NMR)

thesized in 3 steps from benzil, was reacted with **1** at 50 °C to produce disilaoxetane **4c** (eq 4). The reaction was

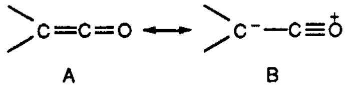


4b,c
4b: R = Me
4c: R = Ph

clean and without side products. Similarly, the dehydrohalogenation of **2b** by NEt_3 produced dimethylketene (**6a**) which subsequently reacted over a period of 3 d with **1** to produce cycloadduct **4b**.[7]

It was observed qualitatively that the reactivity of ketenes toward **1** was substantially less than that of ketones and aldehydes. Ketenes are known to be less nucleophilic than ketones, a fact that can be rationalized by participation of resonance form B in which the oxygen bears a formal positive charge.[8]

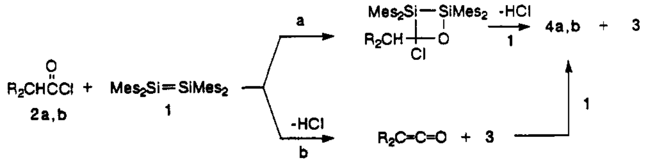
The mechanism of these cycloadditions is believed to be stepwise, occurring either through nucleophilic attack by oxygen or electrophilic attack by carbon on the disilene. In either case participation of resonance form B would reduce the reactivity of ketenes toward disilenes.



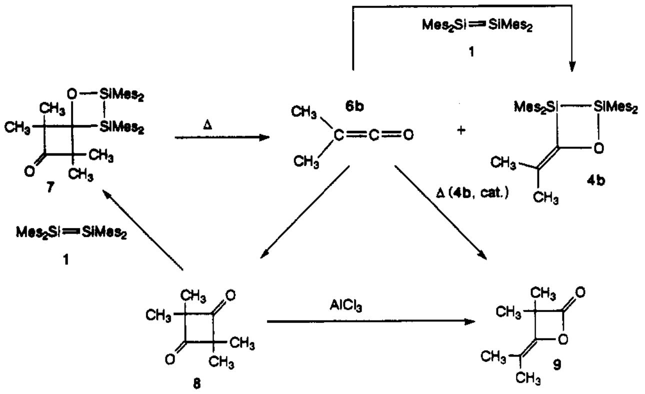
The interaction of dimethylketene with **1** was further explored through the thermolysis of the cyclobutanedione adduct **7**, prepared by reaction of 1,3-cyclobutanedione **8** with **1** as described earlier.[1] Surprisingly, a second equivalent of **1** would not add across the remaining carbonyl bond. Heating a mixture of **7** and **1** to 70 °C resulted in the cleavage of **7** into dimethylketene, as evidenced by its presence in the ^{1}H NMR spectrum, and **4b**. When the volatile products of the reaction were vacuum distilled into another NMR tube, dimethylketene was observed to dimerize to **8**. It was found that heating dimethylketene in the presence of **4b** accelerated the dimerization, but now the β-lactone **9** was formed exclusively. Both **8** and **9** are known dimerization products of dimethylketene, and it has been shown that solvent effects can determine which isomer is preferred.[9] The presence of unsymmetrical dimer **9** was unequivocally proven by reacting it with a catalytic amount of $AlCl_3$ and obtaining symmetrical dimer **8**. The entire reaction sequence is summarized in Scheme II.

The $^1J_{^{29}\mathrm{Si}-^{29}\mathrm{Si}}$ of **4b** and **7** were determined to be 86 and 89 Hz, respectively, by using the INEPT-INADEQUATE pulse sequence adapted for the ^{29}Si nucleus.[22] These coupling constants are similar to that for 4,4-dimethyl-2,3-disilaoxetane (84 Hz). For all three compounds, the Si–Si coupling constants are a little lower than typical values for other three- and four-membered ring heterocycles formed from reactions of disilenes. It is reasonable to expect the $^1J_{^{29}\mathrm{Si}-^{29}\mathrm{Si}}$ of **4b** to be slightly larger than that of **7** since one of the silicon atoms is bonded to a sp^2 center.

Scheme I. Possible Pathways for the Formation of 4a,b



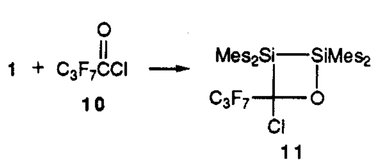
Scheme II. Thermolysis of 7



Reactions of Tetramesityldisilene with Nonenolizable Acid Chlorides

Having established that acid chlorides possessing α-protons react with **1** to form ketenes, we turned next to reactions of **1** with a few acyl chlorides without α-protons.

Heptafluorobutyryl chloride (**10**) reacted rapidly with **1**, producing a clear colorless solution within seconds. A white solid product was isolated, which gave a mass spectrum indicating that **11** was a 1:1 adduct of the starting materials. The ^{1}H NMR exhibited four different aryl-H resonances, and a pattern in the *o*-CH_3 region indicating extremely hindered *o*-methyl rotation. The spectra are consistent with 1,2-disilaoxetane structure **11** (eq 5).



The ^{19}F NMR spectrum showed a C_3F_7 group which was in an asymmetric environment as evidenced by the fact that two AB quartets appeared with large coupling values that are common for geminal fluorines. The $^3J_{F-F}$ values were small or not observed as is often the case in fluorocarbon compounds.[10] No ^{29}Si NMR data could be obtained due to the low solubility of **11** in all solvents tried.

When trimethylacetyl chloride was added to **1**, no cycloaddition took place, perhaps for steric reasons. Reaction was slow, requiring several days at 60 °C, and led only to **3** and *iso*-butene (eq 6). These results are best explained if there was first abstraction of Cl from trimethylacetyl chloride by **1** to form an acyl radical or cation, which could then lose CO to give isobutene.

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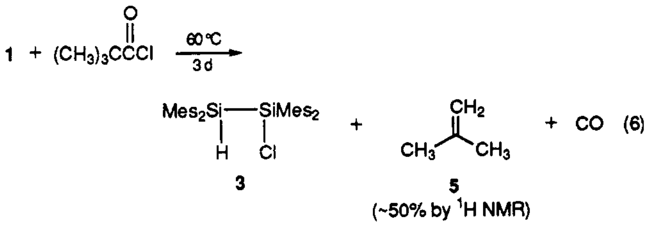
(7) The reactions of 1 with ketenes to produce 4b and 4c were both more rapid than the reaction of 1 with dimethylacetyl chloride to give 4b.

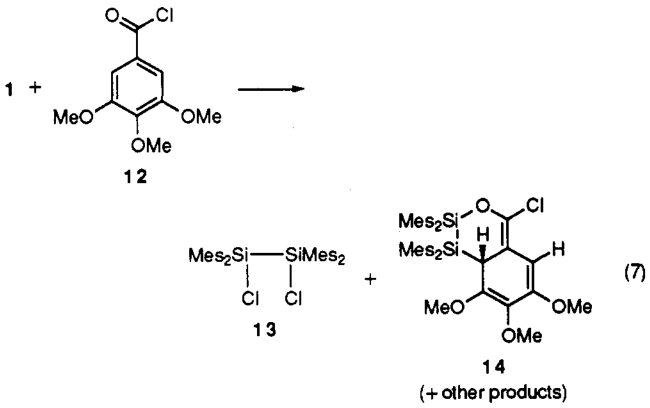
(8) Moore, C. B.; Pimentel, G. C. *J. Chem. Phys.* **1963**, *35*, 2816. Firl, F.; Runge, W. *Z. Naturforsch.* **1974**, *29b*, 393.

(9) Farnum, D. G.; Johnson, J. R.; Hess, R. E.; Marshall, T. B.; Webster, B. *J. Am. Chem. Soc.* **1965**, *87*, 5191.

(10) Emsley, J. W.; Phillips, L.; Wray, V. *Prog. Nucl. Magn. Reson. Spectrosc.* **1975**, *10* (Parts 3 and 4), 1.



A particularly interesting result was obtained in the reaction of 3,4,5-trimethoxybenzoyl chloride (**12**) with **1**. Seconds after addition of **12** to **1**, the yellow color of the disilene changed to deep orange. Analysis of the mixture by preparative gel permeation chromatography showed two main products to be present in addition to several highly colored minor products (eq 7).



The most abundant product was identified as **13** by its published ^{1}H NMR and mass spectra.[5] The other major compound, an air-stable yellow solid, was more difficult to identify. The mass spectrum confirmed that it was a 1:1 adduct of the starting materials. The ^{1}H NMR spectrum was quite complicated, but at higher temperatures it was apparent that eight magnetically different mesityl groups were present. These data are consistent with the yellow compound being a mixture of two diastereomers having structure **14**. Supporting evidence for structure **14** was the absence of any carbonyl stretching frequency in the IR, and chemical shifts for allylic and vinyl ring protons of the methoxy-substituted ring (4.7 and 6.02 ppm, respectively).

The ^{29}Si NMR had four resonances: −3.84, −3.73, 4.99, and 5.60 ppm. The spectrum was acquired using the INEPT refocused pulse sequence with delay times set to give long-range coupling to silicon antiphased to $^{2}J_{\text{Si-H}}$.[11] The spectrum of **14** showed the downfield pair of signals antiphased to the other pair, which agrees with the proposed structure.

The NMR spectra can be best explained if there is hindered rotation of the mesityl groups. When the mesityl groups become locked, two different orientations of the mesityl groups will occur: a right-handed and a left-handed one. Since the molecule is not symmetric, the two orientations will be magnetically inequivalent. Essentially, the mesityl groups align in either orientation, providing a second chiral center in the molecule. The two chiral centers result in a pair of magnetically different diastereomers. The inequivalencies began to dissipate as the compound was heated, forcing the mesityl groups in the direction of free rotation. The ^{29}Si NMR spectrum taken at 65 °C showed the upfield shift had coalesced to a single peak and the other pair of peaks had moved closer together.

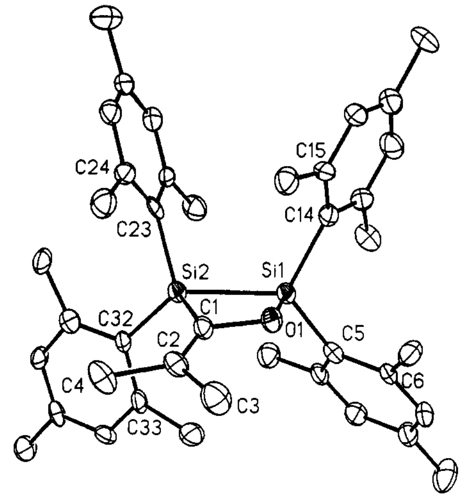


Figure 1. Thermal ellipsoid drawing of **4b**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)–Si(2) 2.373(2), Si(1)–O(1) 1.693(4), Si(2)–C(1) 1.886(5), C(1)–O(1) 1.428(7), C(1)–C(2) 1.329(8); Si(2)–Si(1)–O(1) 78.2(1), Si(1)–Si(2)–C(1) 71.1(2), Si(1)–O(1)–C(1) 106.6(3), Si(2)–C(1)–O(1) 103.5(3), O(1)–C(1)–C(2) 119.1(4), C(1)–C(2)–C(3) 123.5(5), C(3)–C(2)–C(4) 115.2(5).

Cycloaddition reactions of the [2+4] type are unusual for disilenes. The only earlier examples involve 1,2-diketones or 1,2-diketimines, with formation of bonds from silicon to oxygen or nitrogen.[12–14] The reaction shown in eq 7 is unique because it involves only one heteroatom in the diene and an aromatic ring is broken in the process. Cycloaddition reactions involving loss of aromaticity have been described for stable silenes,[15,16] but no such reactions involving disilenes have previously been reported.[17]

The products of eq 7 indicate that competition took place between cycloaddition and chlorine abstraction. The minor products were all highly colored (mostly red and orange) and exhibited complicated ^{1}H NMR spectra. Such products were likely the result of subsequent reactions of the acid chloride after chlorine abstraction, but could not be identified.

Crystal Structure of 4b

The structure of **4b** was confirmed by X-ray crystallography. A thermal ellipsoid diagram for **4b** is shown in Figure 1, and details of the structure determination appear

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(11) Blinka, T. A.; Helmer, B. J.; West, R. *Adv. Organomet. Chem.* **1984**, *23*, 93.

(12) Boudjouk, P.; Han, B.-H.; Anderson, K. R. *J. Am. Chem. Soc.* **1982**, *104*, 4492.

(13) DeYoung, D. J. Dissertation, University of Wisconsin, 1984.

(14) Weidenbruch, M.; Lesch, A. J. *Organomet. Chem.* **1991**, *407*, 31.

(15) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.

(16) Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246.

(17) The aromatic ring is postulated to break in the thermolysis of **1** as shown (see ref 9):

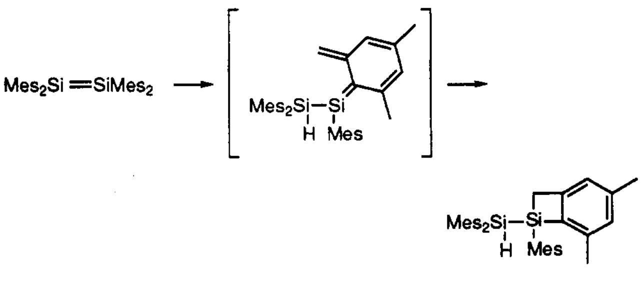
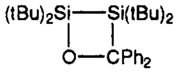


Table I. Crystal and Refinement Data

empirical formula	$C_{40}H_{50}OSi_2$
formula wt	603.0
cryst dimensions, mm	0.15 × 0.25 × 0.30
cryst system	triclinic
space group	*P*1
cell parameters	
a, Å	10.422(2)
b, Å	11.123(2)
c, Å	16.124(3)
α, deg	78.06(3)
β, deg	87.93(3)
γ, deg	72.94(3)
V, Å^3	1751.0(6)
Z	2
density (calcd), g cm^{-3}	1.144
absorption coeff, mm^{-1}	1.118
F(000)	652
temp, K	108(2)
2θ range, deg	3.0–100.0
scan type	Wyckoff
scan speed, deg/min	variable, 6.00–20.00 in ω
scan range	0.60
observed reflections [$F > 4.0\sigma(F)$]	2783
data to parameter ratio	7.1:1
largest difference peak, e/Å^3	0.38
largest difference hole, e/Å^3	−0.28
R, %	5.77
wR, %	7.29
goodness of fit	1.79

in Table I. The only other X-ray crystal structure of a 2,3-disilaoxetane in the literature is for **15**.[18] Structure



15

4b differs from this compound in a number of ways. The ring in **15** is highly puckered, probably because of the steric demands of the *tert*-butyl groups. The Si–Si and Si–C bonds are also abnormally long in **15**, 241 and 202 pm, respectively. For **4b**, the oxetane ring is nearly planar, and the exocyclic double bond is bent out of the plane of the ring by only 12°. The bond lengths within the oxetane ring are also more normal. The Si–Si distance was 237 pm, which is slightly elongated, but less so than for **15**. The Si–C bond length was only 189 pm, which is substantially less than the 202 pm reported for **15**. Additionally, the mesityl groups are almost eclipsed, exhibiting torsion angles for C(5)–Si(1)–Si(2)–C(32) and C(14)–Si(1)–Si(2)–C(23) of −8.3° and 0.4°.

Experimental Section

General Comments. All reactions were performed under argon or nitrogen using either a Schlenk line or a glovebox. Solvents were distilled from a Na/benzophenone mixture immediately prior to use. Liquid acid chlorides were distilled from K_2CO_3 and used promptly. Diphenylketene (**6c**),[19] tetramesityldisilene (**1**),[20] and 1,3-cyclobutadione adduct **7**[1] were prepared according to procedures in the literature.

NMR spectra were determined in C_6D_6 unless otherwise noted. ^{1}H NMR were recorded on a Bruker WP-200 spectrometer. ^{29}Si NMR spectra were recorded on a Bruker AM-500 (99.36 MHz). All ^{29}Si spectra were collected using the INEPT pulse sequence with a ^{1}H refocusing pulse (standard Bruker program INEPTRD: $D1 = 3.0$ s, $D2 = 0.085$ s, $D3 = 0.15$ s). Mass spectra were obtained with a Kratos MS-80 mass spectrometer. Analytical GC was done on a Hewlett-Packard 5890 instrument equipped with a 0.53-mm × 15-m open tubular column coated with methylsilicone containing 5% phenyl groups (DB-5). Preparative gel permeation chromatography (GPC) was done on a Japan Analytical Industry Co. Model LC-908 using a Jaigel-1H column of cross-linked polystyrene and refractive index detection. Toluene was used an an eluent with a flow rate of 3.5 mL/m. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

Reaction of 1 with Acetyl Chloride (2a). In a drybox 60 mg of **1** (0.11 mmol) was placed in an NMR tube with 0.10 g (10× excess) of acetyl chloride and 4 mL of C_6D_6. The tube was evacuated and sealed. Not all of the disilene went into solution, so the tube was periodically shaken to mix the reactants. After 3 h it was apparent that **1** was completely consumed. ^{1}H NMR showed the reaction to be nearly quantitative; **3** and **4a** were formed in 1:1 proportions by integration of Si–H and =CH peaks. The tube was opened and solvent removed *in vacuo*. The compounds were separated by chromatography on a silica gel column, eluted with 90% hexane/10% ether. The HCl adduct **3** (20 mg, 32%) eluted first, followed by **4a** (15 mg, 24%).

3: ^{1}H NMR δ 2.04 (s, 6H, *p*-Me), 2.08 (s, 6H, *p*-Me), 2.35 (s, 12H, *o*-Me), 2.40 (s, 12H, *o*-Me), 5.87 (s, 1H, Si–H), 6.63 (s, 4H, ArH), 6.69 (s, 4H, ArH); ^{29}Si NMR δ 2.25 ($^{2}J_{SiH} = 12.6$ Hz), −52.6 ($^{1}J_{Si\text{-}H} = 182$ Hz); HRMS (EI) *m/z* M$^+$ − Mes calcd 449.1887, found 449.1823.

4a: ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 6H, *p*-Me), 2.20 (s, 12H, *o*-Me), 2.23 (s, 6H, *p*-Me), 2.27 (s, 12H, *o*-Me), 4.98 (d, $J = 2.4$ Hz, 1H, =CH), 5.17 (d, $J = 2.4$ Hz, 1H, =CH), 6.72 (s, 4H, ArH), 6.76 (s, 4H, ArH); ^{29}Si NMR δ 23.96, −2.37; HRMS (EI) *m/z* M$^+$ calcd 574.3087, found 574.3108.

Reaction of 1 with Dimethylacetyl Chloride (2b). In a drybox 90 mg of **1** (0.17 mmol) was placed in an NMR tube with 0.15 g of dimethylacetyl chloride and 3 mL of C_6D_6. The tube was occasionally shaken. After 7 d conversion to **3** and **4b** was observed along with an unisolated side product. The yield by ^{1}H NMR was about 75%. For characterization of **4b** see thermolysis of **7**.

When the reaction was run in the presence of NEt_3, dimethylketene was observed by ^{1}H NMR along with NEt_3HCl as a white precipitate. After standing for 5 d, the ketene peak was gone and **3** and **4b** were present in a ratio of 3:1 by ^{1}H NMR. The mixture could be separated by gel permeation chromatography, giving 20 mg of **4b** (20%) and 60 mg of **3** (64%).

Reaction of 1 with *tert*-Butyl Chloride. To an NMR tube were added 100 mg of **1**·2THF (0.15 mmol) and 14 mg of *tert*-butyl chloride (0.16 mmol) in 3 mL of C_6D_6. The tube was subsequently sealed and heated for 10 d at 70 °C. ^{1}H NMR showed about 20% conversion of **1** to **3** and *iso*-butene (**5**), identified by its ^{1}H NMR spectrum.

5: ($A_3XX'A'_3$ pattern approaching A_6X_2)[21] ^{1}H NMR δ 1.59 (t, $J = 1.1$ Hz, 6H, CH_3), 4.73 (sept, $J = 1.1$ Hz).

Reaction of 1 with Dimethylketene (6b). A 50-mL flask was charged with equimolar amounts of triethylamine and **2b**. The mixture was kept under argon and stored for 2 h. Formation of a white salt was visible after 15 min. Part of the solution was vacuum transferred to an NMR tube. The presence of dimethylketene was established by ^{1}H NMR (δ 1.21 ppm); over a period of 3 d it slowly dimerized to **8** (^{1}H NMR δ 0.96 ppm; HRMS (EI) *m/z* M$^+$ calcd for $C_8H_{12}O$ 140.0839, found 140.0837).

When dimethylketene was distilled into 50 mg of **1**·2THF (0.74 mmol) and left at 50 °C overnight, 26 mg of **4b** was formed (59%).

Reaction of 1 with Diphenylketene (6c). A total of 80 mg of **1**·2THF (0.25 mmol) and 0.05 g (0.25 mmol) of diphenylketene was sealed in an NMR tube with C_7D_8. The solution was heated for 5 d at 50 °C. Kugelrohr distillation (80 °C/0.01 Torr) removed

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[18] Schäfter, A.; Weidenbruch, M. *J. Organomet. Chem.* **1985**, *282*, 305.

[19] Smith, L. I.; Hoehn, H. H. *Org. Synth. Collect.* **1955**, *3*, 356.

[20] It has been observed that the chemistry in solution for **1** and that for **1**·2THF are identical. For the synthesis of tetramesityldisilene, see: Yokelson, H. B.; Gillette, G. R.; Tan, R. P. K.; Millevolte, A. J.; West, R. *Inorg. Synth.*, in press.

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the excess diphenylketene. The product was recrystallized from a toluene/hexane mixture to yield 51 mg of **4c** (58%): ^{1}H NMR (toluene-d_8) δ 2.06 (s, 6H, *p*-Me), 2.11 (s, 6H, *p*-Me), 2.12 (s, 12H, *o*-Me), 2.40 (s, 12H, *o*-Me), 6.57 (s, 4H, ArH), 6.61 (s, 4H, ArH), 6.7–7.65 (m, 10H, Ph); ^{29}Si NMR δ –0.67, 26.06; HRMS (EI) *m*/*z* M$^+$ calcd 726.3713, found 726.3730. Anal. Calcd for $C_{50}H_{54}Si_2O$: C, 82.64; H, 7.44. Found: C, 82.71; H, 7.52.

Thermolysis of 7. A solution of 120 mg of **7** (0.18 mmol) in C_6D_6 was sealed in an NMR tube and heated to 100 °C. After 35 min the tube was cooled to –30 °C and opened under argon, and the volatile contents were vacuum transferred into another NMR tube. This was sealed and the ^{1}H NMR spectrum taken, showing the singlet of dimethylketene at 1.21 ppm. This peak slowly disappeared, and **8** (0.95 ppm) was observed after 2 d. The residue after evaporation of solvent was identified as analytically pure **4b** (103 mg, 96%): ^{1}H NMR δ 1.57 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.03 (s, 6H, *p*-Me), 2.04 (s, 6H, *p*-Me), 2.43 (s, 12H, *o*-Me), 2.49 (s, 12H, *o*-Me), 6.61 (s, 4H, ArH), 6.63 (s, 4H, ArH); ^{29}Si NMR δ –7.37, 22.19: HRMS (EI) *m*/*z* M$^+$ calcd 602.3400, found 602.3388. Anal. Calcd for $C_{40}H_{50}Si_2O$: C, 79.66; H, 8.37. Found: C, 79.20; H, 8.21.

When the solution of **7** was heated to 100 °C in the presence of 1 equiv of **4b**, β-lactone **9**[9] was formed: ^{1}H NMR δ 0.91, 0.94 ppm; HRMS (EI) *m*/*z* M$^+$ calcd for $C_8H_{12}O$ 140.0839, found 140.0842.

It was observed that when 100 mg of **8** was dissolved in benzene with a catalytic amount of $AlCl_3$, **9** was formed in quantitative yield by ^{1}H NMR.

Reaction of 1 with Heptafluorobutyryl Chloride (10). To a 50-mL flask containing 8 mL of benzene were added 500 mg of **1**·2THF (0.74 mmol) and a large excess of 2,2,3,3,4,4,4-heptafluorobutanoic acid chloride. After standing overnight at room temperature, 406 mg of **11** (72%) precipitated from solution as white crystals: mp 176–177 °C; ^{1}H NMR ($CDCl_3$) δ 2.19 (s, 12H, *p*-Me), 2.24 (s, 6H, *o*-Me), 2.28 (br s, 6H, *o*-Me), 2.31 (v br s, 12H, *o*-Me), 6.65 (s, 2H, ArH), 6.69 (s, 2H, ArH), 6.77 (s, 2H, ArH), 6.69 (s, 2H, ArH); HRMS (EI) *m*/*z* M$^+$ – MesH calcd 644.1568, found 644.1583; ^{19}F NMR (ext ref $CFCl_3$) δ –85.7 (t, J = 10.7 Hz, 3F, CF_3), –111.8 (v br d, J = 283 Hz, 1F, $\mathrm{CF_3CFF'C}\mathit{F}\mathrm{F'}$), –113.5 (v br d, J = 283 Hz, 1F, $\mathrm{CF_3CFF'CF}\mathit{F'}$), –123.5 (br ddd, J = 286, 14.5, 2.56 Hz, 1F, $\mathrm{CF_3C}\mathit{F}\mathrm{F'CFF'}$), –125.5 (ddd, J = 286, 14.5, 2.56 Hz, 1F, $\mathrm{CF_3CF}\mathit{F'}\mathrm{CFF'}$). Anal. Calcd for $C_{40}H_{44}Si_2F_7OCl$: C, 67.75; H, 5.79. Found: C, 67.79; H, 5.76.

Reaction of 1 with Trimethylacetyl Chloride. In an NMR tube containing 3 mL of C_6D_6 were placed 100 mg of **1**·2THF (0.15 mmol) and 20 mg (0.165 mmol) of *tert*-butyl chloride. The tube was then sealed. Heating the tube at 65 °C for 8 h gave ~50% conversion to **3** and **5**, as shown by ^{1}H NMR.

Reaction of 1 with 3,4,5-Trimethoxybenzoyl Chloride (12). To 10 mL of benzene was added 200 mg of **1**·2THF (0.3 mmol) and 16 mg of 3,4,5-trimethoxybenzoyl chloride. The reaction mixture became red-orange within a few minutes. The mixture was then run through a preparative GPC using toluene as solvent. Separation of all products required 5 cycles through the column. Compound **14** (50 mg, 22%) was collected as the third fraction and remained a yellow oil after attempts at crystallization. Compound **13** (75 mg, 36%) was isolated as the fifth fraction.

14: ^{1}H NMR (25 °C) 1.96 (s, 6H, *p*-Me), 2.02 (s, 3H, *p*-Me), 2.04 (s, 3H, *p*-Me), 2.05 (s, 3H, *p*-Me), 2.08 (s, 6H, *p*-Me), 2.11 (s, 3H, *p*-Me), 2.39 (s, 6H, *o*-Me), 2.41 (s, 6H, *o*-Me), 2.51 (s, 12H, *o*-Me), 2.55 (s, 24H, *o*-Me), 2.74 (s, 3H, OMe), 3.00 (s, 3H, OMe), 3.13 (s, 3H, OMe), 3.41 (s, 3H, OMe), 3.90 (s, 6H, OMe), 4.71, 5.99, 6.00, 7.02 (4s, 4H, vinyl and allylic CH), 6.54 (s, 2H, ArH), 6.57 (s, 2H, ArH), 6.62 (s, 2H, ArH), 6.63 (s, 2H, ArH), 6.66 (s, 2H, ArH), 6.68 (s, 4H, ArH), 6.72 (s, 2H, ArH); ^{29}Si NMR δ –3.92, –3.80, 4.87, 5.69: HRMS (EI) *m*/*z* M$^+$ calcd 762.3327, found 762.3340. Anal. Calcd for $C_{46}H_{55}Si_2O_4Cl$: C, 72.44; H, 7.21. Found: C, 72.88; H, 7.62.

Structure Determination of 4b. Colorless, blocklike crystals of **4b** were grown by the slow evaporation of hexane from a saturated solution. The X-ray crystallographic experiments were performed with a graphite-monochromated Cu Kα X-radiation source (λ = 1.54178 Å) and a low-temperature device.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)[a]

	x	*y*	*z*	*U*(eq)
Si(1)	4717(1)	6699(1)	2019(1)	21(1)
Si(2)	4748(1)	7901(1)	3071(1)	21(1)
O(1)	5071(1)	8012(1)	1442(1)	23(1)
C(1)	5261(1)	8745(1)	2032(1)	22(1)
C(2)	5858(1)	9658(1)	1780(1)	26(1)
C(3)	6306(1)	10001(1)	894(1)	38(1)
C(4)	6147(1)	10413(1)	2386(1)	39(1)
C(5)	6084(1)	5254(1)	1824(1)	22(1)
C(6)	6395(1)	5145(1)	973(1)	21(1)
C(7)	7364(1)	4073(1)	807(1)	27(1)
C(8)	8061(1)	3092(1)	1438(1)	30(1)
C(9)	7770(1)	3204(1)	2275(1)	29(1)
C(10)	6794(1)	4244(1)	2479(1)	24(1)
C(11)	5720(1)	6185(1)	237(1)	30(1)
C(12)	9105(1)	1940(1)	1249(1)	48(1)
C(13)	6537(1)	4213(1)	3406(1)	34(1)
C(14)	3008(1)	6608(1)	1682(1)	23(1)
C(15)	1993(1)	7731(1)	1306(1)	26(1)
C(16)	759(1)	7631(1)	1079(1)	30(1)
C(17)	473(1)	6468(1)	1195(1)	35(1)
C(18)	1463(1)	5392(1)	1569(1)	35(1)
C(19)	2709(1)	5438(1)	1821(1)	28(1)
C(20)	2152(1)	9065(1)	1119(1)	32(1)
C(21)	–867(1)	6398(1)	914(1)	52(1)
C(22)	3666(1)	4163(1)	2229(1)	38(1)
C(23)	2955(1)	8540(1)	3370(1)	21(1)
C(24)	2163(1)	9845(1)	3170(1)	25(1)
C(25)	862(1)	10177(1)	3434(1)	29(1)
C(26)	260(1)	9311(1)	3891(1)	27(1)
C(27)	1026(1)	8035(1)	4095(1)	29(1)
C(28)	2340(1)	7652(1)	3847(1)	24(1)
C(29)	2718(1)	10901(1)	2708(1)	33(1)
C(30)	–1156(1)	9752(1)	4176(1)	41(1)
C(31)	3111(1)	6240(1)	4107(1)	34(1)
C(32)	5998(1)	7549(1)	3978(1)	20(1)
C(33)	7359(1)	6910(1)	3859(1)	24(1)
C(34)	8278(1)	6526(1)	4538(1)	26(1)
C(35)	7942(1)	6772(1)	5325(1)	27(1)
C(36)	6626(1)	7452(1)	5434(1)	23(1)
C(37)	5656(1)	7850(1)	4786(1)	25(1)
C(38)	7909(1)	6698(1)	3002(1)	35(1)
C(39)	8962(1)	6325(1)	6046(1)	42(1)
C(40)	4304(1)	8645(1)	4999(1)	32(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Unit cell parameters were determined by least-squares refinements based on 25 centered reflections. Three standard reflections were measured after every 50 reflections during the data collection. No significant decrease in the intensity of the standard reflections was observed during the data collection.

The structures were solved by direct methods using the SHELTX PLUS program on a MicroVAX II and refined by the full-matrix least-squares refinement method using the reflections with $F_o > 4.0\sigma(F)$. The non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were placed in idealized positions and refined using a riding model and isotropic thermal parameters. Atomic coordinates and isotropic coordinates are found in Table II. The refinement converged using statistical weights to unweighted and weighted agreement factors of R = 5.77% and wR = 7.29%.

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Supplementary Material Available: Tables of crystallographic data, bond lengths, and bond angles for **4b** (3 pages). Ordering information is given on any current masthead page.

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