Silicon Compounds with Strong Intramolecular Steric Interactions, LVII[◇]

Oxidation and Cycloaddition Reactions of an Unsymmetrically Substituted Disilene[☆]

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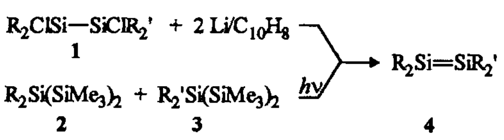
Reaction of the unsymmetrically substituted disilene $R_2Si{=}SiR'_2$ (**4**; R = 2,4,6-$Me_3C_6H_2$, R′ = 2,4,6-$iPr_3C_6H_2$) with *m*-chloroperbenzoic acid (*m*CPBA) or oxygen furnished the correspondingly substituted 1,2,3-oxadisilirane **5** or 1,3,2,4-dioxadisiletane **6**, respectively. The [2 + 2] and [2 + 4] cycloaddition reactions of **4** with benzophenone and 3,5-di-*tert*-butyl-1,2-benzoquinone, respectively, proceeded with a high degree of regioselectivity to yield the 1,2,3-oxadisiletane **9** and the 2,3-dihydro-1,4,2,3-benzodioxadisiline **7**. The latter product was isolated together with a small amount of an isomeric compound **8** in which the substituents at the silicon atoms are reversed. The molecular structures of the products **5**, **6**, and **7** were determined by X-ray crystallography.

Although less than fifteen years have passed since the first reports on the isolation of disilenes[2,3], compounds containing an Si=Si bond, the chemistry of this class of compounds has already been the subject of several review articles[4]. However, most of the published reports are concerned almost exclusively with the symmetrically substituted compounds $R_2Si{=}SiR_2$ or RR′Si=SiRR′ whereas merely ^{29}Si-NMR data[5,6] and hardly any other properties or structural information have been reported to date for unsymmetrically substituted disilenes of the type $R_2Si{=}SiR'_2$ and their oxidation products.

The reason for this is certainly not a lack of interest but rather lies in the difficult accessibility of these compounds. Disilenes with symmetrical substitution patterns are usually obtained simply by photolysis of cyclic or acyclic trisilanes[4] whereas, in contrast, the preparation of compounds of the type **4** is much more laborious. Although cophotolysis of trisilanes bearing different substituents on the respective central silicon atoms does give rise to the formation of the desired products, the symmetrically substituted compounds $R_2Si{=}SiR_2$ and $R'_2Si{=}SiR'_2$ are always formed concomitantly, thus causing major separation problems. Halogen elimination from 1,2-dihalodisilanes of the type 1 offers a possible alternative to the cophotolysis but, in most cases, overshoots the target and finally leads to disilenyl radical anions $R_2Si{=}SiR_2^{\bullet -}$ by a further transfer of electrons to the Si=Si bond[7,8].

Only in the case of 1,2-dichlorotetrakis(2,4,6-triisopropylphenyl)disilane has the halogen elimination afforded the respective substituted disilene[9]. We have recently found that this methodology is also applicable to the disilane **1** and furnishes the disilene **4** in modest yield[10]. The same compound is also accessible from the cophotolysis of the trisilanes **2** and **3**[11]. However, its isolation in the pure state will probably, as mentioned above, only be possible after tedious separation procedures.

Scheme 1. R = 2,4,6-$Me_3C_6H_2$, R′ = 2,4,6-$iPr_3C_6H_2$



We now report on the formation and structures of two oxidation products starting from **4** and on some cycloaddition reactions of **4** which, on account of the different spatial requirements of the substituents R and R′, should preferentially lead to one of the possible isomeric adducts.

Results and Discussion

Although 1,2,3-oxadisiliranes are usually readily accessible from the reaction of nitrous oxide with disilenes[6,12], this procedure fails in the case of **4** because the steric overcrowding in the molecule prevents the reaction sequence presumably initiated by a [3 + 2] cycloaddition of nitrous oxide to the Si=Si bond. In contrast, the reaction of **4** with *meta*-chloroperbenzoic acid (*m*CPBA) – previously used successfully for the preparation of $R_2Si(O)SiR_2$ (R = 2,4,6-

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[◇] Part LVI: Ref.[1].

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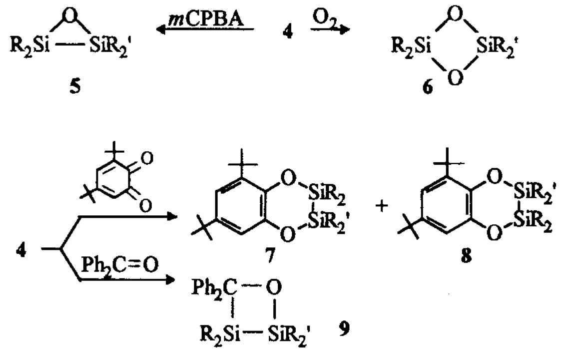
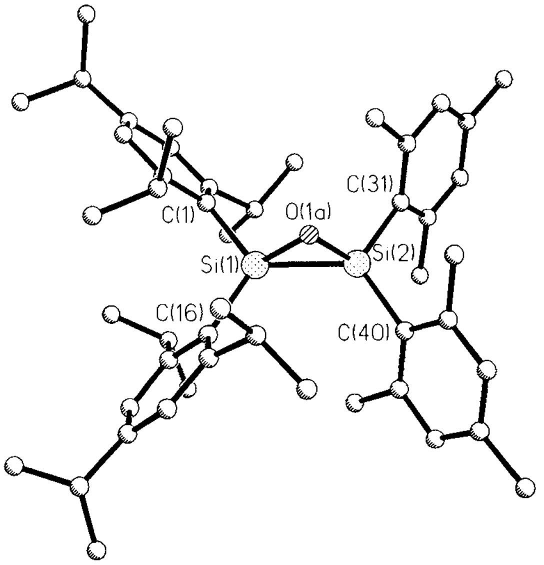
$i\mathrm{Pr_3C_6H_2})^{[13]}$ – proceeds smoothly to furnish the unsymmetrically substituted 1,2,3-oxadisilirane **5** (Scheme 2).

Scheme 2. R = 2,4,6-$\mathrm{Me_3C_6H_2}$, R′ = 2,4,6-$i\mathrm{Pr_3C_6H_2}$



The ^{1}H- and ^{13}C-NMR spectra of **5** indicate extensive hindrance to rotation about the Si–aryl bonds in that, for example, all methyl protons of the two 2,4,6-trimethylphenyl groups appear as separate signals. In the ^{29}Si-NMR spectrum, two signals in the typical region for this three-membered ring structure are observed. However, the $^1J_{\mathrm{Si,Si}}$ value of 122.5 Hz is appreciably larger than those observed for other disilanes with the same substitution pattern – for example, 85.5 Hz for **9** – and approaches the value of 159.5 Hz for the disilene **4**[10]. The only other $^1J_{\mathrm{Si,Si}}$ coupling constant previously determined for a 1,2,3-oxadisilirane, 99 Hz[6], is much smaller than the value reported here.

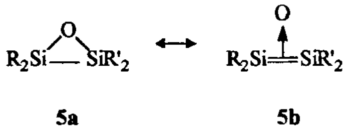
Figure 1. Molecular structure of **5** in the crystal (hydrogen atoms omitted)



Selected bond lengths [pm] and angles [°]: Si(1)–Si(2) 222.9(1), Si(1)–O 172.5(5), Si(2)–O 170.5(5), Si(1)–C(1) 190.8(3), Si(1)–C(16) 192.2(4), Si(2)–C(31) 190.4(4), Si(2)–C(40) 189.3(4), Si(1)–Si(2)–O 49.8(2), Si(2)–O–Si(1) 81.1(2), O–Si(1)–Si(2) 49.1(2), C(1)–Si(1)–C(16) 113.6(2), C(1)–Si(1)–Si(2) 123.8(2), C(16)–Si(1)–Si(2) 122.5(2), C(31)–Si(2)–C(40) 114.3(2), C(31)–Si(2)–Si(1) 124.2(2), C(40)–Si(2)–Si(1) 121.4(2).

The unusual bonding situation in 1,2,3-oxadisiliranes is also reflected in the X-ray structure of **5** (Figure 1) which reveals an Si–Si bond length of 222.9(2) pm, i.e. remarkably shortened in comparison with the normal bond length of approx. 234 pm in sterically unstressed disilanes. When the Si–Si bond length measured here is compared with those in analogously substituted disilanes as **1**[10] or **7**, it is apparent that the bond is shortened by as much as 20 pm. In spite of the different substitution pattern, the two silicon atoms of **5** each exist in a planar environment in relation to the respective *ipso* carbon atoms and the other silicon atom (angular sums in each case: 359.9°). Taken together these data clearly show that 1,2,3-oxadisiliranes, similar to the ethene complexes of transition metals, exist in a continuum between the three-membered ring structure **5a**) and the π-complex structure **5b**)[6,13,14] (Scheme 3).

Scheme 3



The reaction of oxygen with **5** or, more simply, passage of oxygen through an *n*-hexane solution of **4** affords the 1,3,2,4-dioxadisiletane (cyclodisiloxane) **6**. The ^{1}H-NMR spectrum of **6** at ambient temperature contains mainly highly broadened signals, indicating that a slow rotation about the Si–C bonds occurs at this temperature. This rotation is slowed down sufficiently at −20 °C so that sharp signals can be observed for the individual proton groups. The ^{13}C- and ^{29}Si-NMR data are as to be expected for four-membered rings of this type.

Since previously only the structures of symmetrically substituted 1,3,2,4-dioxadisiletanes have been reported[5,13,15], we also characterized **6** by X-ray crystallography (Figure 2). This shows an almost planar four-membered ring with endocyclic angles of about 90°. Worthy of special note is the short transannular Si···Si separation of 236.7(2) pm. This is smaller than the corresponding distances in the benzene or toluene solvates of tetrakis(2,4,6-trimethylphenyl)-1,3,2,4-dioxadisiletane (239 pm)[15] and considerably smaller than the value of 243.2(2) pm[13] for the 2,4,6-triisopropylphenyl-substituted compound. The reason for this small Si···Si separation in comparison to the symmetrically substituted four-membered rings lies in the somewhat narrower Si–O–Si angles which bring the two silicon atoms closer together. Although the Si···Si separations observed here are equal in size or even smaller than, for example, the Si–Si bond lengths in the disilanes **1**[10] or **7**, the existence of bonding interactions between the two silicon atoms can presumably be excluded[14,15].

In addition to the influence of the unsymmetrical substitution pattern in **4** on the structure of the oxidation products, we were also interested in the additions of this disilene to unsymmetrical reaction partners since, in such cases, the formation of two isomeric cycloadducts would be possible. As first trapping reagent, we selected 3,5-di-*tert*-butyl-1,2-

benzoquinone since its bulky *tert*-butyl groups are so distant from the reaction centers that they should exert only a slight influence on the [4 + 2] cycloaddition. Indeed, the cycloadducts **7** and **8** were isolated, albeit in a ratio of about 5.5:1; the major isomer is assumed to have the constitution **7** in which the less bulky SiR_2 unit with R = 2,4,6-$Me_3C_6H_2$ is in the neighborhood of the more proximal *tert*-butyl group. This assumption is supported by the ^1H-NMR spectra of **7** and **8** in which, as expected, an appreciably larger hindrance to rotation is observed for **8**.

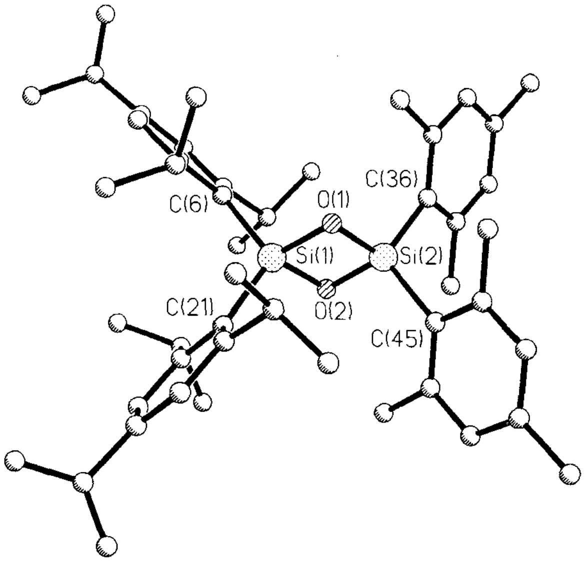


Figure 2. Molecular structure of **6** in the crystal (hydrogen atoms omitted)

Selected bond lengths [pm] and angles [°]: Si(1)–O(1) 168.1(4), Si(1)–O(2) 168.3(4), Si(2)–O(1) 164.6(4), Si(2)–O(2) 165.4(4), Si(1)···Si(2) 236.7(2), Si(1)–C(6) 190.5(3), Si(1)–C(21) 191.2(3), Si(2)–C(36) 189.2(3), Si(2)–C(45) 188.6(3), Si(1)–O(1)–Si(2) 90.3(2), O(1)–Si(1)–O(2) 88.4(2), O(1)–Si(2)–O(2) 90.5(2), Si(1)–O(2)–Si(2) 90.3(2).

These constitutional assignments were confirmed by the X-ray structural analysis of **7** (Figure 3). A conspicuous feature of the structure of **7** is the rather long Si–Si bond length in spite of its incorporation in a six-membered ring. This bond is longer than that in the acyclic compound **1**[10] and, moreover, longer than the non-bonding separation in the 1,3,2,4-dioxadisiletane **6**.

A typical reaction mode for disilenes is the [2 + 2] cycloaddition of the Si=Si bond to the C=O bond of ketones[16–19]. Since the different spatial requirements of the substituents at the two silicon atoms should be particularly apparent in such cases, we allowed **4** to react with benzophenone. The cycloadduct **9** in which the less bulky SiR_2 group has undergone addition to the carbon atom and the more bulky SiR'_2 group to the oxygen atom of the C=O bond was isolated as the sole product in 80% yield. On account of the considerable hindrance to rotation about the Si–C bonds detected in the ^1H- and ^{13}C-NMR spectra, the concomitant formation of the sterically less favorable isomer with the more bulky SiR'_2 group directly adjacent to the Ph_2C group under the prevailing reaction conditions seems hihgly unlikely.

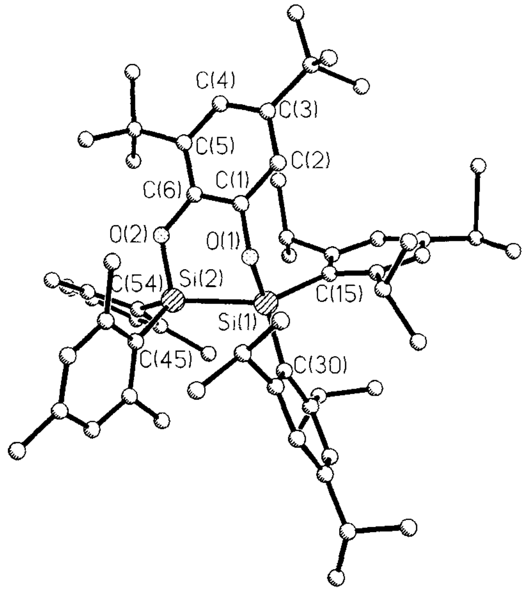


Figure 3. Molecular structure of **7** in the crystal (hydrogen atoms omitted)

Selected bond lengths [pm] and angles [°]: Si(1)–Si(2) 242.8(2), Si(1)–O(1) 168.7(3), Si(2)–O(2) 167.8(3), Si(1)–C(15) 192.6(5), Si(1)–C(30) 190.6(5), Si(2)–C(45) 188.9(5), Si(2)–C(54) 190.8(5), Si(1)–Si(2)–O(2) 99.0(1), Si(2)–Si(1)–O(1) 86.1(1).

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Experimental

All manipulations were performed by using standard Schlenk techniques under dry nitrogen or argon. Solvents were purified, dried, and distilled under argon. – ^1H and ^{13}C NMR: Bruker AM 300. – ^{29}Si NMR: Bruker AMX 300. – MS: Varian MAT 212. – Elemental analyses: Analytische Laboratorien, D-51647 Gummersbach, Germany.

3,3-Bis(2,4,6-triisopropylphenyl)-2,2-bis(2,4,6-trimethylphenyl)-1,2,3-oxadisilirane (**5**): A solution of *m*CPBA (173 mg, 1.00 mmol) in 20 ml of toluene was added dropwise to a solution of **4** (700 mg, 1 mmol) in 30 ml of toluene at 25 °C until the solution became almost colourless. The solution was evaporated and the resulting solid was dissolved in 50 ml of *n*-hexane. *m*-Chlorobenzoic acid was filtered off and the resulting solution was cooled to −30 °C. The precipitate was recrystallized three times from *n*-hexane to provide 510 mg (70%) colourless crystals of **5**, m.p. 232–235 °C. – ^1H NMR (C_6D_6, 25 °C): δ = 0.56 (d, 3H, $^3J_{H,H}$ = 6.5 Hz), 0.60 (d, 3H, $^3J_{H,H}$ = 6.5 Hz), 0.70 (d, 3H, $^3J_{H,H}$ = 6.5 Hz), 0.82 (d, 3H, $^3J_{H,H}$ = 6.5 Hz), 1.13 (d, 12H, $^3J_{H,H}$ = 6.5 Hz), 1.41 (d, 9H, $^3J_{H,H}$ = 6.5 Hz), 1.55 (d, 3H, $^3J_{H,H}$ = 6.5 Hz), 2.00 (s, 3H), 2.05 (s, 3H), 2.49 (s, 3H), 2.52 (s, 3H), 2.66 (s, 3H), 2.69 (s, 3H), 2.70 (sept, 2H), 3.42 (sept, 1H), 3.90 (sept, 1H), 4.28 (sept, 1H), 4.71 (sept, 1H), 6.55 (s, 1H), 6.63 (s, 3H), 6.97 (s, 1H), 7.03 (s, 1H), 7.08 (s, 1H), 7.12 (s, 1H). – ^{13}C NMR (C_6D_6, 25 °C): δ = 20.89 (CH_3), 21.12 (CH_3), 22.55 (CH_3), 22.86 (CH_3), 23.46 (CH_3), 23.62 (CH_3), 23.96 (CH_3), 24.21 (CH_3), 24.47 (CH_3), 25.54 (CH_3), 24.77 (CH_3), 24.91 (CH_3), 25.03 (CH_3), 25.86 (CH_3), 26.03 (CH_3), 29.52

(CH), 33.47 (CH), 34.58 (CH), 36.44 (CH), 37.13 (CH), 120.46 (CH), 121.34 (CH), 122.08 (CH), 123.18 (CH), 130.53 (CH), 130.75 (CH), 130.90 (CH), 131.50 (CH), 132.86 ($\mathrm{C_q}$), 133.05 ($\mathrm{C_q}$), 139.50 ($\mathrm{C_q}$), 139.84 ($\mathrm{C_q}$), 143.67 ($\mathrm{C_q}$), 145.45 ($\mathrm{C_q}$), 145.98 ($\mathrm{C_q}$), 150.97 ($\mathrm{C_q}$), 151.52 ($\mathrm{C_q}$), 154.56 ($\mathrm{C_q}$), 154.93 ($\mathrm{C_q}$), 156.34 ($\mathrm{C_q}$), 156.93 ($\mathrm{C_q}$). – ^{29}Si NMR ($\mathrm{C_6D_6}$, 25°C, TMS ext.): $\delta = -25.92$ (Si2), -31.52 (Si3), $^{1}J_{\mathrm{SiSi}} = 122.5$ Hz. – MS (CI, isobutane), *m/z* (%): 718 (100) [MH$^+$]. – $\mathrm{C_{48}H_{68}OSi_2}$ (717.2): calcd. C 80.38, H 9.46; found C 80.19, H 9.54.

4,4-Bis(2,4,6-triisopropylphenyl)-2,2-bis(2,4,6-trimethylphenyl)-1,3,2,4-dioxadisiletane (**6**): Dry oxygen was bubbled through a yellow-orange solution containing 2.1 g (3.0 mmol) of **4** in 50 ml *n*-hexane at 25°C until the solution became nearly colourless. Approx. 20 ml of *n*-hexane were removed by evaporation and the remaining solution was cooled to −30°C. The resultant solid was crystallized three times from *n*-hexane yielding 1.1 g (50%) of colourless crystals of **6**; m.p. 225–227°C. – ^{1}H NMR (500 MHz, [D$_8$]toluene, −20°C): $\delta = 0.73$ (d, 6H, $^3J_{\mathrm{H,H}} = 6.6$ Hz), 0.77 (d, 6H, $^3J_{\mathrm{H,H}} = 6.6$ Hz), 1.12 (d, 6H, $^3J_{\mathrm{H,H}} = 6.9$ Hz), 1.15 (d, 6H, $^3J_{\mathrm{H,H}} = 6.9$ Hz), 1.42 (d, 6H, $^3J_{\mathrm{H,H}} = 6.6$ Hz), 1.53 (d, 6H, $^3J_{\mathrm{H,H}} = 6.6$ Hz), 2.04 (s, 6H), 2.49 (s, 6H), 2.62 (s, 6H), 2.68 (sept, 2H, $^3J_{\mathrm{H,H}} = 6.9$ Hz), 3.55 (sept, 2H, $^3J_{\mathrm{H,H}} = 6.6$ Hz), 4.68 (sept, 2H, $^3J_{\mathrm{H,H}} = 6.6$ Hz), 6.55 (s, 2H), 6.57 (s, 2H), 7.00 (s, 2H), 7.16 (s, 2H). – ^{13}C NMR ($\mathrm{C_6D_6}$, 25°C): $\delta = 21.08$ ($\mathrm{CH_3}$), 22.55 ($\mathrm{CH_3}$), 23.46 ($\mathrm{CH_3}$), 23.87 ($\mathrm{CH_3}$), 25.12 ($\mathrm{CH_3}$), 25.42 ($\mathrm{CH_3}$), 30.74 (CH), 34.55 (CH), 35.62 (CH), 120.89 (CH), 122.67 (CH), 128.71 (CH), 129.71 (CH), 130.71 ($\mathrm{C_q}$), 131.22 ($\mathrm{C_q}$), 140.21 ($\mathrm{C_q}$), 143.93 ($\mathrm{C_q}$), 144.96 ($\mathrm{C_q}$), 151.55 ($\mathrm{C_q}$), 155.17 ($\mathrm{C_q}$), 156.09 ($\mathrm{C_q}$). – ^{29}Si NMR ($\mathrm{C_6D_6}$, 25°C, TMS ext.): $\delta = -3.26$ (Si 2), -5.43 (Si 4). – MS (CI, isobutane), *m/z* (%): 733 (12) [M$^+$], 613 (65) [M$^+$ − $\mathrm{C_9H_{12}}$]. – $\mathrm{C_{48}H_{68}O_2Si_2}$ (733.2): calcd. C 78.63, H 9.35; found C 78.30, H 9.39.

5,7-Di-tert-butyl-2,2-bis(2,4,6-triisopropylphenyl)-3,3-bis(2,4,6-trimethylphenyl)-2,3-dihydro-1,4,2,3-benzodioxadisiline (**7**) and *5,7-di-tert-butyl-3,3-bis(2,4,6-triisopropylphenyl)-2,2-bis(2,4,6-trimethylphenyl)-2,3-dihydro-1,4,2,3-benzodioxadisiline* (**8**): To a solution of 700 mg (1.00 mmol) of **4** in 20 ml of *n*-hexane was added dropwise a dark green solution of 220 mg (1.00 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone in 20 ml of toluene. The solvents were removed in vacuo and the residue was recrystallized firstly from diethyl ether and then from toluene to provide 500 mg (54%) of colourless needles of **7**; m.p. 218°C. – ^{1}H NMR ([D$_8$]toluene, 75°C): $\delta = 0.89$ (d, 12H, $^3J_{\mathrm{H,H}} = 6.1$ Hz), 0.96 (d, 12H, $^3J_{\mathrm{H,H}} = 6.1$ Hz), 1.14 (s, 9H, *t*Bu), 1.16 (d, 12H, $^3J_{\mathrm{H,H}} = 6.8$ Hz), 1.39 (s, 9H, *t*Bu), 2.03 (s, 6H), 2.43 (s, 12H), 2.72 (sept, 2H, $^3J_{\mathrm{H,H}} = 6.8$ Hz), 3.48 (sept, 4H, $^3J_{\mathrm{H,H}} = 6.1$ Hz), 6.60 (s, 4H), 7.0–7.1 (broad), 7.1 (s, 2H). – ^{13}C NMR ($\mathrm{C_6D_6}$, 25°C): $\delta = 20.89$ ($\mathrm{CH_3}$), 23.92 ($\mathrm{CH_3}$), 24.06 ($\mathrm{CH_3}$), 24.40 ($\mathrm{CH_3}$), 24.51 ($\mathrm{CH_3}$), 24.63 ($\mathrm{CH_3}$), 24.90 ($\mathrm{CH_3}$), 26–28 (very broad, $\mathrm{CH_3}$), 31.38 ($\mathrm{CH_3}$, *t*Bu), 31.61 ($\mathrm{CH_3}$, *t*Bu), 34.44 ($\mathrm{C_q}$, *t*Bu), 34.54 ($\mathrm{C_q}$, *t*Bu), 35.48 (CH), 36–38 (very broad, CH), 117.80 (CH), 118.66 (CH), 121.69 (CH), 121.89 (CH), 122.11 (CH), 122.07 (CH), 128.33 (CH), 129.25 (CH), 129.90 (CH), 130.52 (CH), 139.05 ($\mathrm{C_q}$), 139.84 ($\mathrm{C_q}$), 143.36 ($\mathrm{C_q}$), 143.74 ($\mathrm{C_q}$), 145.38 ($\mathrm{C_q}$), 150.58 ($\mathrm{C_q}$), 155.22 ($\mathrm{C_q}$), 155.56 ($\mathrm{C_q}$). The *ipso*-carbon atoms were not observed. – ^{29}Si NMR ($\mathrm{C_6D_6}$, 25°C, TMS ext.): $\delta = -10.15$. – MS (field desorption), *m/z* (%): 922 (100) [M$^+$]. – $\mathrm{C_{62}H_{88}O_2Si_2}$ (921.6): calcd. C 80.81, H 9.62; found C 80.59, H 9.55.

After isolation of **7**, the mother liquor was stripped, the residue was redissolved in a minimum amount of diethyl ether, and the solution was cooled to −30°C. This procedure yielded 90 mg (10%) of colourless rhombic crystals of **8**, m.p. 249°C. – ^{1}H NMR ($\mathrm{C_6D_6}$, 25°C): $\delta = 0.13$ (d, 3H, $^3J_{\mathrm{H,H}} = 6.7$ Hz), 0.49 (d, 3H, $^3J_{\mathrm{H,H}} = 6.7$ Hz), 0.49 (d, 3H, $^3J_{\mathrm{H,H}} = 6.7$ Hz), 1.06 (s, 9H, *t*Bu), 1.14–1.23 (broad, 12H, $\mathrm{CH_3}$), 1.35 (d, 3H, $^3J_{\mathrm{H,H}} = 6.7$ Hz), 1.39 (d, 3H, $^3J_{\mathrm{H,H}} = 6.7$ Hz), 1.47 (d, 3H, $^3J_{\mathrm{H,H}} = 6.7$ Hz), 1.49 (d, 3H, $^3J_{\mathrm{H,H}} = 6.7$ Hz), 1.54 (s, 9H, *t*Bu), 1.57 (d, 3H, $^3J_{\mathrm{H,H}} = 6.7$ Hz), 1.98 (s, 6H), 2.09 (s, 3H), 2.15 (s, 3H), 2.16 (s, 3H), 2.63 (sept, 1H), 2.66 (s, 3H), 2.74 (sept, 2H), 3.93 (sept, 1H), 4.10 (sept, 1H), 4.34 (sept, 1H), 6.47 (s, 1H), 6.55 (s, 1H), 6.57 (s, 1H), 6.64 (s, 1H), 6.70 (d, 1H, $^4J_{\mathrm{H,H}} = 2.5$ Hz), 6.81 (s, 1H), 6.99 (s, 1H), 7.05 (d, 1H), 7.11 (s, 1H), 7.33 (s, 1H). – ^{13}C NMR ($\mathrm{C_6D_6}$, 25°C): $\delta = 20.93$ ($\mathrm{CH_3}$), 22.43 ($\mathrm{CH_3}$), 23.82 ($\mathrm{CH_3}$), 23.92 ($\mathrm{CH_3}$), 24.07 ($\mathrm{CH_3}$), 24.21 ($\mathrm{CH_3}$), 24.41 ($\mathrm{CH_3}$), 24.65 ($\mathrm{CH_3}$), 24.89 ($\mathrm{CH_3}$), 25.39 ($\mathrm{CH_3}$), 25.63 ($\mathrm{CH_3}$), 25.74 ($\mathrm{CH_3}$), 26.57 ($\mathrm{CH_3}$), 27.10 ($\mathrm{CH_3}$), 28.39 ($\mathrm{CH_3}$), 29.07 ($\mathrm{CH_3}$), 30.83 ($\mathrm{CH_3}$, *t*Bu), 31.34 ($\mathrm{CH_3}$, *t*Bu), 34.10 (CH), 34.15 (CH), 34.44 ($\mathrm{C_q}$, *t*Bu), 34.56 ($\mathrm{C_q}$, *t*Bu), 34.75 (CH), 35.29 (CH), 35.73 (CH), 35.89 (CH), 117.37 (CH), 118.76 (CH), 121.30 (CH), 122.39 (CH), 123.19 (CH), 123.57 (CH), 124.48 (CH), 129.25 (CH), 129.70 (CH), 130.42 (CH), 131.40 ($\mathrm{C_q}$), 133.60 ($\mathrm{C_q}$), 133.90 ($\mathrm{C_q}$), 135.50 ($\mathrm{C_q}$), 138.50 ($\mathrm{C_q}$), 139.19 ($\mathrm{C_q}$), 139.60 ($\mathrm{C_q}$), 143.44 ($\mathrm{C_q}$), 143.56 ($\mathrm{C_q}$), 143.73 ($\mathrm{C_q}$), 146.20 ($\mathrm{C_q}$), 147.20 ($\mathrm{C_q}$), 150.73 ($\mathrm{C_q}$), 153.10 ($\mathrm{C_q}$), 154.40 ($\mathrm{C_q}$), 157.40 (CO), 157.50 (CO). – ^{29}Si NMR ($\mathrm{C_6D_6}$, 25°C, TMS ext.): $\delta = -13.0$, -7.93. – MS (field desorption), *m/z* (%): 922 (100) [M$^+$].

Table 1. Crystallographic data for **5**, **6**, and **7**

	5	**6**	**7**
Formula	$\mathrm{C_{48}H_{68}OSi_2}$	$\mathrm{C_{48}H_{68}O_2Si_2}$	$\mathrm{C_{62}H_{88}O_2Si_2}$ · 1/2 toluene
Mol. mass	717.20	733.20	921.55
Cryst. size [mm]	0.64×0.64×0.42	1.18×0.87×0.65	1.02×0.53×0.30
Cryst. system	tetragonal	tetragonal	monoclinic
Space group	$I4_1/a$	$I4_1/a$	$C2/c$
a [pm]	3604.7(3)	3627.5(3)	4673.8(3)
b [pm]	3604.7(3)	3627.5(3)	1081.3(1)
c [pm]	1438.5(1)	1440.7(1)	2430.4(2)
β [°]			92.41(1)
V [× 10^6 pm^3]	1869.2(3)	1895.8(3)	1227.2(2)
Z	16	16	8
$d_{\mathrm{calcd.}}$ [g cm^{-3}]	1.019	1.028	1.047
Diffractometer		Siemens AED 2	
Radiation (Graphite-monochromated) [pm]	Mo-K_α 71.073	Mo-K_α 71.073	Mo-K_α 71.073
T [K]	296(2)	296(2)	296(2)
μ [mm^{-1}]	0.107	0.108	0.098
Scan-method	ω–2θ	ω–2θ	ω–2θ
2θ (max) [°]	46	48	46
Total no. of reflexions	6884	7680	8656
No of unique reflexions	6489	7406	8536
No. of observed reflexions [$I > 2\sigma(I)$]	6484	7406	8530
No. of parameters refined	416	421	600
GOF (F^2)	1.023	0.913	0.997
$R1$	0.086	0.090	0.076
$wR2$	0.190	0.238	0.165
Residual electron density [e nm^{-3}]	353, −207	371, −286	442, −270

2,2-Bis(2,4,6-triisopropylphenyl-3,3-bis(2,4,6-trimethylphenyl)-4,4-diphenyl-1,2,3-oxadisiletane (**9**): A solution of 182 mg (1.00 mmol) of benzophenone in 20 ml of *n*-hexane was added dropwise to a solution of 700 mg (1.00 mmol) of **4** in 50 ml of *n*-hexane. The orange-yellow solution was heated under reflux for 20 h, after which time it was cooled to 20°C. The solvent was distilled off and the residue was chromatographed on silica gel 60 with *n*-hexane/diethyl ether (9:1) yielding a yellow solid which was recrystallized from diethyl ether to afford 704 mg (80%) of colourless crystals of **9**; m.p. 241°C. – ^{1}H NMR ($\mathrm{C_6D_6}$, 25°C): $\delta = 0.36$ (d, 3H, $^3J_{\mathrm{H,H}} = 6.2$ Hz), 0.50 (d, 3H, $^3J_{\mathrm{H,H}} = 6.2$ Hz), 0.73 (d, 3H, $^3J_{\mathrm{H,H}} = 6.2$ Hz), 0.97 (d, 3H, $^3J_{\mathrm{H,H}} = 6.2$ Hz), 1.18 (m, 18H, $\mathrm{CH_3}$), 1.32 (d, 6 H, $^3J_{H,H}$ = 6.2 Hz), 1.81 (s, 3 H), 1.99 (s, 3 H), 2.03 (s, 3 H), 2.22 (s, 3 H), 2.45 (s, 3 H), 2.54 (s, 3 H), 2.75 (sept, 2 H), 3.03 (sept, 1 H), 3.46 (sept, 1 H), 3.63 (sept, 1 H), 4.78 (sept, 1 H), 6.52, 6.57, 6.61, 6.83, 6.85, 6.88, 6.93, 6.98, 7.02, 7.05, 7.22, 7.42, 7.49, 7.51, 7.60, 7.62, 7.63, 7.71. – ^{13}C NMR (C_6D_6, 25 °C): δ = 20.74 (CH_3), 20.84 (CH_3), 23.15 (CH_3), 23.72 (CH_3), 23.94 (CH_3), 24.12 (CH_3), 24.63 (CH_3), 24.72 (CH_3), 25.22 (CH_3), 25.49 (CH_3), 25.68 (CH_3), 25.79 (CH_3), 26.53 (CH_3), 26.77 (CH_3), 28.96 (CH_3), 29.81 (CH_3), 34.41 (CH), 36.38 (CH), 37.47 (CH), 95.55 (CO), 121.63 (CH), 122.24 (CH), 122.54 (CH), 123.91 (CH), 126.37 (CH), 126.42 (CH), 127.36 (CH), 128.88 (CH), 129.72 (CH), 130.02 (CH), 135.76 (C_q), 137.20 (C_q), 138.13 (C_q), 138.36 (C_q), 139.01 (C_q), 143.71 (C_q), 144.55 (C_q), 145.00 (C_q), 145.40 (C_q), 149.52 (C_q), 150.27 (C_q), 151.68 (C_q), 152.94 (C_q), 153.08 (C_q), 155.80 (C_q), 156.10 (C_q). – ^{29}Si NMR (C_6D_6, 25 °C, TMS ext.): δ = 24.07, 32.55; $^1J_{Si,Si}$ = 85.5 Hz. – MS (CI, isobutane), m/z (%): 883 (33) [M^+]. – $C_{61}H_{78}OSi_2$ (883.46): calcd. C 82.93, H 8.90; found C 82.72, H 8.74.

X-ray Structural Analyses of Compounds **5**, **6**, *and* **7**: Single crystals were grown from saturated solutions in *n*-hexane (**5** and **6**) or toluene (**7**). Compound **7** crystallized as a solvate **7** · 1/2 toluene. The structures were solved by direct methods and refined by full-matrix least squares techniques against all F^2 data with $[I > 2\sigma(I)]$[20]. The oxygen atom of **5** is disordered occupying two positions with the occupancy factors of 0.75 and 0.25.

Crystal data and numerical data of the structure determinations are given in Table 1[21].

☆ Dedicated to Professor *Manfred Regitz* on the occasion of his 60th birthday.

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