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Decamethylsilicocene Chemistry: Reaction with Representative Aldehydes and Ketones

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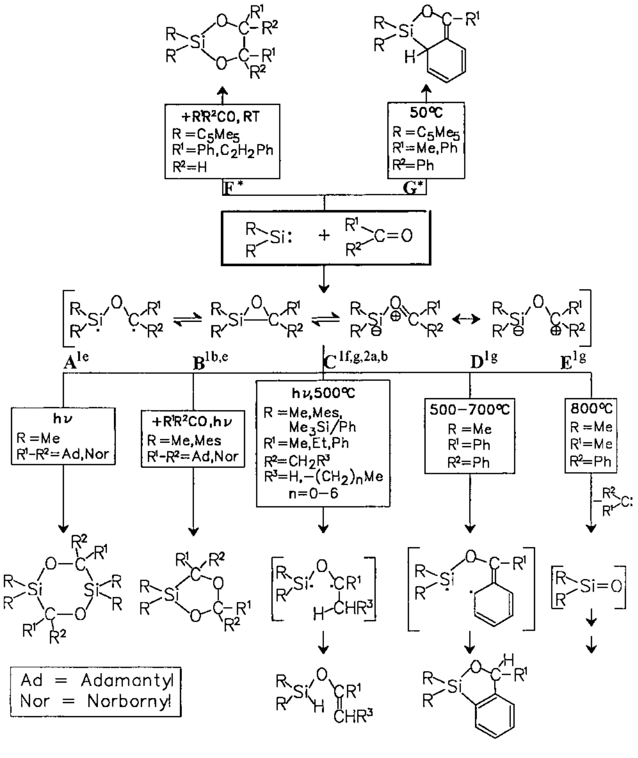
Reactions of decamethylsilicocene, $(Me_5C_5)_2Si$ (**1**), with representative organic carbonyl compounds are described. They proceed via [2 + 1] cycloaddition products of the oxasilirane type as reactive intermediates to give different types of compounds. The formal oxidation state of silicon is changed from +II in the substrate to +IV in the final products; at the same time the hapticity of the pentamethylcyclopentadienyl ligands changes from η^5 to η^1. In the reaction of **1** with aldehydes such as benzaldehyde and *trans*-cinnamaldehyde as well as with acetone, formation of the respective dioxasilolane derivatives **2**, **3**, and **5** takes place. Here, C−C bond formation is observed for the first time in the reaction of a divalent silicon compound; reaction with the aldehydes is stereospecific. In the reaction of **1** with acetophenone or benzophenone, the bicyclic ring systems **6** and **7**, respectively, containing an oxasilacyclopentene unit are formed by rearrangement of the transient oxasiliranes. The 1,3,2-dioxasilole **9** is the product of the reaction of **1** with benzil. The new compounds are characterized by NMR (^1H, ^{13}C, ^{29}Si) spectroscopy and by mass spectrometry and microanalytical data. The X-ray crystal structure analysis of **2** is presented.

Introduction

The reactions of transient silylenes (silanediyls) with organic carbonyl compounds such as aldehydes, ketones, and α-diketones have been studied in detail during the last two decades in the research groups headed by Ando[1] and Ishikawa.[2] The silylenes investigated (dimethylsilylene, dimesitylsilylene, and (trimethylsilyl)phenylsilylene) were generated by photochemically or thermally induced elimination processes. In their reactions with organic carbonyl compounds, the products obtained are the result of the formation of highly reactive intermediates (oxasiliranes or ring-opened biradical or ionic isomers) which are stabilized in quite different ways, as described in Scheme 1, steps **A**−**E**.

Scheme 1. Products and Pathways in Reactions of Silylenes with Organic Carbonyl Compounds[a]



[a] The asterisks denote pathways found in this work.

Decamethylsilicocene, $(C_5Me_5)_2Si$ (**1**), was the first stable silicon(II) compound described in the literature.[3] It allows chemical reactions under ordinary conditions in a normal temperature range.[4] Due to its structure and reactivity, **1** is regarded as a hypercoordinated, nucleophilic silylene. In this context, the reaction of **1** with several electrophilic π-systems was investigated.[4e,f]

In the following we describe the behavior of **1** toward representative carbonyl compounds and compare the results with those obtained with the transient silicon(II) compounds mentioned above.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

[1] (a) Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270. (b) Ando,W.; Hamada,Y.; Sekiguchi, A. *J. Chem. Soc., Chem. Commun.* **1983**, 952. (c) Ando, W.; Hamada, Y.; Sekiguchi, A. *Tetrahedron Lett.* **1982**, *23*, 5323. (d) Ando, W., Ikeno, M. *J. Chem. Soc., Chem. Commun.* **1979**, 655. (e) Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **1978**, *100*, 3614. (f) Ando, W.; Ikeno, M. *Chem. Lett.* **1978**, 609. (g) Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **1977**, *99*, 6447.

[2] (a) Ishikawa, K.; Nishimara, K.; Sagisawa, H.; Kumada, M. *J. Organomet. Chem.* **1980**, *194*, 147. (b) Ishikawa, K.; Nakagawa, K.-I.; Kumada, M. *J. Organomet. Chem.* **1977**, *134*, C45.

[3] (a) Jutzi, P.; Holtmann, U.; Kanne, D.; Krüger, C.; Blohm, A; Gleiter, R.; Hyla-Kryspin, I. *Chem. Ber.* **1989**, *122*, 1629. (b) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164.

[4] (a) Jutzi, P.; Bunte, E.-A.; Holtmann, U.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **1993**, *446*, 139. (b) Jutzi, P.; Bunte, E.-A. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1605. (c) Jutzi, P. In *Frontiers of Organosilicon Chemistry*; Bassindale, A. R., Gaspar, P. P., Eds.; Royal Society of Chemistry: Cambridge, England, 1991. (d) Jutzi, P.; Möhrke, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 893. (e) Jutzi, P.; Möhrke, A.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1518. (f) Jutzi, P.; Möhrke, A. *Angew. Chem. Int., Ed. Engl.* **1989**, *28*, 762.

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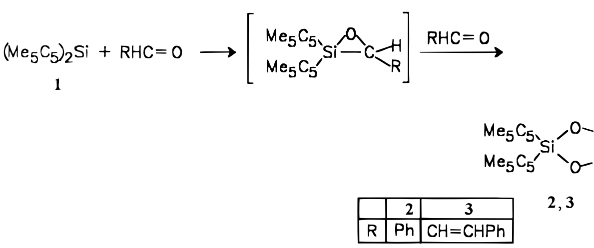
Scheme 2



	2	3
R	Ph	CH=CHPh

Results and Discussion

Decamethylsilicocene (**1**) reacted in toluene solution and under mild conditions with 2 equiv of benzaldehyde to give the 1,3-dioxasilolane **2** in good yield (see Scheme 2). Compound **2** was obtained as colorless air-stable crystals, which are soluble in all common organic solvents. The reaction is highly regio- and stereospecific; only the *trans* isomer of **2** was formed. Furthermore, the product formation was independent of the stoichiometry of the reactants.

Under comparable conditions, reaction of decamethylsilicocene (**1**) with *trans*-cinnamaldehyde led to the 1,3-dioxasilolane **3** as a pale yellow powder, which showed physical properties similar to those of **2** (see Scheme 2).

Compounds **2** and **3** were characterized unambiguously by NMR spectroscopic and microanalytical data; compound **2** was further characterized by an X-ray diffraction analysis (vide infra; Figure 1).

^{1}H and ^{13}C NMR spectra give information about the stereochemistry of the heterocycles **2** and **3**. Thus, the *trans* orientation of the ligands R (Ph, CH═CHPh) causes the prochirality of the silicon atom. As a consequence, the five C—Me positions within the σ-bonded pentamethylcyclopentadienyl ligands are magnetically nonequivalent.

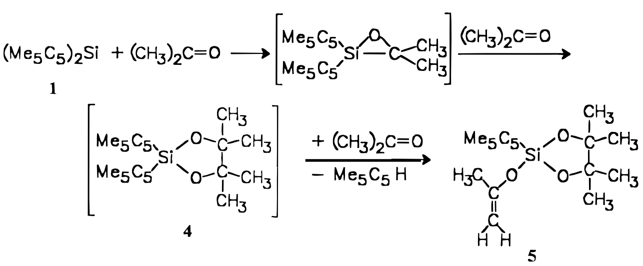
For the reactions of **1** with benzaldehyde and with *trans*-cinnamaldehyde we propose the following reaction pathway (see Scheme 2). The first intermediate is a highly reactive formal [2 + 1] cycloaddition product, which is subsequently attacked by a further substrate molecule. Regio- and stereospecific insertion into the silicon−carbon bond of the intermediate results in the formation of the final products **2** and **3**, respectively. This type of reaction has so far not been described in silylene chemistry. Similar results were obtained in the reaction of stannylenes with aldehydes.[5]

Ando et al.[1c] isolated a stable oxasilirane derivative in the reaction of Mes_2Si with tetramethyl-2-indanone. Electron spectroscopy investigation at low temperature (−196 °C) demonstrated that a intensely blue silacarbonyl ylide was an intermediate in the formation of the oxasilirane.[1a]

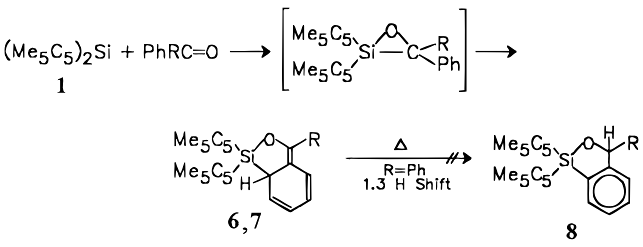
In the reaction of **1** with benzaldehyde or *trans*-cinnamaldehyde, the formation of silacarbonyl ylides as intermediates seems to be less probable, since no color change during the reactions was observed. Furthermore, compound **1** has to be regarded as a nucleophilic and not as an electrophilic silylene.

More drastic conditions were necessary to initiate the reaction of decamethylsilicocene (**1**) with acetone. After a solution of **1** was heated in toluene with excess acetone for 6 h at 80 °C, a colorless oily product was obtained. Purification by sublimation or crystallization has been unsuccessful. NMR spectroscopic investigations showed the presence of the 1,3-dioxasilolane derivative **5** in about 80% yield (see Scheme 3). Reaction of **1** with acetone in a 1:2 stoichiometry did not lead to the 1,3-dioxasilolane **4** as the final product.

Scheme 3



Scheme 4



R	Me	Ph
	6	7

In analogy to the reaction of **1** with aldehydes, we propose the formation of the dioxasilolane **4** as an intermediate, which reacts under the more drastic conditions with a further molecule of acetone to form the vinyloxo-substituted dioxasilolane **5** and pentamethylcyclopentadiene. As in many other processes, the pentamethylcyclopentadienyl ligand acts as a leaving group.[6]

In the reaction of decamethylsilicocene (**1**) with acetophenone, the five-membered heterocyclic ring system **6** was isolated in about 30% yield after a reaction time of 3 days at 50 °C (see Scheme 4). Compound **6** was obtained as a pale yellow powder. Under similar conditions (6 days at 50 °C), reaction of **1** with benzophenone resulted in the formation of **7** as a yellow powder in good yield.

Compounds **6** and **7** were characterized by NMR spectroscopic, mass spectrometric, and microanalytical data.

The pathway of the reactions of **1** with acetophenone and with benzophenone is discussed as follows (see Scheme 4). The first intermediate is a highly reactive formal [2 + 1] cycloaddition product, which is unstable under the reaction conditions. This intermediate gains stabilization by a concerted rearrangement process leading to compounds **6** or **7**.

Ando et al.[1g] discussed a biradical intermediate in the reaction of dimethylsilylene with benzophenone at high temperatures (500−700 °C) and suggested a further intermediate such as **7**, which finally was stabilized by a 1,3-H shift (see Scheme 1, pathway **D**). Similarly, in

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(5) Neumann, W. P.; Schwarz, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 812.

(6) (a) Jutzi, P.; Kanne, D.; Hursthouse, M.; Howes, A. J. *Chem. Ber.* **1988**, *121*, 1299. (b) Jutzi, P.; Holtmann, U.; Bögge, H.; Müller, A. *J. Chem. Soc., Chem. Commun.* **1988**, 305.

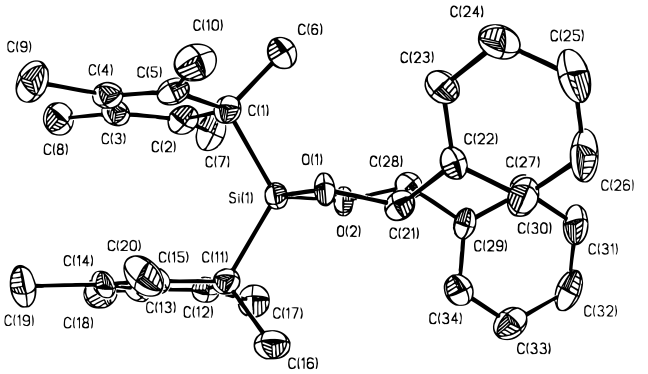
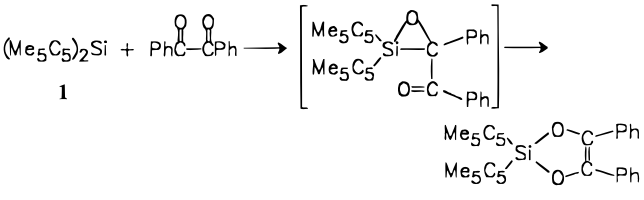


Figure 1. Molecular structure of **2**.

Scheme 5



1

9

the reaction of dimethylsilylene with acetophenone at high temperatures (500 °C) a biradical intermediate was found, from which a silyl enol ether is formed as the final product (see Scheme 1, pathway **C**).[1g]

In the reaction of **1** with acetophenone or benzophenone, the formation of biradical intermediates seems to be less probable, due to the rather low reaction temperatures.

It is worth mentioning that in **7** a 1,3-hydrogen shift is not observed; thus heating a solution of **7** in $CDCl_3$ at 80 °C for 6 days did not lead to the aromatic compound **8** (see Scheme 4).

The reaction of decamethylsilicocene (**1**) with benzil needs even more drastic conditions. Reaction in toluene as solvent at 100 °C for 3 days led to the 1,3,2-dioxasilole **9** in good yield (see Scheme 5). Compound **9** was characterized by NMR spectroscopic, mass spectrometric, and microanalytical data.

For the reaction of **1** with benzil we propose the following pathway (see Scheme 5). Once more the first reaction step leads to a formal [2 + 1] cycloaddition product, in which a highly reactive oxasilirane is formed. This intermediate reacts with the other carbonyl group of the α-diketone to give the stable product **9**. A comparable pathway has been described by Ando et al.[1d] for the reaction of dimethylsilylene with various α-diketones.

X-ray Crystal Structure of 2. The molecular structure of **2** is presented in Figure 1; selected bond lengths and bond angles are displayed in Table 2, and crystallographic data are given in Table 1.

Table 1. Crystallographic Data[a]

empirical formula	$C_{34}H_{42}O_2Si$
cryst size, mm^3	0.60 × 0.15 × 0.10
fw	510.77
cryst syst	triclinic
space group	$P\bar{1}$
lattice params	
a, Å	9.944(7)
b, Å	12.004(6)
c, Å	12.983(12)
α, deg	102.16(6)
β, deg	102.03(6)
γ, deg	95.66(5)
V, Å^3	1465(2)
Z	2
d_{calc}, g/cm^3	1.158
diffractometer	Siemens P2$_1$
F(000)	552
μ(Mo Kα), mm^{-1}	0.108
temp, °C	−100(2)
$2\theta_{max}$, deg	3.30−50.00
no. of data collected	5509
no. of params refined	344
no. of obs data ($F > 4\sigma(F)$)	2165
residuals: R_F, wR_{F^2} for obs data	0.1127, 0.2148
largest peak in final diff map, e/Å^3	0.4
abs cor	none

[a] X-ray structure determination: a single crystal was coated with a layer of hydrocarbon oil, attached to a glass fiber, and cooled to 173 K for data collection. Crystallographic programs used for structure solution and refinement were from SHELXTL PLUS and SHELXL-93. The structure was solved by using direct methods and was refined by using full-matrix least squares on F^2 of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at the calculated positions with $U(H) = 1.2U_{eq}$ for CH and CH_2 groups, and $U(H) = 1.5U_{eq}$ for CH_3 groups.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of 2

	Bond Lengths		
Si1−C1	1.904(8)	O2−C28	1.452(8)
Si1−C11	1.891(8)	C21−C28	1.554(10)
Si1−O1	1.663(5)	C21−C22	1.495(10)
Si1−O2	1.673(5)	C28−C29	1.499(9)
O1−C21	1.446(8)		
	Bond Angles		
C1−Si1−C11	119.1(3)	Si1−O2−C28	111.3(4)
O1−Si1−O2	96.3(2)	O1−C21−C28	106.8(6)
O1−Si1−C1	108.4(3)	O1−C21−C22	111.0(6)
O1−Si1−C11	112.2(3)	O2−C28−C21	105.1(6)
O2−Si1−C1	110.9(3)	O2−C28−C29	111.0(5)
O2−Si1−C11	107.6(3)	C22−C21−C28	112.0(6)
Si1−O1−C21	110.1(4)	C29−C28−C21	114.2(6)

The structure of compound **2** shows a corrugated heterocyclic five-membered 1,3,2-dioxasilolane ring system. The Cp* ligands are σ-bonded to the Si atom and have a nearly parallel sandwichlike orientation. The distances between the allylic C(Cp*) atoms and the Si atom are rather long (∼1.90 Å). The angle between the allylic C(Cp*) atoms and the Si atom (119.1°) deviates drastically from the value expected for an sp^3-hybridized Si atom. These data are consistent with the well-known steric requirements of σ-bonded pentamethylcyclopentadienyl ligands.[4a] The two phenyl ligands are *trans* oriented.

The Si−O bond lengths (∼1.67 Å) are slightly longer than in other 1,3,2-dioxasilolane derivates.[7,8] The O−Si−O angle is 96.3°. This angle contraction and the elongation of the Si-O bond lengths are a result of the ring strain of the heterocyclic ring as well as of the expansion of the angle between the allylic C(Cp*) atoms and the Si atom.

Conclusion

The results obtained in the reactions of decamethylsilicocene (**1**) with organic carbonyl compounds can be summarized as follows.

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(7) Schomburg, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 65.

(8) Nakadaira, Y.; Nomura, T.; Kanouchi, S.; Sato, R.; Kabuto, C.; Sakurai, H. *Chem. Lett.* **1983**, 209.

(1) In all reactions described, a change of hapticity of the pentamethylcyclopentadienyl ligands from η^5 in **1** to η^1 in the products and also a change of the oxidation state of silicon from +II to +IV is observed. Compound **1** reacts as a nucleophilic silylene, which is in accord with earlier investigations.[4c,e,f]

(2) Quite different conditions are required. Mild conditions (room temperature) are sufficient in the reactions of **1** with aldehydes such as benzaldehyde or *trans*-cinnamaldehyde; more drastic conditions (50−80 °C) are neccessary to perform the reaction with ketones. This might be due to the different steric demands of the carbonyl substrates: compound **1** possesses two bulky pentamethylcyclopentadienyl ligands and prefers reactions with small substrates.

(3) In the reaction of **1** with aldehydes and with acetone C−C bond formation is observed (see Schemes 2 and 3 and pathway **F** in Scheme 1). To the best of our knowledge, C−C bond formation in reactions of transient or stable silylenes with organic carbonyl compounds has not been described in the literature.

(4) The reactions of **1** with aldehydes such as benzaldehyde and *trans*-cinnamaldehyde are highly regio- and stereospecific; only the *trans* isomers are formed (see Scheme 2).

(5) In the reaction of **1** with acetophenone and benzophenone the heterocyclic compounds **6** and **7** are formed (see Scheme 4 and pathway **G** in Scheme 1). It is worth mentioning that the formation of the cyclohexadiene system is preferred over the formation of an aromatic system by a 1,3-hydrogen shift.

(6) With α-diketones, **1** reacts in the same way as other silylenes do, i.e. with formation of 1,3,2-dioxasilole derivatives.

(7) Scheme 1 gives the different pathways observed so far in the reactions of silylenes with organic carbonyl compounds.

Experimental Section

General Considerations. Standard Schlenk techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods and distilled under argon prior to use. The reagents PhCHO, PhC_2H_2CHO, $PhCOCH_3$, Ph_2CO, $(CH_3)_2CO$, and PhCOCOPh were procured commercially and used without further purification.

Physical Measurements. IR spectra were obtained from KBr pellets using a Mattson Perkin Polaris FTIR spectrophotometer. Mass spectra (EI) were run on a Varian 311 A mass spectrometer (70 eV, 300 μA emission) and NMR spectra were obtained using a Bruker AM 300 spectrometer (^{1}H, 300.13 MHz; ^{13}C, 75.47 MHz; ^{29}Si, 59.60 MHz). NMR spectra were referenced to the residual protic impurities of the deuteriated solvents C_6D_6, $CDCl_3$, and toluene-d_8. Elemental analyses were performed by the Microanalytical Laboratory of the University of Bielefeld. Melting points (uncorrected) were measured with a Büchi 510 melting point apparatus using sealed capillary tubes.

Synthesis of 2,2-Bis(pentamethylcyclopentadienyl)-4,5-diphenyl-1,3,2-dioxasilolane (2). A 0.70 g (6.60 mmol) portion of benzaldehyde was added to a solution of 0.99 g (3.30 mmol) of **1** in 15 mL of toluene at 0 °C. The reaction mixture was stirred at 0 °C for 4 h and at room temperature for 36 h. The mixture was reduced to dryness in vacuo. The residue was dissolved in *n*-hexane; cooling of this solution to −67 °C led to a colorless powder, which was crystallized in toluene. Compound **2** (mp 123−125 °C dec) was obtained as colorless crystals (0.58 g, 34% yield). ^{1}H NMR ($CDCl_3$; δ): 1.20 (s, 6H, allyl $C_5(\mathit{CH}_3)_5$); 1.72, 1.78, 2.02 (s, 6H:12H:6H, $C_5(\mathit{CH}_3)_5$); 4.78 (s, 2H, C*H*); 7.21, 7.30 (m, 4H:6H, aryl *H*). ^{13}C NMR ($CDCl_3$; δ): 11.5, 12.3, 17.3 ($C_5(\mathit{C}H_3)_5$); 55.6 (allyl $\mathit{C}_5(CH_3)_5$); 84.5 (*C*(H)-Ph); 126.9, 127.9, 128.2 (aryl *C*); 136.1, 136.6, 139.4 (vinyl $\mathit{C}_5(CH_3)_5$ and aryl *C*). ^{29}Si NMR ($CDCl_3$; δ): 6.2. Anal. Calcd for $C_{34}H_{42}SiO_2$: C, 79.94; H, 8.28. Found C, 79.64; H, 8.32. MS (*m*/*z*): 510 (M^+). IR(KBr): ν_{Si-O} 1020 (s) cm^{-1}.

Synthesis of 2,2-Bis(pentamethylcyclopentadienyl)-4,5-bis(-2-phenylethenyl)-1,3,2-dioxasilolane (3). A solution of 0.42 g (1.41 mmol) of **1** and 0.18 g (1.41 mmol) of PHC_2H_2CHO in 10 mL of toluene was stirred at room temperature for 1 day. The solvent was removed and the residue extracted with 20 mL of petroleum ether. Compound **3** was crystallized in the petroleum ether extract. After it was dried, **3** was obtained as a pale yellow powder (0.21 g, 54% yield). ^{1}H NMR (C_6D_6; δ): 1.28, 1.76, 1.79, 2.00, 2.18 (s, 6H:6H.6H:6H:6H, $C_5(\mathit{CH}_3)_5$); 4.52−4.56 (m, 2H, allyl *H*); 6.36 (ddd, ^3J = 5.1 Hz, ^4J = 1.7 Hz, 2H, vinyl *H*); 6.89 (d, ^3J = 15.8 Hz, 2H, vinyl *H*); 7.02−7.15 (m, 6H, aryl *H*); 7.31 (d, ^3J = 8.4 Hz, 4H, aryl *H*). ^{13}C NMR (C_6D_6; δ): 11.5, 12.0, 16.6 ($C_5(\mathit{C}H_3)_5$); 55.0 (allyl $\mathit{C}_5(CH_3)_5$); 81.2 ($\mathit{C}(H)C_2H_2Ph$); 126.6, 127.7, 127.8, 128.6, 131.6 (aryl *C*); 135.9, 136.3, 136.6 (vinyl $\mathit{C}_5(CH_3)_5$ and aryl *C*). ^{29}Si NMR (C_6D_6; δ): 8.0. Anal. Calcd for $C_{38}H_{46}SiO_2$: C, 81.09; H, 8.24. Found: C, 80.82; H, 8.44. MS (*m*/*z*): 562 (M^+).

Synthesis of 2-(1-Propen-2-yloxy)-2-(pentamethylcyclopentadienyl)-4,4,5,5-tetramethyl-1,3,2-dioxasilolane (5). A solution of 1.15 g (3.86 mmol) of **1** and 15 mL of acetone in 4 mL of toluene was heated at 80 °C for 6 h. The solvent was removed in vacuo, and a colorless oily residue was obtained, which contained the product **5** and some byproducts. Purification by sublimation (0.01 bar, 100 °C) or crystallization was unsuccessful. NMR spectroscopic investigations indicated that the reaction mixture gave the product **5** in about 80% yield. ^{1}H NMR ($CDCl_3$; δ): 1.05 (s, 3H, $C_5(\mathit{CH}_3)_5$); 1.20 (s, 12H, $-OC(\mathit{CH}_3)_2$); 1.72, 1.80 (s, 6H:6H, $C_5(\mathit{CH}_3)_5$); 1.81 (s, 3H, $-OC\mathit{CH}_3$); 4.08, 4.24 (s, 1H:1H, $-OC{=}\mathit{CH}_2$). ^{13}C NMR ($CDCl_3$; δ): 11.0, 13.2, 15.8 ($C_5(\mathit{C}H_3)_5$); 22.5 ($-OC\mathit{C}H_3$); 26.7 ($-OC(\mathit{C}H_3)_2$); 63.6 (allyl $\mathit{C}_5(CH_3)_5$); 79.4 ($-O\mathit{C}(CH_3)_2$); 91.8 ($-OC{=}\mathit{C}H_2$); 135.3, 140.6 (vinyl $\mathit{C}_5(CH_3)_5$); 154.2 ($-O\mathit{C}{=}CH_2$). ^{29}Si NMR ($CDCl_3$; δ): −74.6. MS (*m*/*z*): 336 (M^+).

Synthesis of 2,2-Bis(pentamethylcyclopentadienyl)-7-methyl-1-oxa-2-silabicyclo[4.3.0]nona-3,5,7-triene (6). A solution of 1.0 g (3.30 mmol) of **1** and 0.80 g (6.60 mmol) of acetophenone in 30 mL of toluene was heated to 50 °C over a period of 3 days. Volatiles were removed, and the yellow oily residue was dissolved in 3 mL of *n*-hexane. Cooling this solution to −60 °C afforded crystals which were recrystallized twice in *n*-hexane. Compound **6** (mp 90−91 °C) was obtained as pale yellow crystals (0.43 g, 31% yield). ^{1}H NMR (C_6D_6; δ): 1.09, 1.21, 1.74, 1.78, 1.94, 2.00 (s, 3H:3H:12H:6H:3H:3H, $C_5(\mathit{CH}_3)_5$); 1.85 (d, ^5J = 4.8 Hz, 3H, $-OC\mathit{CH}_3$); 3.54 (m, 1H, O-Si-C*H*-CH=); 5.67 (m, 1H, OSiCHC*H*=); 5.85 (m, 2H, −CH=C-*HCH*=); 6.23 (d, ^3J = 9.5 Hz, 1H, MeC=CC*H*=). ^{13}C NMR (C_6D_6; δ): 11.5, 12.2 ($C_5(\mathit{C}H_3)_5$); 14.7 ($-OC\mathit{C}H_3$); 17.6 ($C_5(\mathit{C}H_3)_5$); 30.2 (OSi*C*HCH=); 55.4 (allyl $\mathit{C}_5(CH_3)_5$); 119.2, 123.0, 123.6, 126.8 (vinyl −*C*H= (cyclohexadiene system); 136.2, 137.1 (vinyl $\mathit{C}_5(CH_3)_5$); 139.1 (−OC=*C*−); 150.6 (−O*C*=C−). ^{29}Si NMR (C_6D_6; δ): 30.3. Anal. Calcd for $C_{28}H_{38}OSi$: C, 80.38%; H, 9.09%. Found: C, 78.90%; H, 8.89%.[9] MS (*m*/*z*): 418 (M^+), 417($M^+ - H$), 416 ($M^+ - 2H$), 282 ($M^+ - C_5(CH_3)_5H$). IR (KBr): ν_{SiO} 1107 (s) cm^{-1}; $\nu_{C=C}$ 1449 cm^{-1} (m); ν_{C-O} 1205 cm^{-1} (s).

Synthesis of 2,2-Bis(pentamethylcyclopentadienyl)-7-phenyl-1-oxa-2-silabicyclo[4.3.0]nona-3,5,7-triene (7). A solution of 0.90 g (3.02 mmol) of **1** and 0.55 g (3.02 mmol) of benzophenone in 20 mL of toluene was heated to 50 °C over a period of 6 days. The reaction mixture was yellow. The solvent was removed in vacuo, and the yellow oily residue was dissolved in 10 mL of *n*-pentane. Cooling of this solution to

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[9] NMR investigations indicated the presence of low-volatility organic compounds.

−60 °C gave compound **7** (mp 126−128 °C), which was obtained as a yellow powder (0.98 g, 68% yield). ^{1}H NMR (CDCl$_3$; δ): 1.07, 1.70, 1.80, 1.95 (br s, 6H:9H:12H:3H, C$_5$(CH_3)$_5$); 3.52 (s, 1H, SiC*H*CH=) 5.70 (m, 1H, OSiCHC*H*=); 5.78 (m, 2H, −CH=C*H*C*H*=); 6.62 (d, $^{3}J = 9.6$ Hz, 1H, PhC=C-C*H*=); 7.28, 7.37, 7.63 (t, $J = 7.3$ Hz, t, $J = 7.3$ Hz, d, $J = 7.6$ Hz, 1H:2H:2H, aryl H). ^{13}C NMR (CDCl$_3$; δ): 11.5, (C$_5$(CH$_3$)$_5$); 17.5 (C$_5$(CH$_3$)$_5$); 31.2 (OSi*C*HCH=); 55.4 (allyl C_5(CH$_3$)$_5$); 116.2, 121.8, 122.0, 123.4 (vinyl −*C*H= (cyclohexadiene system)); 127.3, 127.5, 128.1, 134.9 (aryl C_6H$_5$); 136.6, 137.1 (vinyl C_5(CH$_3$)$_5$); 138.9 (−OC=*C*−); 149.8 (−O*C*=C−). ^{29}Si NMR (CDCl$_3$; δ): 29.4. Anal. Calcd for C$_{33}$H$_{40}$OSi: C, 82.40%; H, 8.58%. Found: C, 82.44%; H, 8.38%. MS (*m/z*): 480 (M$^+$); 479 (M$^+$ − H); 478 (M$^+$ − 2H); 344 (M$^+$ − C$_5$(CH$_3$)$_5$H). IR (KBr): $\nu_{\mathrm{Si-O}}$ 1097 cm^{-1} (s); $\nu_{\mathrm{C=C}}$ 1442 cm^{-1} (m); $\nu_{\mathrm{C-O}}$ 1219 cm^{-1} (s).

Synthesis of 2,2-Bis(pentamethylcyclopentadienyl)-4,5-diphenyl-1,3,2-dioxasilole (9). A solution of 0.91 g (3.05 mmol) of **1** and 0.64 g (3.05 mmol) of benzil in 25 mL of toluene was stirred at 100 °C over a period of 3 days. The solvent was removed under reduced pressure, and the yellow residue was dissolved in diethyl ether. Colorless crystals of **9** (mp 130 °C dec) formed upon cooling this solution to −60 °C (0.84 g, 54% yield). ^{1}H NMR (CDCl$_3$; δ): 1.73 (s, 30H, C$_5$(CH_3)$_5$); 7.28, 7.51 (m, 6H:4H, aryl *H*). ^{1}H NMR (toluene-d_8, −60$^{\mathrm{o}}$ C; δ): 1.26, 1.63, 2.02 (s, 6H:12H:12H, C$_5$(CH_3)$_5$); 7.10, 7.78 (m, 6H:4H, aryl *H*). ^{13}C NMR (CDCl$_3$; δ): 12.3 (C$_5$(CH$_3$)$_5$); 127.0, 127.4, 128.1, 133.4 (aryl *C*); 136.9 (C_5(CH$_3$)$_5$); 139.1 (=*C*(Ph)O−). ^{29}Si NMR (CDCl$_3$; δ): 7.8. Anal. Calcd for C$_{34}$H$_{40}$O$_2$Si: C, 80.26; H, 7.92. Found: C, 79.27; H, 7.91.[9] MS (*m/z*): 508 (M$^+$). IR (KBr): $\nu_{\mathrm{Si-O}}$ 1050 (s) cm^{-1}.

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Supporting Information Available: Tables of crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **2** (6 pages). Ordering information is given on any current masthead page.

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