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Solution and Solid-State Oxidation Chemistry of Tetrakis(2,4,6-triisopropylphenyl)disilene

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The air oxidation of tetrakis(2,4,6-triisopropylphenyl)disilene (**1**) has been investigated. In benzene solution the first oxidation product is the 1,2-disiladioxetane **2**, which rearranges to give the 1,3-cyclodisiloxane **3** in addition to a compound with the 1-oxa-2-silacyclopent-3-ene structure (**4**). The same products are obtained when solid **1** is oxidized. Conditions for the rearrangement of **2** which provide either **3** or **4** pure are also described. Oxidation of **1** with 1 equiv of *m*-chloroperbenzoic acid produces the disilaoxirane **5** and, with excess oxidant, **3**. The X-ray crystal structures of **3** and **5** are reported.

Introduction

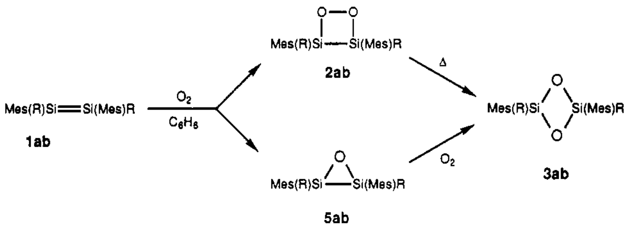
The air oxidation of several disilenes was one of the first reactions to be studied following the discovery of these compounds 10 years ago.[1] The usual course of the oxidation is illustrated in Scheme I. This reaction has been particularly well studied for tetramesityldisilene (**1a**) and 1,2-di-*tert*-butyl-1,2-dimesityldisilene (**1b**). For these compounds, air oxidation in solution produces initially the 1,2-disiladioxetane **2a** or **2b** as the major product along with some of the 1,2-disilaoxirane **5a** or **5b**. In a slower reaction, the 1,2-disiladioxetanes rearrange to the 1,3-cyclodisiloxanes **3a** or **3b**; if excess oxygen is present the latter compounds are also formed by further oxidation of **5a,b**. Oxidation of the solid disilenes **1a** and **1b** also lead to eventual formation of **3a** and **3b**.[2]

Recently, Watanabe and co-workers reported that the air oxidation of solid tetrakis(2,4,6-triisopropylphenyl)disilene (**1**) yielded a novel compound (**4**) with a 1-oxa-2-sila-cyclopent-3-ene structure as the only product.[3] The striking difference between these results and our earlier observations led us to investigate the oxidation of **1**, both in solution and as a solid.[4]

Results and Discussion

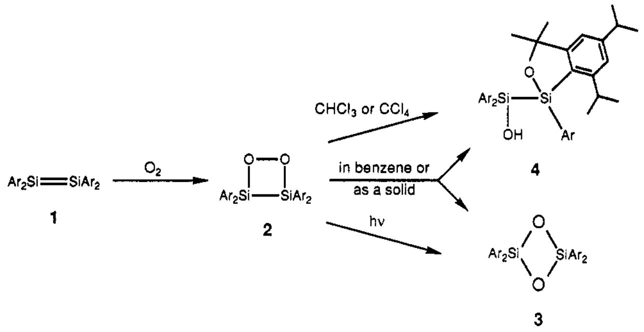
A. Air Oxidation of 1. The experiment of Watanabe and co-workers was first repeated, by exposing a sample of solid **1** to oxygen for 18 h at 25 °C. When the colorless product was dissolved in benzene and examined by ^{29}Si NMR spectroscopy, it displayed four resonances at 37.18, 0.88, –6.39, and –7.49 ppm, in an approximate ratio 1:1:2:1. None of the original disilene was present. Exposure of solid **1** to oxygen for 2 days resulted in the appearance of only three signals at 0.88, –6.39, and –7.49 ppm, in a 1:2:1 ratio.

Scheme I. Oxygenation of 1ab[a]



[a] R = mesityl for **1a**, **2a**, **3a**, and **5a**; R = *tert*-butyl for **1b**, **2b**, **3b**, and **5b**. Mes = 2,4,6-trimethylphenyl.

Scheme II. Oxygenation of 1[a]



[a] Ar = 2,4,6-triisopropylphenyl.

Compound **4** should give only two equal ^{29}Si NMR resonances, and in fact those at –0.88 and –7.49 ppm are due to **4**. Evidently, air oxidation of solid **1** leads, finally, not to a single product but to an approximately 1:1 mixture of two compounds. As will be shown below, the second compound is the 1,3-cyclodisiloxane **3** (Scheme II).

Air oxidation of **1** was then carried out in benzene solution, allowing greater control over the reaction. Oxidation of **1** in solution is perceptibly slower than for the less hindered disilenes **1a** and **1b** but is still rapid. When oxygen is bubbled rapidly into a solution of **1** in benzene, decolorization of the disilene occurs with a half-time of about 1 min, compared to ~10 s for **1a** and **1b**. After complete oxidation, the sole product is the compound with a ^{29}Si NMR resonance at 37.18 ppm. Deshielded silicon resonances in this region are usual for 1,2-disiladioxetanes, which are normally the major initial oxidation products of disilenes.[5] Accordingly, we assign this compound structure **2**. In benzene or cyclohexane solution, **2** rearranges with $t_{1/2}$ = 5 h to a 1:2 mixture of **3** and **4**.

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[1] (a) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531. (b) Yokelson, H. B.; Millevolte, A. J.; Adams, B. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 4116. (c) West, R.; Yokelson, H. B.; Gillette, G. R.; Millevolte, A. J. In *Silicon Chemistry*; Corey, J. R., Corey, E., Gaspar, P. P., Eds.; Ellis Horwood; Chichester, U.K., 1988; Chapter 26, p 269. (d) McKillop, K. L.; Gillette, G. R.; Powell, D. R.; West, R. Unpublished studies.

[2] The air oxidation of (*E*)- and (*Z*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene to **2b** and **5b** occurs stereospecifically, and the rearrangement of **2b** to **3b** and the air oxidation of **5b** to **3b** are also stereospecific. Pure (*E*)-**1b** oxidized to (*E*)-**2b** and (*E*)-**5b**, which gave (*E*)-**3b** upon rearrangement or further oxidation. Air oxidation of a mixture of (*E*)- and (*Z*)-**1b** gave mixtures of (*E*)- and (*Z*)-**2b** and -**5b** in the same ratio as the initial mixture of **1b**. The rearrangement of mixtures of (*E*)- and (*Z*)-**2b** to **3b** and further oxidation of (*E*)- and (*Z*)-**5b** to **3b** both give ratios of **3b** similar to that of the starting materials. Michalczyk, M. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1525.

[3] Watanabe, H.; Takeuchi, K.; Nakajima, K.; Nagai, Y.; Goto, M. *Chem. Lett.* **1988**, 1343.

[4] Masamune, S.; Batcheller, S. A.; Park, J.; Davis W. M.; Yamashita, O.; Ohta, Y.; Kabe, Y. *J. Am. Chem. Soc.* **1989**, *111*, 1888.

[5] Yokelson, H. B. Ph.D. Thesis, University of Wisconsin—Madison, 1987.

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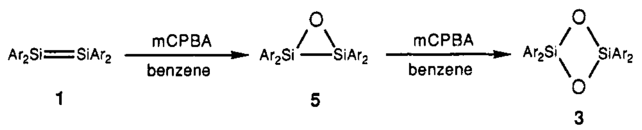
Scheme III. mCPBA Oxidation of 1[a]



[a] Ar = 2,4,6-triisopropylphenyl.

Attempts to separate mixtures of **3** and **4** were met with difficulty. Both compounds are very soluble in all but the most polar solvents. Crystallization from ethanol, the method used by Watanabe and co-workers to obtain a crystal of **4** for an X-ray structure analysis, afforded batches of colorless crystals, which proved to be mixtures of **3** and **4** in a similar proportion to that in the original solutions. After many attempts small samples of pure **3** and **4** were isolated by fractional crystallization. Small amounts of pure **3** and **4** were also obtained by preparative gel permeation chromatography after 25 cycles in toluene.

B. Preparation of Pure 3 and 4 by the Rearrangement of 2. Fortunately, it proved possible to find conditions for the rearrangement of **2** which produced either **3** or **4** in pure form and in larger quantity. After examination of many solvent systems and temperatures, it was found that **2** rearranged in both $CHCl_3$ and CCl_4 at 55 °C to yield **4** quantitatively.[6]

No solvent was found in which **2** rearranged exclusively to **3**. Compound **3** could, however, be obtained pure by photolysis of **2**. When **2** was photolyzed in hexane at −50 °C, the sole product was a compound with a single ^{29}Si NMR resonance at −6.39 ppm. Crystals were obtained from ethanol and a crystallographic analysis was performed, verifying that the compound was **3**; the structure is described in section E.

C. Synthesis of Disilaoxirane 5. The reaction of **1** with dinitrogen oxide was attempted in order to obtain the disilaoxirane **5**. Although this oxidation occurs for other disilenes[7] and digermenes,[4] a benzene solution of **1** saturated with dinitrogen oxide remained completely unchanged after 1 week at 25 °C and 3 days at 80 °C.[8] For comparison, **1a** reacts completely with dinitrogen oxide in benzene solution at 25 °C within 2 h.[7] Trimethylamine *N*-oxide also did not react with **1** in benzene solution after 3 days at 80 °C. However, a benzene solution of **1** was rapidly decolorized upon addition of an equal molar equivalent of *m*-chloroperbenzoic acid (mCPBA). A single product was obtained which had the composition R_4Si_2O (R = 2,4,6-triisopropylphenyl). This compound had only one signal in the ^{29}Si NMR spectrum at −30.39 ppm, in the region characteristic for disilaoxiranes. Its structure was determined to be **5** by X-ray crystallography. The stability of **5** toward further oxidation by atmospheric oxygen is in marked contrast to other disilaoxiranes which react rapidly with oxygen. Only after addition of another equivalent of mCPBA was the ^{29}Si NMR signal of **5** replaced by that of **3** (Scheme III). This reaction provides an alternate route for synthesis of pure **3**.

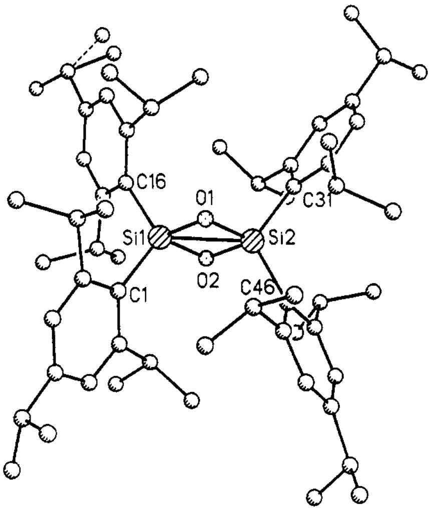


Figure 1. Structure of **3** determined from a crystallographic analysis. Hydrogen atoms are omitted for clarity.

Table I. Selected Bond Lengths and Angles for 3

	Bond Lengths (pm)		
Si(1)–Si(2)	243.1 (2)	Si(1)–O(1)	169.9 (4)
Si(1)–O(2)	169.2 (4)	Si(1)–C(1)	188.3 (6)
Si(1)–C(16)	190.0 (6)	Si(2)–O(1)	169.9 (4)
Si(2)–O(2)	170.8 (4)	Si(2)–C(31)	189.8 (6)
Si(2)–C(46)	190.4 (6)		
	Bond Angles (deg)		
Si(2)–Si(1)–O(1)	44.3 (1)	Si(2)–Si(1)–O(2)	44.6 (1)
O(1)–Si(1)–O(2)	89.0 (2)	Si(2)–Si(1)–C(1)	120.7 (2)
O(1)–Si(1)–C(1)	109.3 (2)	O(2)–Si(1)–C(1)	114.0 (2)
Si(2)–Si(1)–C(16)	121.8 (2)	O(1)–Si(1)–C(16)	114.1 (2)
O(2)–Si(1)–C(16)	109.6 (2)	C(1)–Si(1)–C(16)	117.5 (3)
Si(1)–Si(2)–O(1)	44.3 (1)	Si(1)–Si(2)–O(2)	44.1 (1)
O(1)–Si(2)–O(2)	88.5 (2)	Si(1)–Si(2)–C(31)	123.2 (2)
O(1)–Si(2)–C(31)	109.7 (2)	O(2)–Si(2)–C(31)	116.1 (2)
Si(1)–Si(2)–C(46)	120.6 (2)	O(1)–Si(2)–C(46)	115.1 (2)
O(2)–Si(2)–C(46)	108.1 (2)	C(31)–Si(2)–C(46)	116.3 (3)
Si(1)–O(1)–Si(2)	91.3 (2)	Si(1)–O(2)–Si(2)	91.2 (2)

D. Comparison with the Previous Literature Report. The air oxidation of **1**, as shown above, is much more complicated than reported in the earlier communication.[3,11] In addition, the ^{1}H NMR data and melting point reported in the literature for **4** actually match those which we observed for **3**. The X-ray crystal structure for **4**, determined earlier by Watanabe and co-workers,[3] was repeated, establishing that our compound **4** was the same substance described previously.

These findings, along with our own difficulty in separating mixtures of **3** and **4** leads us to conclude that pure **3** and **4** crystallize nearly simultaneously as separate crystals. In fact, examination of the crystals by microscope shows crystals with different topological features.

Evidently, the crystals which Watanabe and co-workers chose for performing a melting point determination and ^{1}H NMR and X-ray crystal structure analyses were taken from a mixture of crystals. Those chosen for a melting point determination and ^{1}H NMR spectroscopy were mostly those of **3**, while the single crystal chosen for a crystallographic analysis was that of **4**.[11]

E. X-ray Crystal Structure of 1,3-Cyclodisiloxane 3. The structure of **3** was determined by X-ray diffraction.

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(6) An attempt to observe the analogous 1-oxa-2-silacyclopent-3-ene **4a** by conducting the rearrangement of tetramesityl-1,2-disiladioxetane **2a** in CCl_4 at 55 °C was unsuccessful; only formation of **3a** was noted.

(7) Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865.

(8) This suggests that the reaction of dinitrogen oxide with other disilenes is a 3 + 2 cycloaddition reaction followed by loss of nitrogen and ring closure. The 3 + 2 approach of dinitrogen oxide toward disilene **1** would be more subject to the increased steric bulk of this disilene than an *N*-oxide end-on donation of an oxygen atom would be. Similar 3 + 2 cycloaddition reaction mechanisms have also been proposed for the reactions of the isoelectronic diazomethane[9] and organic azides[10] with disilenes as well as the reaction of dinitrogen oxide with digermenes.[4]

(9) Masamune, S.; Murakami, S.; Tobita, H.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 7776.

(10) Gillette, G. R.; West, R. *J. Organomet. Chem.* **1990**, *394*, 45.

(11) After this paper was written, Prof. Watanabe and co-workers repeated the oxidation of **1**, with results similar to ours. Private communication from Prof. H. Watanabe.

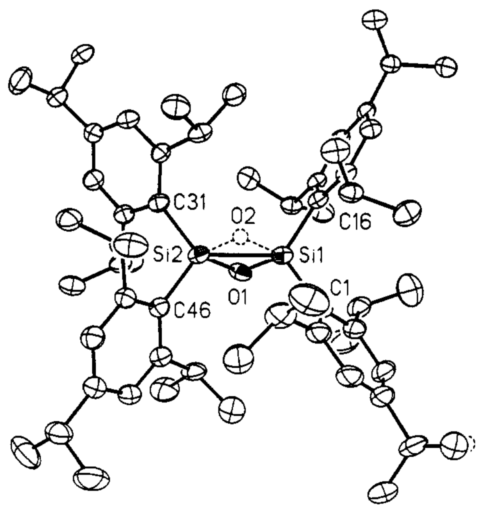


Figure 2. Structure of **5** determined from a crystallographic analysis. Hydrogen atoms are omitted for clarity.

Table II. Selected Bond Lengths and Angles for 5

	Bond Lengths (pm)		
Si(1)-Si(2)	225.4 (2)	Si(1)-O(1)	172.2 (3)
Si(1)-C(1)	188.6 (5)	Si(1)-C(16)	188.8 (3)
Si(2)-O(1)	171.7 (3)	Si(2)-C(31)	189.0 (5)
Si(2)-C(46)	189.4 (4)		
	Bond Angles (deg)		
Si(2)-Si(1)-O(1)	49.0 (1)	Si(2)-Si(1)-C(1)	123.7 (1)
O(1)-Si(1)-C(1)	112.4 (2)	Si(2)-Si(1)-C(16)	121.5 (1)
O(1)-Si(1)-C(16)	113.0 (2)	C(1)-Si(1)-C(16)	114.5 (2)
Si(1)-Si(2)-O(1)	49.1 (1)	Si(1)-Si(2)-C(31)	125.8 (10)
O(1)-Si(2)-C(31)	112.6 (2)	Si(1)-Si(2)-C(46)	121.9 (1)
O(1)-Si(2)-C(46)	113.3 (2)	C(31)-Si(2)-C(46)	112.1 (2)
Si(1)-O(1)-Si(2)	81.9 (1)		

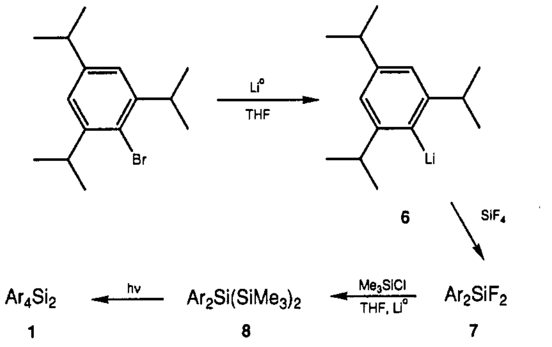
The molecular structure is shown in Figure 1.

The features of the oxygen–silicon framework are quite similar to those of other 1,3-cyclodisiloxanes, but **3** has a slightly longer cross-ring Si–Si distance of 243 pm (Table I). For comparison, the Si–Si separations in other 1,3-cyclodisiloxanes are 231 pm for **3a**·(toluene) and 240 pm for (*E*)-**3b**.[1a] The oxygen–silicon bond lengths in **3** are all close to 170 pm, and the ring is nearly planar. One of the four para isopropyl groups is disordered, and this is accounted for in the model.

F. X-ray Crystal Structure of Disilaoxirane 5. The structure of **5** was confirmed by an X-ray diffraction study. The thermal ellipsoid plot is shown in Figure 2. Disilaoxirane **5** is the second disilaoxirane to be examined by X-ray diffraction. The first, tetramesityldisilaoxirane **5a**, was found to possess some unusual structural features: a very short Si–Si distance of 223 pm and a planar geometry of the non-oxygen atoms around each silicon atom.[7] Less extreme examples of this type of geometry have also been found in related three-membered rings where the oxygen has been replaced by CH_2,[9] by a nitrene moiety,[10] or by other chalcogen atoms.[12]

The structure of **5** is very similar to that of **5a**. It has a short Si–Si bond length (225 pm) and an essentially planar arrangement of O, C and Si atoms around each silicon (Table II). It is of interest to note that the aryl substituents are bent back from the central ring with C–Si–C bond angles of about 113°, probably to minimize cross-ring steric interactions. In the tetramesityldisilaoxirane **1b** and 1,3-cyclodisiloxane **3** these angles are about 117°. There is some disorder in the structure of **5**, with 16% of the oxygen atoms residing in a nearly equivalent position on the other side of the Si–Si axis and a para isopropyl group which has taken more than one orientation.

Scheme IV. Synthesis of 1[a]



[a] Ar = 2,4,6-triisopropylphenyl.

G. Preparation of 1. Several preparations of **1** have been described in the literature.[3,13,14] We employed photolysis of the trisilane **8** for the preparation of **1** as previously reported by Ando and co-workers.[14] Here we report the details of the synthesis of **8** and its photolysis (Scheme IV). Although the earlier workers describe the photolysis of **8** in hydrocarbon matrix, they have not published a synthetic route or physical data for **8**.

We encountered difficulty in synthesizing bis(2,4,6-triisopropylphenyl)dichlorosilane from 2-lithio-1,3,5-triisopropylbenzene (**6**) and silicon tetrachloride. Much better results were obtained by treating **6** with silicon tetrafluoride. The resultant bis(2,4,6-triisopropylphenyl)difluorosilane (**7**) was then successfully coupled with trimethylchlorosilane to give a high yield of **8**, which was then photolyzed to give a good yield of **1**.

Experimental Section

General Procedures. All reactions involving disilene **1**, halosilanes, or lithium reagents were carried out under an atmosphere of dry nitrogen or argon. The corresponding solvents were distilled from Na/K and benzophenone. Silicon tetrachloride and trimethylchlorosilane were distilled from potassium carbonate under an atmosphere of dry nitrogen. The preparation of 1-bromo-2,4,6-triisopropylbenzene was performed as described in the literature.[15] The gel permeation chromatography was carried out on a Japan Analytical Industry Co. Model LC-908 HPLC system equipped with a styrene-DVB JAIGEL-1H column.

The ^1H NMR spectra were obtained on a Bruker WP-270 NMR spectrometer. Proton chemical shifts were referenced to an internal standard of tetramethylsilane. The ^{29}Si NMR spectra were obtained on a Bruker AM-500 NMR spectrometer proton decoupled using a refocused INEPT (ERNST) pulse sequence. The ^{29}Si NMR chemical shifts were referenced to an external tetramethylsilane standard. IR spectra were taken on a Mattson Instrument Polaris FT-IR spectrometer. Mass spectra were recorded on a Kratos MS-80 instrument.

Synthesis of Tetrakis(2,4,6-triisopropylphenyl)disilene (1). Preparation of 2-Lithio-1,3,5-triisopropylbenzene (6). Lithium wire (2.8 g, 0.40 mol/1% sodium content) was cut into a flask containing 150 mL of anhydrous diethyl ether cooled to 0 °C in an ice bath under a flow of argon. A solution of 26.0 g (0.092 mol) of 1-bromo-2,4,6-triisopropylbenzene in 75 mL of anhydrous diethyl ether was added to the flask over 1 h with stirring. The reaction was shown to be complete after 7 h (85%

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(12) Tan, R.; Gillette, G. R.; Powell, D. R.; West, R. *Organometallics* **1991**, *10*, 546.

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

(14) Ando, W.; Fujita, M.; Yoshida, H.; Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3310.

(15) Miller, A. R.; Curtin, D. Y. *J. Am. Chem. Soc.* **1976**, *98*, 1860.

by GC). The lithium reagent was not isolated but instead filtered through a filter cannula or fritted funnel under nitrogen into another flask which was to be used in the next reaction. Protonation of 6 by rapid addition of water gave a quantitative conversion to 1,3,5-triisopropylbenzene (if the addition of water was too slow, a second quenching product was also formed by the reaction of the lithium reagent with oxygen). The proton NMR spectrum of the quenching product matched that of an authentic sample of 1,3,5-triisopropylbenzene. ^{1}H NMR (CDCl$_3$): δ 1.23 (d, 18 H), 2.76 (sep, 3 H), 6.90 (s, 3 H).

Preparation of Bis(2,4,6-triisopropylphenyl)difluorosilane (7). The solution from the previous step was cooled to −78 °C with stirring *in a fume hood*. Silicon tetrafluoride was bubbled through the solution at 10-min intervals until conversion was complete (90% by GC). This typically required three to five cycles of gas over the course of 1 h or more. Dry nitrogen was then flushed through the system to remove excess silicon tetrafluoride. Water (100 mL) was added to quench the reaction. The mixture was then washed four times with 100-mL portions of water and dried over MgSO$_4$. Removal of solvent yielded a brown mass which was crystallized from methanol to give large colorless needles (crystallization often took days to initiate) or from which the volatile impurities were removed by a Kugelrohr distillation at 120 °C, 0.65 Torr to yield 20 g of 92% pure 7 which was used successfully in the next step. ^{1}H NMR (C$_6$D$_6$): δ 1.16 (d, 12 H), 1.20 (d, 24 H), 2.72 (sept, 2 H), 3.68 (sept, 4 H), 7.13 (s, 4 H). ^{29}Si NMR (C$_6$D$_6$): δ −23.78 (triplet, $^1J_{Si-F}$ = 301 Hz). HR/MS: M$^+$ calc, *m/e* 472.3337; found, *m/e* 472.3336.

Preparation of Bis(2,4,6-triisopropylphenyl)-1,1,1,3,3,3-hexamethyltrisilane (8). Lithium wire (2.1 g, 0.30 mol) was cut into a flask containing 70 mL of THF and 18.8 mL (0.16 mol) of trimethylchlorosilane under a positive argon flow. The mixture was cooled to 0 °C, and 17.5 g (0.037 mol) of 7 in 80 mL of anhydrous THF was added dropwise over 1 h with stirring. After 1 h the solution was allowed to warm to room temperature, and after 30 h the reaction was complete (96% by GC). Unreacted lithium metal was filtered away from the mixture, the solvent was removed, and the residue was redissolved in 100 mL of hexane. The resultant suspension was washed with four 100-mL portions of water and twice with 75-mL portions of brine. The hexane layer was dried over MgSO$_4$ and evaporated to a brown oil. Purification was accomplished by recrystallization from hexane, yielding 14.6 g (0.025 mol, 68%) of 8, >99% pure by GC. ^{1}H NMR (CDCl$_3$): δ −0.01 (d, 6 H), 0.25 (s, 18 H), 1.10 (d, 6 H), 1.17 (d, 12 H), 1.30 (d, 6 H), 1.33 (d, 6 H), 2.79 (sept, 2 H), 2.86 (sept, 2 H), 3.37 (sept, 2 H), 6.76 (s, 1 H), 6.78 (s, 1 H), 6.96 (s, 1 H), 6.98 (s, 1 H). ^{29}Si NMR (C$_6$D$_6$): δ −11.9, −53.4. GC/MS: *m/e* 507 (m + 1 − TMS).

Synthesis of Tetrakis(2,4,6-triisopropylphenyl)disilene (1). In a dry quartz photolysis tube was placed 2.0 g (3.4 mmol) of 8. The solid was pumped on, and then the tube was back-filled with nitrogen. Via syringe, 80 mL of dried, deolefinated pentane was added to the tube. After five freeze–pump–thaw cycles, the solution was photolyzed at −50 °C under vacuum with stirring for 48 h. A yellow color developed immediately upon photolysis and became progressively darker as the reaction proceeded. The crude photolysate was 85–90% pure. The product was recrystallized from a minimum amount of dried, degassed benzene in a drybox to provide 1.2 g (1.4 mmol, 82%) of pure 1. Both the ^{1}H NMR and ^{29}Si NMR data match those reported in the literature.[13] ^{1}H NMR (C$_6$D$_6$): δ 0.63 (d, 12 H), 0.64 (d, 12 H), 1.14 (d, 12 H), 1.17 (d, 12 H), 1.40 (d, 12 H), 1.44 (d, 12 H), 2.72 (sept, 4 H), 3.83 (sept, 4 H), 4.57 (sept, 4 H), 6.98 (*d* = 1.5 Hz, 4 H), 7.07 (*d* = 1.5 Hz, 4 H). ^{29}Si NMR (C$_6$D$_6$): δ 53.27.

Air Oxidation of Tetrakis(2,4,6-triisopropylphenyl)disilene (1) in Benzene or Cyclohexane. Pure triplet oxygen was bubbled through a deep yellow-orange solution containing 75 mg (8.6 × 10^{-2} mmol) of disilene 1 in 0.5 mL of solvent at 25 °C in an NMR tube. The solution became decolorized with a $t_{1/2}$ ~ 1 min; the colorless solution showed only one signal in the ^{29}Si NMR spectrum at 37.18 ppm, assigned to 2. With time the intensity of this signal diminished while three new signals at 0.88, −6.39, and −7.49 ppm with intensities of ~1:1:1 appeared until no signal for 2 could be observed. This process occurred with $t_{1/2}$ = 5 h. Physical data for 2: ^{1}H NMR (C$_7$D$_8$): δ 0.35 (d, 6 H), 0.56 (d, 6 H), 0.63 (d, 6 H), 1.11 (d, 12 H), 1.18 (d, 12 H), 1.19 (d, 12 H), 1.32 (d, 6 H), 1.39 (d, 12 H), 2.70 (sept, 4 H), 2.91 (sept, 2 H), 3.34 (sept, 4 H), 5.21 (sept, 2 H), 6.94 (s, 4 H), 7.13 (s, 2 H), 7.21 (s, 2 H); ^{29}Si NMR (C$_6$D$_6$): δ 37.18.

Air Oxidation of Tetrakis(2,4,6-triisopropylphenyl)disilene (1) as a Solid. Disilene 1 (75 mg, 8.6 × 10^{-2} mmol) was exposed to triplet oxygen at 25 °C for 18 h. Examination of the solid by ^{29}Si NMR spectroscopy in benzene showed that there was no disilene 1 left. The peak for 2 and peaks at 0.88, −6.39, and −7.49 were observed in an approximate 1:1:2:1 ratio.

When the experiment was repeated and the solid was allowed to stand in contact with air for 2 days, only three signals at 0.88, −6.39, and −7.49 ppm in an approximate 1:2:1 ratio were observed in the ^{29}Si NMR spectrum.

Synthesis of Pure 3 by the Photolytic Rearrangement of 2. Pure triplet oxygen was bubbled through a deep yellow-orange solution containing 150 mg (1.7 × 10^{-1} mmol) of disilene 1 in 3 mL of benzene at 25 °C until the solution became colorless. The benzene was then evaporated away and the colorless product was dissolved in 20 mL of dry hexane. The solution was photolyzed with 254-nm light at −50 °C for 12 h. The resulting solution was evaporated to a colorless solid which was dissolved in benzene. Examination by ^{29}Si NMR spectroscopy showed only one signal at −6.39 ppm. The product was crystallized by slowly cooling an ethanol solution, and a single crystal was chosen for an X-ray crystallographic analysis; the product was then determined to be 3. ^{1}H NMR (CDCl$_3$): δ 0.27 (d, 12 H), 0.64 (d, 12 H), 1.10 (d, 12 H), 1.15 (d, 24 H), 1.29 (d, 12 H), 2.77 (sept, 4 H), 3.29 (sept, 4 H), 4.17 (sept, 4 H), 6.84 (s, 4 H), 6.88 (s, 4 H). ^{29}Si NMR (C$_6$D$_6$): δ −6.39. HR/MS: M$^+$ calc, *m/e* 900.6636; found *m/e* 900.6621. Mp: 244.0–244.5 °C.

Preparation of Pure 4 by the Thermal Rearrangement of 2 in Chloroform or Carbon Tetrachloride. Pure triplet oxygen was bubbled through a deep yellow-orange solution containing 150 mg (1.7 × 10^{-1} mmol) of disilene 1 in 3 mL of benzene at 25 °C until the solution became colorless. The benzene was then evaporated away and the colorless product dissolved in 3 mL of solvent. The solution was heated in an oil bath for 5 h. The resulting solution was evaporated to a colorless solid which was dissolved in benzene. Examination by ^{29}Si NMR spectroscopy showed two signals at +0.88 and −7.49 ppm in a 1:1 ratio. ^{1}H NMR (C$_6$D$_6$): complex methyl region δ 0.25–2.25 (72 H), 2.70 (m, 3 H), 3.02 (sept, 1 H), 3.41 (m, 2 H), 3.63 (sept, 1 H), 3.88 (sept, 2 H), 4.25 (s, 1 H), 4.34 (sept, 1 H), 4.55 (sept, 1 H), 6.88 (s, 1 H), 6.96 (s, 2 H), 7.01 (s, 1 H), 7.06 (s, 1 H), 7.09 (s, 2 H), 7.21 (s, 1 H). ^{29}Si NMR (C$_6$D$_6$): δ 0.88, −7.49. HR/MS: M$^+$ calc, *m/e* 900.6636; found, *m/e* 900.6368. IR ν(unassociated OH) 3690 cm^{-1} (sharp). Mp: 182.5–183.0 °C.

The structure of 4 was verified by repeating the X-ray crystal structure determination. Data for 4, C$_{60}$H$_{92}$O$_2$Si$_2$: colorless prisms were grown by the slow cooling of an ethanol solution of 4. The crystals were triclinic and belonged to the space group *P*1 with *a* = 13.034 (6) Å, *b* = 13.553 (7) Å, *c* = 17.738 (9) Å, α = 86.82 (4)°, β = 84.34 (4)°, γ = 69.22 (4)°, V = 2915 (3) Å^3, and d_{calcd} = 1.027 g/cm^3 for *Z* = 2. Data were collected at 113 K on a Siemens P3f diffractometer using Cu Kα radiation (λ = 1.54178 Å). A total of 8746 reflections were collected with 8746 independent reflections (R_{int} = 1.33%) and 5726 observed reflections (*F* >'4.0σ(*F*)). The structure was solved by direct methods and refined by full-matrix least-squares procedures, using SHELXTL-PLUS software. Hydrogen atoms were added at calculated positions. Final *R* indices: *R* = 9.63%, R_w = 11.66%.

Synthesis of Tetrakis(2,4,6-triisopropylphenyl)disilaoxirane (5). mCPBA (60 mg, 2.9 × 10^{-4} mol/85% pure) in 5 mL of dried, degassed benzene was added dropwise to 250 mg of 1 in 15 mL of dried, degassed benzene in a glovebox. Addition of the mCPBA solution was stopped after the solution became nearly colorless. The mixture was placed in a separatory funnel along with 20 mL of hexane and washed three times with 75 mL of a saturated solution of Na$_2$SO$_3$ to quench any remaining mCPBA and remove the resulting acid. The solution was washed three times with 75 mL of water, and the solvent was removed under vacuum to yield 5 quantitatively. ^{1}H NMR (C$_6$D$_6$): δ 0.51 (d, 6 H), 0.63 (d, 6 H), 0.74 (d, 6 H), 0.84 (d, 6 H), 1.11–1.20 (mult, 24 H), 1.39 (d, 6 H), 1.40 (d, 6 H), 1.46 (d, 6 H), 1.53 (d, 6 H), 2.70 (sept, 2 H), 2.71 (sept, 2 H), 3.46 (sept, 2 H), 3.93 (sept, 2 H), 4.20 (sept, 2 H), 4.79 (sept, 2 H), 6.95 (*d* = 1.5 Hz, 2 H), 7.02 (*d* = 1.5

Hz, 2 H), 7.05 (d = 1.5 Hz, 2 H), 7.12 (d = 1.5 Hz, 2 H). ^{29}Si NMR (C_6D_6): δ -30.39. MS:M$^+$ m/e 885. HR/MS: M$^+$ - $(CH_3)_2CH$ calc, m/e 841.6141; found, m/e 841.6000. Mp: 212-231 °C.

Synthesis of Tetrakis(2,4,6-triisopropylphenyl)-1,3-cyclodisiloxane (3). Disilene 1 was oxidized using the same procedure as for the synthesis of 5, except that a large excess of mCPBA was used. The conversion to 3 was quantitative.

Purification of 3 and 4 from a Mixture. A mixture of solid 3 and 4 from the oxidation of 1 was washed with ethanol until a small amount of the mixture had visibly dissolved. The volume of the ethanol was then reduced by boiling and eventually cooled to 0 °C for 2 weeks. If only a few crystals formed they were, sometimes, either pure 3 or pure 4. Small amounts of pure compounds were isolated in this way. However, this procedure was difficult to reproduce. Most often either crystallization did not occur or, if it did, it produced crystals of both 3 and 4. Gel permeation chromatography with toluene as the eluant afforded an additional 5 mg of pure 3 and 4 after recycling 25 times in toluene over 12 h.

X-ray Crystal Structure Data for 1,3-Disilaoxirane 3 ($C_{60}H_{92}O_2Si_2$). Colorless prisms were grown by the slow cooling of an ethanol solution of 3. The crystals were monoclinic and belonged to the space group $P2_1/c$ with a = 10.420 (2) Å, b = 15.184 (3) Å, c = 37.410 (7) Å, β = 95.02 (3)°, V = 5896 (2) Å^3, and d_{calcd} = 1.016 g/cm^3 for Z = 4. Data were collected at 113 K on a Siemens P3f diffractometer using Mo Kα radiation (λ = 0.710 73 Å). A total of 9889 reflections were collected with 9469 independent reflections (R_{int} = 4.05%) and 4580 observed reflections ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by full-matrix least-squares procedures, using SHELXTL-PLUS software. Hydrogen atoms were added at calculated positions. Final R indices: R = 7.81%, R_w = 7.56%.

X-ray Crystallography Data for Disilaoxirane 5 ($C_{60}H_{92}OSi_2$). Colorless prisms were grown by the slow cooling of an ethanol solution of 5. The crystals were triclinic and belonged to the space group $P1$ with a = 13.049 (4) Å, b = 13.607 (4) Å, c = 17.567 (5) Å, α = 88.69 (2)°, β = 85.38 (2)°, γ = 68.90 (2)°, V = 2900.5 (15) Å^3, and d_{calcd} = 1.014 g/cm^3 for Z = 2. Data were collected at 113 K on a Siemens P3f diffractometer using Cu Kα radiation (λ = 1.541 78 Å). A total of 8241 reflections were collected with 7815 independent reflections (R_{int} = 1.33%) and 6034 observed reflections ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by full-matrix least-squares procedures, using SHELXTL-PLUS software. Hydrogen atoms were added at calculated positions. Final R indices: R = 6.50%, R_w = 8.10%.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates and anisotropic thermal parameters, and bond lengths and angles for 3 and 5 (23 pages); listings of observed and calculated structure factor amplitudes for 3 and 5 (62 pages). Ordering information is given on any current masthead page.

Group 4 Metallocene Olefin Hydrosilylation Catalysts

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The hydrosilylation of olefins such as styrene, 1-hexene, and 2-pentene with diphenylsilane can be carried out with catalysts generated from zirconocene dichloride and 2 equiv of butyllithium. Complete regioselectivity is observed as only terminal organosilicon products are produced (~90%). In the case of styrene, three major products are formed: phenethyldiphenylsilane, *trans*-1-phenyl-2-(diphenylsilyl)ethene, and ethylbenzene. The product distribution was found to be dependent on reagent concentrations: reactions run with excess diphenylsilane favored diphenylphenethylsilane; excess styrene favored *trans*-1-(diphenylsilyl)-2-phenylethene. Reactivity as a function of silane, olefin, and catalyst was examined. Secondary silanes are generally superior to primary and tertiary silanes for hydrosilylation. Silane coupling reactions compete with hydrosilylation with less sterically hindered silanes to produce oligomeric products. Sterically hindered silanes, such as triphenylsilane, react only at elevated temperature and yield vinylsilane as the major product. Extensive H/D exchange is observed in the hydrosilylation of styrene with Ph_2SiD_2. Stoichiometric reactions indicate that dibutylzirconocene reacts to form a zirconocene-butene complex at room temperature. The possibility of an "olefin first" mechanism is discussed.

Transition-metal-catalyzed olefin hydrosilylation is one of the most important methods for the preparation of organosilicon compounds.[1] The vast majority of hydrosilylation catalysts are derived from group 8 metals due to their exceptional catalytic activity. Because of the utility of these later-transition-metal catalysts, relatively little effort has been devoted to early-transition-metal hydrosilylation catalysts[2] despite the possibility that such catalysts might display improved chemo- or stereoselectivities. Recent results[3] revealed that early-transition-metal metallocenes are active catalyst precursors for olefin hydrosilylation. These results, combined with the recent

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