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Reactions of the 1,1-Diphenylacetone-Derived Dianion as a C,O-Dinucleophile with Organohalosilanes and -germanes

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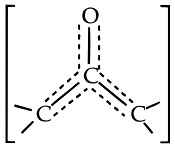
1,1-Diphenylacetone dianion reacts with diorganodichlorosilanes to give 1,1,5,5-tetraorgano-3,7-bis(diphenylmethylene)-1,5-disila-2,8-dioxacyclooctanes, while 1,1-diphenylacetone dianion reacts with diorganodifluorosilanes to give a positional isomer, 1,1,5,5-tetraorgano-3,7-bis(diphenylmethylene)-1,5-disila-2,6-dioxacyclooctane. The structures of 1,1,5,5-tetraphenyl-3,7-bis(diphenylmethylene)-1,5-disila-2,8-dioxyacyclooctane and 1,1,5,5-tetraphenyl-3,7-bis(diphenylmethylene)-1,5-disila-2,6-dioxacyclooctane were determined by X-ray crystallography. A 10-membered cyclic compound and a 6-membered cyclic compound also were prepared by the reaction of 1,1-diphenylacetone dianion with 1,2-dichlorotetramethyldisilane and 1,3-dichlorohexamethyltrisilane, respectively. The structure of 1,1,2,2,6,6,7,7-octamethyl-4,9-bis(diphenylmethylene)-1,2,6,7-tetrasila-3,10-dioxacyclodecane was determined by X-ray crystallography. 1,1-Diphenylacetone dianion reacts with diphenyldichlorogermane and diphenyldifluorogermane to give 1,1,5,5-tetraphenyl-3,7-bis(diphenylmethylene)-1,5-digerma-2,6-dioxacyclooctane. The structure of 1,1,5,5-tetraphenyl-3,7-bis(diphenylmethylene)-1,5-digerma-2,6-dioxacyclooctane was determined by X-ray crystallography. A possible explanation for the difference in the reactions observed with Ph_2SiCl_2 and Ph_2SiF_2 is presented. Experiments involving reactions of the 1,1-diphenylacetone dianion with monochlorosilanes indicate that a Si−CH_2, not an Si−O, bond is formed first.

Introduction

Acetone dianions **1** are ambident dinucleophiles in their reactions with metal dihalides. The dianion derived from dibenzyl ketone reacted with *cis*-$(Ph_3P)_2PtCl_2$ and *trans*-$(Ph_3P)_2PdCl_2$ as a C,C-dinucleophile to give products of type **2a**,[1] and the acetone-derived dianion on reaction with *cis*-$(Ph_3P)_2PtCl_2$ gave **2b**.[2] In contrast, the dianions derived from 1,1-diphenylacetone and acetone reacted with the bis(η^5-cyclopentadienyl) dichlorides of zirconium and hafnium as C,O-dinucleophiles. The products, dinuclear cyclic compounds of type **3**, presumably were formed by dimerization of initially formed **4**, very likely via the coordination dimer **5** (Scheme 1). This different mode of reaction, i.e., to form a M−O and M−C bond vs two M−C bonds, is a result of the oxophilicity of zirconium and hafnium in contrast to the low oxophilicity of palladium and platinum. On this basis, one would predict that acetone-derived dianions also would react as C,O-dinucleophiles with halides of the very oxophilic silicon. Our studies of the reactions of the dianion prepared by double deprotonation of 1,1-diphenylacetone have confirmed this prediction, and we report here details of the reactions that we have studied.



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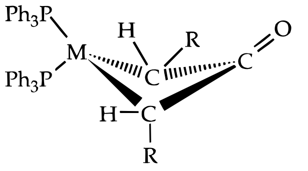

2: a, M = Pt, Pd; R = Ph
b, M = Pt; R = H

Results and Discussion

1,1-Diphenylacetone-derived dianion **6**, prepared by treatment of 1,1-diphenylacetone successively with 1 molar equiv each of KH and *n*-BuLi in THF,[4] reacted readily with diorganodichlorosilanes (Ph_2SiCl_2, Me_2SiCl_2, Et_2SiCl_2, $MeSiHCl_2$) at 0 °C in THF to give solid products in 40−70% yield. The use of higher reaction temperatures decreased the product yield, but lower reaction temperatures did not result in an increase in product yield. It is likely that in a competitive reaction

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

(1) (a) Chiu, K. W.; Henderson, W.; Kemmitt, R. D. W.; Prouse, L. J. S.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1988**, 427. (b) For a discussion of the bonding in such complexes, see: Fawcett, J.; Henderson, W.; Jones, M. D.; Kemmitt, R. D. W.; Russell, D. R.; Lam, B.; Kang, S. K.; Albright, T. A. *Organometallics* **1989**, *8*, 1991. (c) Short review: Kemmitt, R. D. W.; Moore, M. R. *Transition Met. Chem.* **1993**, *18*, 348.

(2) Wang, T. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1994.

(3) Seyferth, D.; Wang, T.; Davis, W. M. *Organometallics* **1994**, *13*, 4134.

(4) (a) Trimitsis, G. B.; Hinkley, J. M.; TenBrink, R.; Poli, M.; Gustafson, G.; Erdman, J.; Rop, D. *J. Am. Chem. Soc.* **1977**, *99*, 4838. (b) Hubbard, J. S.; Harris, T. M. *J. Am. Chem. Soc.* **1980**, *102*, 2110.

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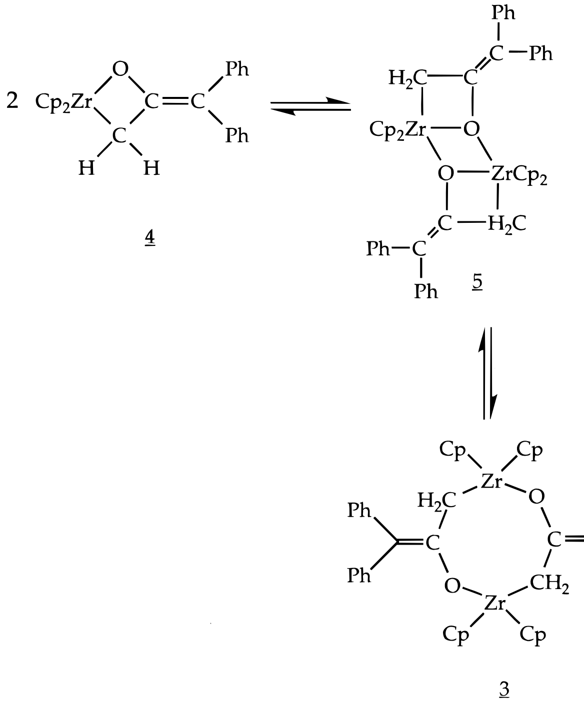
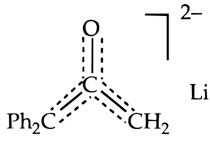
Scheme 1



the dianion slowly attacks the THF solvent. The product yields decreased as the size of the substituents on the silicon atom increased; methyldichlorosilane gave the highest yield (70%) while diphenyldichlorosilane gave the lowest (40%) yield of the product. Di-*tert*-butyldichlorosilane did not react with dianion **6**.

The crystalline product obtained in the reaction of **6** with diphenyldichlorosilane was studied in detail. This product was expected to be either the 1,2-silaoxetane **7** or its dimer **8**, the latter analogous to the solid product of the **6**/(η^5-C_5H_5)$ZrCl_2$ reaction. However, surprisingly, the product was neither of these, although its C,H analysis was in agreement with the values calculated for **7** and **8** and its molecular weight (VPO and MS) was the same as that of **8**. Compound **8** contains two equivalent Si atoms, so its ^{29}Si NMR spectrum should show only one resonance. The ^{29}Si NMR spectrum of the **6**/Ph_2SiCl_2 reaction product showed *two* resonances at δ_{Si} −9.4 and −36.6 indicative of the presence of chemically nonequivalent silicon atoms. On the basis of the ^{29}Si NMR and the molecular weight data, structure **9** was assigned to the **6**/Ph_2SiCl_2 product. This was confirmed by an X-ray diffraction study. Figure 1 shows the molecular structure of **9**.



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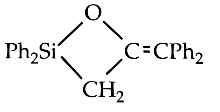

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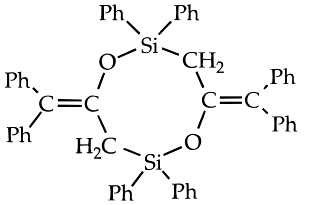

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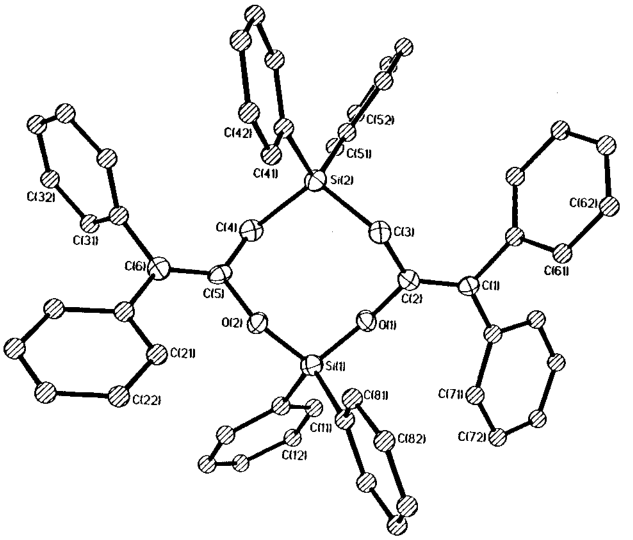
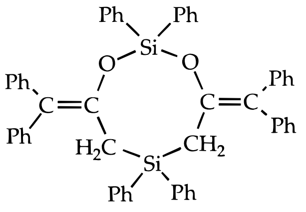


Figure 1. ORTEP plot of the structure of **9**, showing 35% probability ellipsoids.

Table 1. Selected Intramolecular Bond Distances (Å) and Angles (deg) for 9

Si(1)−O(1)	1.648(6)	Si(1)−O(2)	1.633(6)
Si(1)−C(16)	1.839(8)	Si 1)−C(86)	1.850(8)
Si(2)−C(3)	1.910(8)	Si(2)−C(4)	1.895(8)
Si(2)−C(46)	1.870(8)	Si(2)−C(56)	1.856(8)
O(1)−C(2)	1.390(10)	O(1)−C(5)	1.382(10)
C(1)−C(2)	1.340(11)	C(2)−C(3)	1.492(11)
C(4)−C(5)	1.490(12)	C(5)−C(6)	1.358(12)
O(1)−Si(1)−O(2)	112.6(3)	O(1)−Si(1)−C(16)	103.7(3)
O(2)−Si(1)−C(16)	112.4(3)	O(1)−Si(1)−C(86)	110.3(3)
O(2)−Si(1)−C(86)	103.3(3)	C(16)−Si(1)−C(86)	114.8(4)
C(3)−Si(2)−C(4)	111.4(4)	C(3)−Si(2)−C(46)	104.0(3)
C(4)−Si(2)−C(46)	109.1(4)	C(3)−Si(2)−C(56)	111.8(4)
C(4)−Si(2)−C(56)	109.5(4)	C(46)−Si(2)−C(56)	110.8(4)
Si(1)−O(1)−C(2)	129.3(5)	Si(1)−O(2)−C(5)	132.9(5)
O(1)−C(2)−C(3)	113.1(7)	C(2)−C(1)−C(76)	125.4(7)
Si(2)−C(3)−C(2)	117.5(5)	O(1)−C(2)−C(1)	119.7(7)
O(2)−C(5)−C(4)	114.6(7)	C(1)−C(2)−C(3)	127.2(7)
C(4)−C(5)−C(6)	126.3(8)	Si(2)−C(4)−C(5)	113.8(5)
C(5)−C(6)−C(36)	118.0(7)	O(2)−C(5)−C(6)	118.7(7)
Si(1)−C(16)−C(15)	121.5(6)	Si(1)−C(16)−C(11)	120.5(7)
Si(2)−C(46)−C(42)	122.8(6)	Si(2)−C(46)−C(41)	120.1(6)
Si(2)−C(56)−C(55)	122.2(6)	Si(2)−C(56)−C(51)	121.6(6)
Si(1)−C(86)−C(85)	121.8(6)	Si(1)−C(86)−C(81)	121.2(6)

The eight-membered ring of **9** is crown-shaped. Important bond distances and angles are given in Table 1. The Si−O and Si−C bond distances of the ring are normal and in the ranges (1.630−1.677 Å and 1.872−1.894 Å, respectively) observed in diverse cyclic silicon compounds containing Si−O and Si−C(sp^3) bonds in the ring.[5] The C(1)−C(2) and C(5)−C(6) bond distances are typical of C−C double bonds.[6]



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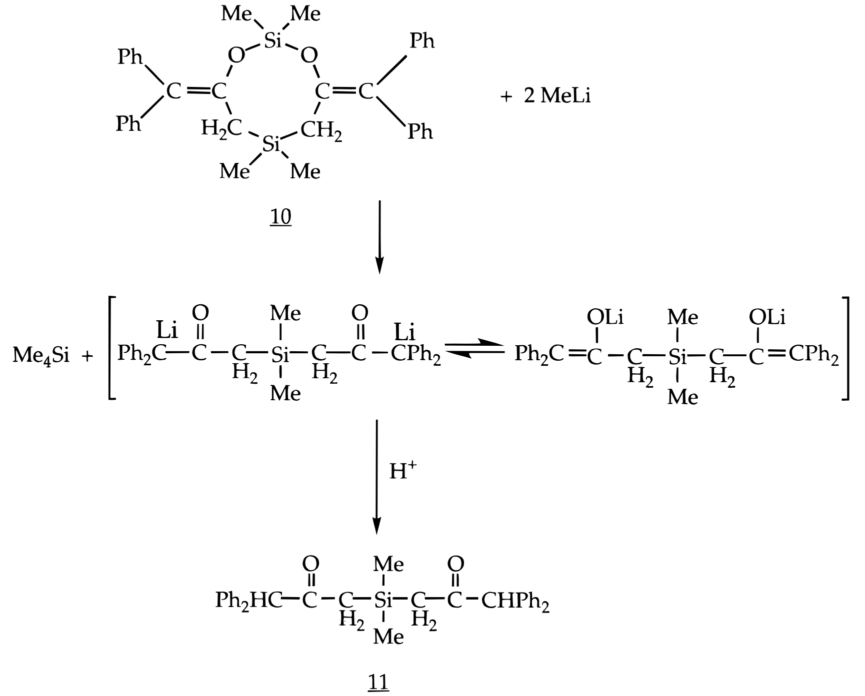
The reaction of the dimethylsilylene analog, **10**, with 2 equiv of methyllithium in diethyl ether at 0 °C gave, after aqueous work-up, the diketone **11** in 80% yield.

Scheme 2



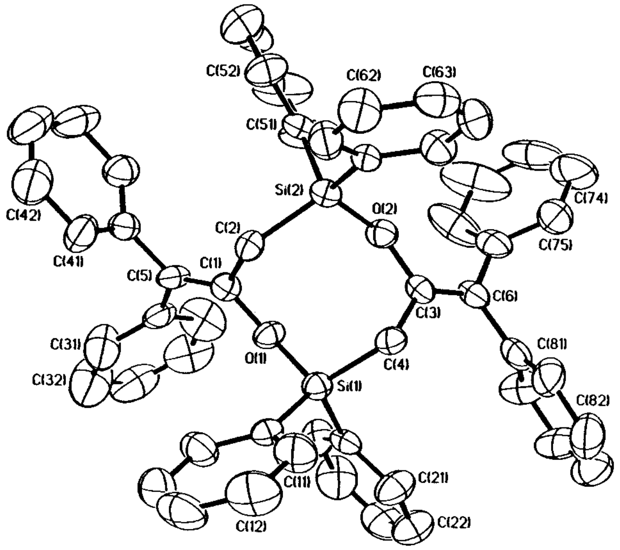


Figure 2. ORTEP plot of the structure of **8**, showing 35% probability ellipsoids.

Table 2. Selected Intramolecular Bond Distances (Å) and Angles (deg) for 8

Si(1)−O(1)	1.643(6)	Si(1)−C(4)	1.873(8)
Si(1)−C(16)	1.853(8)	Si(1)−C(26)	1.861(9)
Si(2)−O(2)	1.641(6)	Si(2)−C(2)	1.862(7)
Si(2)−C(56)	1.853(9)	Si(2)−C(66)	1.869(8)
O(1)−C(1)	1.388(10)	O(2)−C(3)	1.384(11)
C(1)−C(2)	1.510(12)	C(1)−C(5)	1.321(13)
C(3)−C(4)	1.507(11)	C(3)−C(6)	1.321(13)
O(1)−Si(1)−C(4)	112.2(3)	O(1)−Si(1)−C(16)	109.1(4)
C(4)−Si(1)−C(16)	109.5(4)	O(1)−Si(1)−C(26)	103.5(3)
C(4)−Si(1)−C(26)	109.5(3)	C(16)−Si(1)−C(26)	112.9(3)
O(2)−Si(2)−C(56)	113.4(3)	O(2)−Si(2)−C(56)	104.7(3)
C(2)−Si(2)−C(56)	107.4(3)	O(2)−Si(2)−C(66)	108.5(3)
C(2)−Si(2)−C(66)	109.6(3)	C(56)−Si(2)−C(66)	113.2(3)
Si(1)−O(1)−C(1)	129.0(5)	Si(2)−O(2)−C(3)	133.5(5)
O(1)−C(1)−C(2)	114.7(7)	O(1)−C(1)−C(5)	118.0(8)
C(2)−C(1)−C(5)	127.1(8)	Si(2)−C(2)−C(1)	115.1(5)
O(2)−C(3)−(4)	114.4(7)	O(2)−C(3)−C(6)	118.1(8)
C(4)−C(3)−C(6)	127.5(8)	Si(1)−C(4)−C(3)	113.5(6)
Si(1)−C(16)−C(11)	121.8(3)	Si(1)−C(16)−C(15)	118.2(3)
Si(1)−C(26)−C(21)	120.3(2)	Si(1)−C(26)−C(25)	119.7(2)
Si(2)−C(56)−C(51)	122.1(2)	Si(2)−C(56)−C(55)	117.7(2)
Si(2)−C(66)−C(61)	121.6(2)	Si(2)−C(66)−C(65)	118.4(2)

Its formation, as Scheme 2 shows, provides further (chemical) proof for the structure of **9**.

The other products of the 1,1-diphenylacetone-derived dianion/R_2 $SiCl_2$ reactions also contained nonequivalent silicon atoms (by ^{29}Si NMR spectroscopy) and had molecular weights (EI/MS and VPO) equivalent to those of eight-membered rings. The **6**/R_2SiCl_2 reaction, thus, appears to be a general process.

The results of the reaction of **6** with Ph_2SiF_2 were quite unexpected in view of the minor change at first sight in the organosilicon substrate: substitution of F for Cl as the leaving group. That the product of this reaction was not the expected **9** (on the basis of the Ph_2SiCl_2 reaction) was obvious from its ^{29}Si NMR spectrum, which showed only a single, sharp resonance at δ_{Si} −10.7. The melting point of this product was different from that of **9**, but its C,H analysis was essentially the same, as was its molecular weight (780 by EI/MS and 813 by VPO). The **6**/Ph_2SiF_2 product, thus, was an isomer of **9**. On the basis of this evidence, it was assigned the structure **8**, i.e., the one originally expected, the silicon analog of the (η^5-$C_5H_5)_2ZrCl_2$-derived product. The molecular structure of **8** was confirmed by an X-ray diffraction study (Figure 2). The eight-membered ring is crown-shaped and the Si−O and Si−C bonds are normal (Table 2), within the ranges for tetrahedral silicon.[5] Thus, the **6**/Ph_2SiF_2 reaction gives a product in which each silicon atom is bonded to one oxygen and one methylene carbon atom. Dianion **6** reacted with Et_2SiF_2 to give a product analogous to **8**

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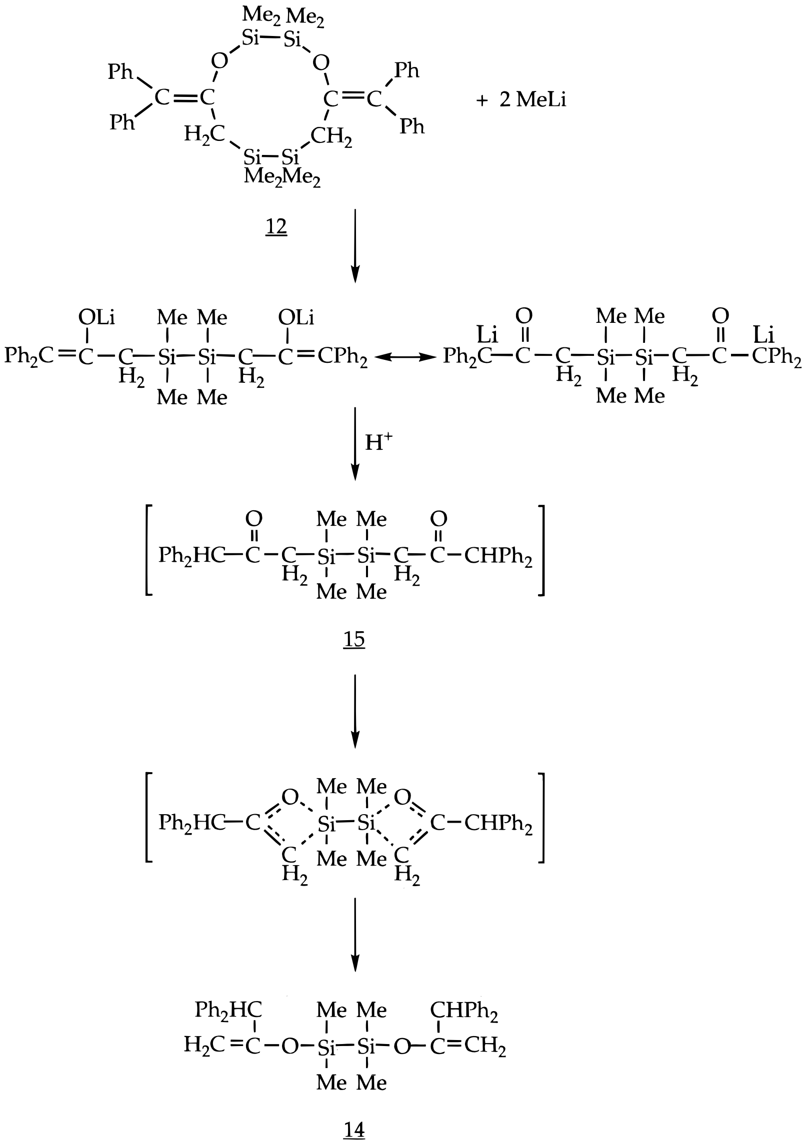
(5) Lukevics, E.; Pudova, O.; Strukovich, R. *Molecular Structure of Organosilicon Compounds*; Ellis Horwood: Chichester, 1989; Chapter 14.

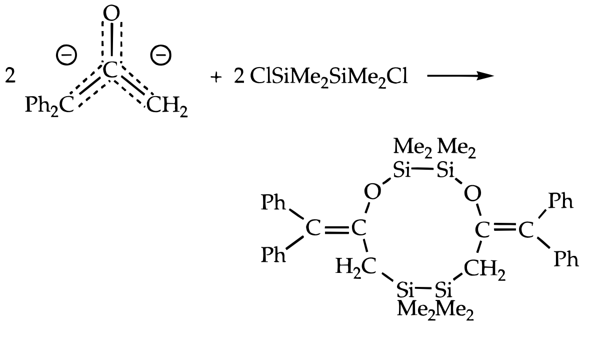
(6) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 519.

Scheme 3



in structure, which suggests that the difference in reactivity between R_2SiCl_2 and R_2SiF_2 toward **6** is general.

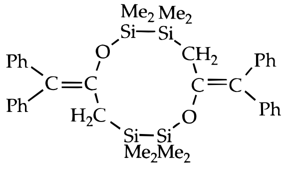
The 1,1-diphenylacetone-derived anion reacted with 1,2-dichlorotetramethyldisilane to give a crystalline product containing a 10-membered ring, **12** (eq 1). The



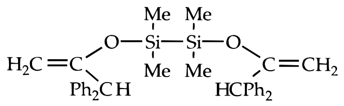
(1)

12

EI/MS showed the molecular ion ($M^+ = 648$), and the solution molecular weight (672) showed the dimer to be present. The ^{29}Si NMR spectrum, which showed two resonances at δ_{Si} −14.7 and 10.0, provided no structural information since the ^{29}Si NMR spectrum of the other possible product, **13**, should also exhibit two resonances.



13



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Here, reaction of the product with 2 molar equiv of methyllithium provided chemical proof of the structure. The product of this reaction, after hydrolytic workup, was **14**. The formation of **14** from **12** can be rationalized as shown in Scheme 3. The intermediate diketone **15** is equivalent to the final product **11** of the **6**/2MeLi reaction. In the case of **12**, however, intermediate **15** undergoes a Brook rearrangement,[7] as shown in Scheme 3, under rather mild conditions, facilitated, perhaps, by the fact that a disilane is involved. The structure of **12** was confirmed by an X-ray diffraction study (Figure 3).

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[7] (a) Brook, A. G.; Macrae, D. M.; Limburg, W. W. *J. Am. Chem. Soc.* **1967**, *89*, 5493. (b) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

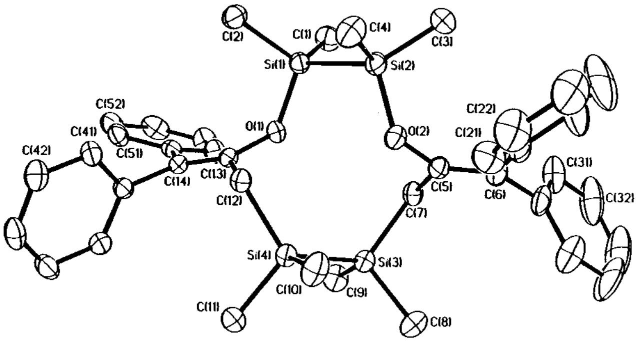
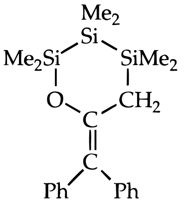


Figure 3. ORTEP plot of the structure of **13**, showing 35% probability ellipsoids.

Table 3 gives important bond distances and angles. The Si−Si distances are typical of Si−Si single bonds.[5] The Si−O and Si−C bond distances are normal, within the ranges for tetrahedral silicon.

In the reactions of dianion **6** with Ph_2SiCl_2 and $ClSiMe_2SiMe_2Cl$, the alternatives to the observed products were the strained silaoxetane **7** and the five-membered disilaoxacyclopentane. The case of 1,3-dichlorohexamethyltrisilane, thus, was of interest since its reaction with **6** could result in unstrained 6- or 12-membered ring products. Treatment of $Cl(SiMe_2)_3Cl$ with **6** gave a crystalline product whose measured molecular weight (EI/MS and VPO) was equivalent to that of the monomer **16**. Its ^1H, ^{13}C, and ^{29}Si NMR spectra were in agreement with the structure shown.



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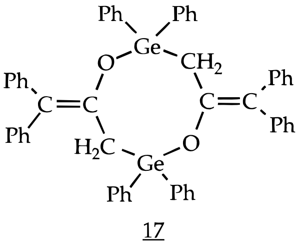
These studies were extended to the diphenyldihalogermanes, since it was of interest to see whether their reactivity toward the 1,1-diphenylacetone-derived dianion **6** would be the same as that observed with the diphenyldihalosilanes. The reaction of dianion **6** with Ph_2GeCl_2 was strikingly different from that of Ph_2SiCl_2. It gave the same product as was obtained in the reaction of **6** with Ph_2GeF_2, the eight-membered ring compound **17**. The structure of **17** was determined in an X-ray diffraction study (Figure 4). The eight-membered ring is crown-shaped, as the side view (Figure 5) shows. Table 4 lists important bond distances and angles. The Ge−O and Ge−C bond distances are normal and in the ranges (1.73−1.79 Å[8] and 1.90−1.98 Å, respectively[9]) observed for tetrahedral germanium.



17

Table 3. Selected Intramolecular Bond Distances (Å) and Angles (deg) for 13

Si(1)−Si(2)	2.373(2)	Si(1)−O(1)	1.676(3)
Si(2)−O(2)	1.664(3)	Si(3)−Si(4)	2.342(2)
Si(3)−C(7)	1.886(4)	Si(4)−C(12)	1.897(4)
O(1)−C(13)	1.381(5)	O(2)−C(5)	1.388(5)
C(5)−C(6)	1.338(5)	C(5)−C(7)	1.491(5)
C(12)−C(13)	1.491(5)	C(13)−C(14)	1.347(5)
Si(2)−Si(1)−O(1)	110.2(1)	O(1)−C(13)−C(12)	113.1(3)
Si(1)−Si(2)−O(2)	109.0(1)	C(12)−C(13)−C(14)	125.8(4)
Si(4)−Si(3)−C(7)	117.1(1)	Si(3)−Si(4)−C(12)	117.9(1)
Si(1)−O(1)−C(13)	122.0(2)	Si(2)−O(2)−C(5)	124.2(2)
O(2)−C(5)−C(6)	120.1(3)	O(2)−C(5)−C(7)	112.4(3)
C(6)−C(5)−C(7)	127.4(4)	Si(4)−C(12)−C(13)	115.0(3)
Si(3)−C(7)−C(5)	113.6(3)	O(1)−C(13)−C(14)	120.9(3)

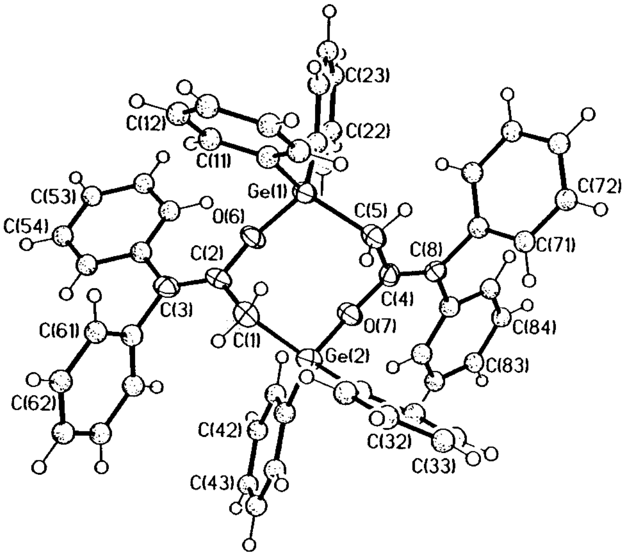


Figure 4. ORTEP plot of the structure of **17**, showing 35% probability ellipsoids.

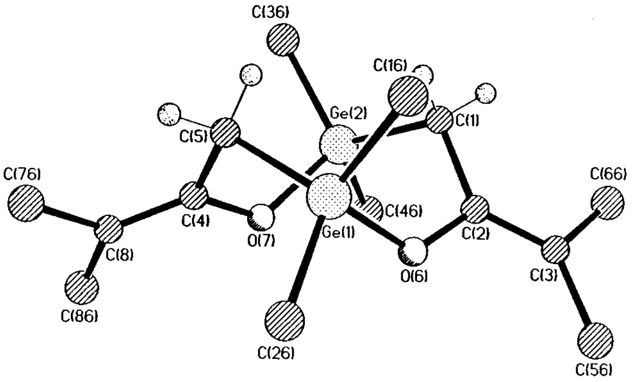


Figure 5. Side view of the crown-shaped eight-membered ring of **17**.

When considering the results of these experiments, two questions arise: Why are the products formed in the reactions of dianion **6** with R_2SiCl_2 and R_2SiF_2 different and why are they the same in reactions with Ph_2GeCl_2 and Ph_2GeF_2? If one is to consider the mechanisms of the reactions of the 1,1-diphenylacetone-derived dianion **6** with organosilicon halides another question must be answered: in the action of **6** on an R_2SiX_2 compound, which is formed first, the Si−C or the Si−O bond?

An answer to the first question may be found in the studies of Sommer and co-workers on the stereochem-

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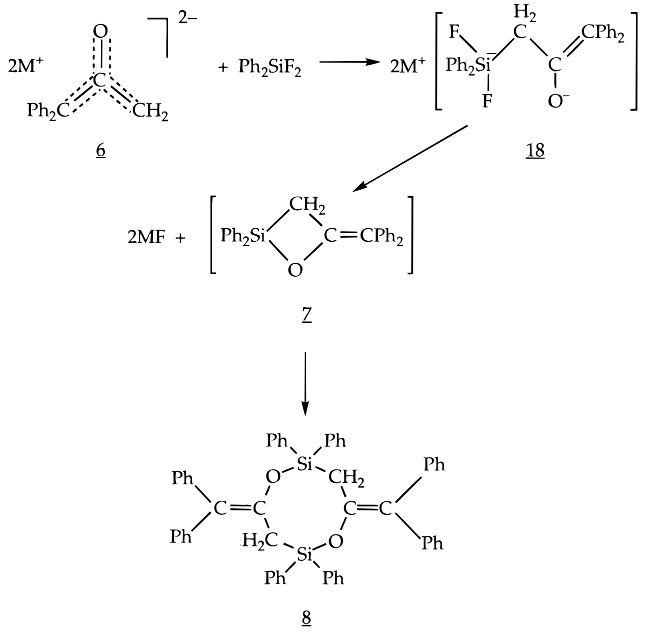
(8) Ross, L.; Dräger, M. *Z. Naturforsch.* **1984**, *39b*, 868.

(9) Dräger, M.; Ross, L.; Simon, D. *Rev. Silicon, Germanium, Tin Lead Compd.* **1983**, *7*, 299.

Table 4. Selected Intramolecular Bond Distances (Å) and Angles (deg) for 17

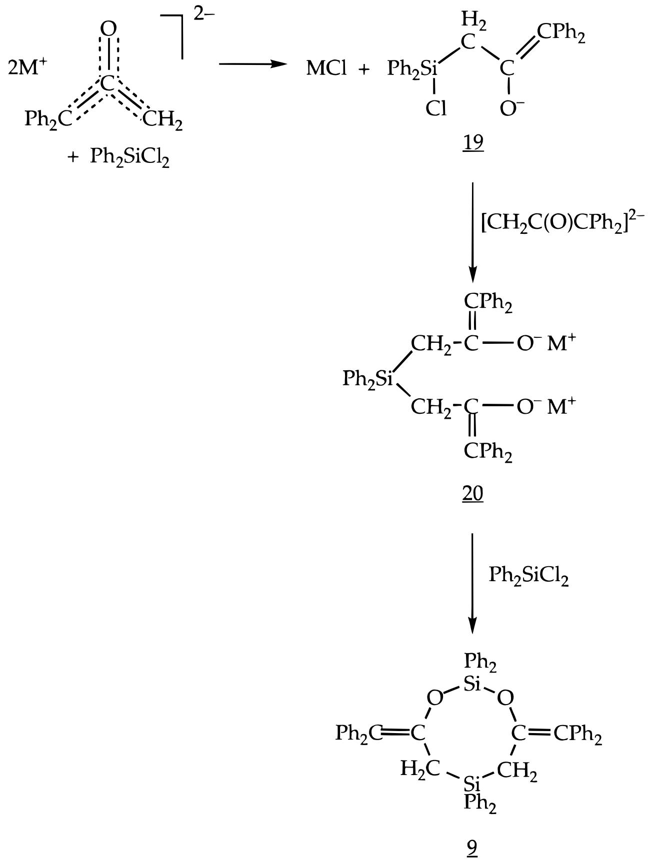
Ge(1)−O(6)	1.778(9)	Ge(2)−O(7)	1.791(10)
Ge(1)−C(5)	1.962(13)	Ge(2)−C(1)	1.955(13)
C(1)−C(2)	1.524(20)	C(4)−C(5)	1.484(20)
O(6)−C(2)	1.368(19)	O(7)−C(4)	1.363(18)
C(2)−C(3)	1.341(23)	C(4)−C(8)	1.329(22)
C(5)−Ge(1)−O(6)	111.4(5)	Ge(1)−C(5)−C(4)	111.7(10)
C(5)−C(4)−O(7)	114.6(12)	Ge(2)−O(7)−C(4)	126.4(8)
C(1)−Ge(2)−O(7)	109.5(5)	Ge(2)−C(1)−C(2)	111.0(9)
C(1)−C(2)−O(6)	113.1(13)	Ge(1)−O(6)−C(2)	129.9(9)
C(1)−C(2)−C(3)	125.6(14)	C(3)−C(2)−O(6)	121.3(14)
C(5)−C(4)−C(8)	125.6(14)	O(7)−C(4)−C(8)	119.8(13)
C(56)−C(3)−C(66)	125.8(13)	C(76)−C(8)−C(86)	114.4(11)

Scheme 4



istry of reactions of organosilicon halides over 30 years ago[10] and later work of Corriu and co-workers.[11] For instance, it was found by Sommer et al. that the reaction of an optically active chlorosilane with ethyllithium in diethyl ether proceeded with inversion of configuration at silicon, i.e., *via* an S_N2 process.[12] On the other hand, the analogous optically active fluorosilane reacted with ethyllithium with retention of configuration at silicon. This was explained in terms of an initial, rapid equilibrium formation of an anionic, pentacovalent silicon intermediate, Li[$R^1R^2R^3$EtSiF], *via* front-side attack of the nucleophile. Thus, assuming that the initial nucleophilic attack by $[Ph_2C(O)CH_2]^{2-}$ at the “hard” silicon occurs *via* the CH_2 terminus to form an Si−C bond (an assumption which was shown to be correct, *vide infra*), the reaction with Ph_2SiF_2 is similar to that of EtLi with a fluorosilane and may be expected to proceed *via* a pentacovalent intermediate, **18**, as shown in Scheme 4. Such anionic intermediates, Corriu and co-workers have shown,[13] have enhanced reactivity. Apparently, the leaving ability of the fluoride substituent in an anionic fluorosilicate is greater than that of a fluorine in a neutral fluorosilane because the Si−F bond is lengthened and the negative charge on the fluorine atom is increased in the anionic fluorosilicate.[14] In the case of intermediate **18**, intramolecular ring closure *via* displacement of F^- by O^- to give the 1,2-silaoxetane, **7**, is facilitated. The latter then undergoes ring-opening cyclodimerization to give the observed product, **8**.

Scheme 5



In the case of the dianion **6**/Ph_2SiCl_2 reaction, we suggest that a pentacovalent intermediate is not formed and, thus, there is not enhanced reactivity of the second Si−Cl bond after the first has reacted with dianion **6**. The result is that intermediate **19** (Scheme 5) is sufficiently long-lived to undergo reaction with another equivalent of **6**, as shown in Scheme 5. Intermediate **20** thus formed could react with Ph_2SiCl_2 to give the final product, **9**. Intramolecular ring closure of **19** to give silaoxetane **7** is excluded since this would lead to formation of the other isomer, **8**.

Germanium chlorides more readily form hypervalent species on reaction with negatively charged nucleophiles than do silicon chlorides,[15] so the mechanism in Scheme 4 for Ph_2SiF_2 is a likely one for Ph_2GeCl_2 as well as for Ph_2GeF_2. Thus, it is understandable that the same product, **17**, is formed in the reactions of dianion **6** with either of these halides. The conversion of a 1,2-germaoxetane to the eight-membered ring dimer has precedence. For instance, Castel and Satgé reported that insertion of Ph_2Ge into an oxirane ring led to a 1,2-

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[10] Sommer, L. H. *Steroechemistry, Mechanism and Silicon*; McGraw-Hill: New York, 1965; Chapter 4.

[11] (a) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231. (b) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E *Top. Stereochem.* **1984**, *15*, 43.

[12] Sommer, L. H.; Rodewald, P. G.; Parker, G. A. *Tetrahedron Lett.* **1962**, 821.

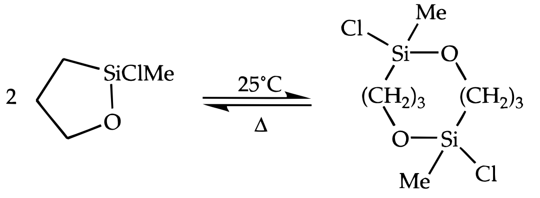
[13] Bréfort, J.-L.; Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Wong Chin Man, W.W. C. *Organometallics* **1990**, *9*, 2080.

[14] Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 7197.

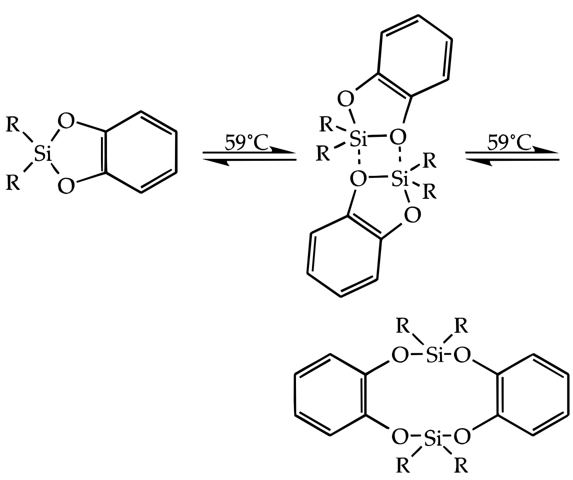
[15] (a) Holmes, R. R.; Day, R. O.; Sau, A. C.; Holmes, J. M. *Inorg. Chem.* **1986**, *25*, 600. (b) Holmes, R. R.; Day, R. O.; Sau, A. C.; Poutane, C. A.; Holmes, J. M. *Inorg. Chem.* **1986**, *25*, 607 and references cited therein.

germaoxetane which dimerized to give a digermadioxacane.[16]

Some comments concerning the proposed 1,2-silaoxetane intermediate **7** in Scheme 4 are in order. 1,2-Silaoxetanes are known compounds but are rather rare. Some more sterically hindered members of this class have been isolated by reaction of a silene with a ketone,[17] but none of them underwent ring-opening cyclodimerization to an eight-membered ring product. Such a process has, however, been reported for a 1,2-silaoxacyclopentane, which gave a 10-membered ring product[18] (eq 2), and for 3,4-benzo-1-sila-2,5-dioxacyclopentene[19] (eq 3).



(2)



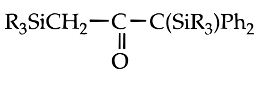
(3)

If a 1,2-silaoxetane intermediate indeed is involved in the formation of the eight-membered ring product **8**, then this process is not reversible. In contrast to the (η^5-C_5H_5)$_2$Zr analog of **8** (Scheme 1), the molecular weight of **8** in $CHCl_3$ solution, as determined by VPO, was that of the eight-membered ring compound, not of the 1,2-silaoxetane. The same was found to be the case for the Ph_2GeX_2/**6** product, **17**. Presumably, the transannular interactions that lead from **4** to the coordination dimer **5** (Scheme 1) do not occur in the organosilicon and -germanium analogs.

However, more energetic conditions do cause reversion of the eight-membered rings, **8** and **17**, to the respective sila- and germaoxetanes. This was shown in their 70 eV electron impact mass spectra. The mass spectra of **8** and its diethylsilylene analog showed ions corresponding to M^+ and 0.5 M^+. This reversion to the four-membered rings was especially pronounced in the case of **17**, whose mass spectrum showed ions corresponding to the molecular ion $[\mathbf{17}]^+$ (30), 0.5 M^+ (100), and ions resulting from the fragmentation of the latter $[Ph_2GeO]^+$ (66) and $[Ph_2C{=}C{=}CH_2]^+$ (20). A known germaoxetane has been reported to fragment in the mass spectrometer in both possible ways.[20]

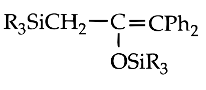
The discussion above is predicated on the assumption that the first bond formed when the 1,1-diphenylacetone-derived dianion **6** reacts with a halosilane is an Si−C bond involving the CH_2 terminus. Further studies were devoted to exploring this question. An answer should be more easily obtained using monochlorosilanes rather than dichlorosilanes as the electrophilic reactants.

In principle, the 1,1-diphenylacetone dianion could react with 2 molar equiv of a triorganochlorosilane, R_3SiCl, to give one, two, three, or all four of the following products: **21**, **22**, **23**, and, least likely, **24**.



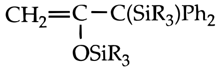
$R_3SiCH_2-\underset{\underset{O}{\|}}{C}-C(SiR_3)Ph_2$

21



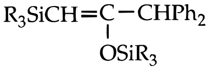
$R_3SiCH_2-\underset{\underset{OSiR_3}{|}}{C}=CPh_2$

22



$CH_2=\underset{\underset{OSiR_3}{|}}{C}-C(SiR_3)Ph_2$

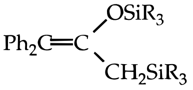
23



$R_3SiCH=\underset{\underset{OSiR_3}{|}}{C}-CHPh_2$

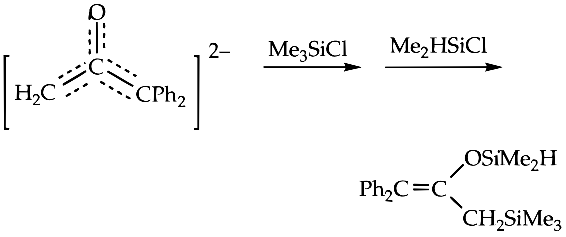
24

In practice, when 2 molar equiv of a monochlorosilane was added to a THF solution of the dianion salt, [Li,K] $[CH_2C(O)CPh_2]$, a single product, **25**, a 2-siloxyallylsilane, was obtained.



25 a, $R_3Si = Me_3Si$ (71%)
b, $R_3Si = Me_2HSi$ (82%)
c, $R_3Si = Ph_2MeSi$ (56%)

(2-Siloxyallylsilanes have demonstrated synthetic utility, reacting with electrophiles in the presence of a Lewis acid to give 1,3-disubstituted acetones.[21]) Treatment of the 1,1-diphenylacetone dianion in succession with 1 molar equiv each of two different monochlorosilanes gave, as the major product, the 2-siloxyallylsilane that contained two different silyl substituents. The silyl group of the chlorosilane that was added first to the dianion solution was attached to the CH_2 terminus of the $[CH_2C(O)CPh_2]^{2-}$ anion, and the silyl group of the chlorosilane that was added second was bonded to the oxygen terminus (eq 4).



(4)

This regioselectivity is general, as the results collected in Table 5 show. A minor byproduct (<20% yield) in these reactions was the 2-siloxyallylsilane, in which both silyl groups were derived from the chlorosilane that had been added first ($Ph_2C{=}C(CH_2SiMe_3)(OSiMe_3)$) in the case of

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(16) Castel, A.; Rivière, P.; Satgé, J.; Cazes, A. *Compt. Rend. Acad. Sci. Paris* **1978**, *287* (C), 205. See also: Satgé, J. *Pure Appl. Chem.* **1984**, *56*, 137.

(17) (a) Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246. (b) Wiberg, N.; Preiner, G.; Schurz, K.; Fischer, G. *Z. Naturforsch.* **1988**, *43b*, 1468. (c) Toltl, N. P.; Leigh, W. J. *Organometallics* **1996**, *15*, 2554.

(18) Rossmy, G.; Koerner, G. *Makromol. Chem.* **1964**, *73*, 85.

(19) Cragg, R. H.; Lane, R. D. *J. Organomet. Chem.* **1984**, *270*, 25.

(20) Lazraq, M.; Couret, C.; Escudié, J.; Satgé, J.; Dräger, M. *Organometallics* **1991**, *10*, 1771.

(21) Hosomi, A.; Hayashida, H.; Tominaga, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3254.

Table 5. Reactions of $[CH_2C(O)CPh_2]^{2-}$ with 1 Molar Equiv Each of Two Different Monochlorosilanes in Succession

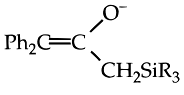
experi-ment	first chlorosilane added	second chlorosilane added	product[a]	% yield
1	Me_3SiCl	Me_2HSiCl	Ph2C=C(CH_2SiMe_3)($OSiMe_2H$)	72
2	Me_3SiCl	$MePh_2SiCl$	$Ph_2C{=}C(CH_2SiMe_3)$(OSiMePh2)	71
3	Me_3SiCl	t-$BuMe_2SiCl$	$Ph_2C{=}C(CH_2SiMe_3)(OSiMe_2$-t-Bu)	82
4	Me_2HSiCl	t-$BuMe_2SiCl$	$Ph_2C{=}C(CH_2SiMe_2H)(OSiMe_2$-t-Bu)	72
5	t-$BuMe_2SiCl$	Me_2HSiCl	$Ph_2C{=}C(CH_2SiMe_2$-t-Bu)($OSiMe_2H$)	22[b]

[a] Byproduct in ~20% yield or less was $Ph_2C{=}C(CH_2SiR_3)(OSiR_3)$ derived solely from the first-added chlorosilane, except for experiment 5, in which the major product was $Ph_2C{=}C(CH_2SiMe_2H)(OSiMe_2H)$. [b] $Ph_2C{=}C(CH_2SiMe_2H)(OSiMe_2H)$, 61% yield.

the reaction of eq 4). Such a byproduct is not unexpected since the first chlorosilane was added quite slowly to the dianion solution and the second chlorosilane was added 10 min after the completion of the addition of the first. Obviously, the dianion is significantly more reactive than the monoanion formed in the first chlorosilane addition. If that were not so, the yields of the 2-siloxyallylsilanes containing two different silyl groups would be quite low or even zero.

The reaction in which t-$BuMe_2SiCl$ was added to the dianion solution first, followed by addition of Me_2HSiCl, requires special comment. When the procedure mentioned above, i.e., a 10 min interval between the completion of the addition of the first chlorosilane and the addition of the second chlorosilane, was followed, the major product (61%) was $Ph_2C{=}C(CH_2SiMe_2H)(OSiMe_2H)$ and the expected $Ph_2C{=}C(CH_2SiMe_2$-t-Bu)($OSiMe_2H$) was formed in only 22% yield. Clearly, the first silylation of the dianion with the bulky t-$BuMe_2SiCl$ was quite slow and was largely incomplete when the Me_2HSiCl was added after the usual 10 min interval. An attempt was made to deal with this problem by extending the time between addition of the first and the second chlorosilane to 3 h and 12 h, respectively. This did not help much. The yield of $Ph_2C{=}C(CH_2SiMe_2$-t-Bu)($OSiMe_2H$) was increased to 40 and 41% yield, respectively, in these experiments, and in place of $Ph_2C{=}C(CH_2SiMe_2H)(OSiMe_2H)$ the second major product was $Ph_2C{=}C(CH_3)(OSiMe_2H)$ formed in 30% yield (GC) in each experiment. This change may be rationalized by the assumption that the $[CH_2C(O)CPh_2]^{2-}$ anion is not stable with time in THF at room temperature, deprotonating the solvent to form the enolate anion, $Ph_2C{=}C(CH_3)O^-$, which then is one of the species present when Me_2HSiCl is added. Deprotonation of THF results in the formation of $CH_2{=}CHOLi$,[22] which will divert some of the added Me_2HSiCl so that the yield of the diphenylacetone-derived products will be low.

The key observation made in the case of the reactions listed in Table 1, i.e., that the silyl group of the chlorosilane that was added first became bonded to the CH_2 terminus of the 1,1-diphenylacetone dianion, could not by itself be taken as proof that the initial reaction of the $[CH_2C(O)CPh_2]^{2-}$ anion occurs at the CH_2 terminus, giving the monoanion **26**. There is an alternate route to the products in Table 1 in which the initial attack results in formation of a Si−O bond giving the monoanion **27**, which subsequently undergoes 1,3 O → C silyl migration of the type reported by Corey and Rücker[23] giving **7**, with which the second chlorosilane then reacts. The reaction times reported by Corey and Rücker in their study of the 4-*tert*-butylcyclohexanone-derived enol ether anions of type **28** were long (5−24 h) compared to our 10 min interval before the second chlorosilane was added, but such a silyl migration cannot be discounted in our reactions.



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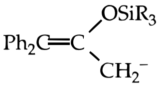

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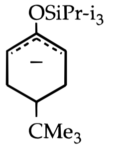
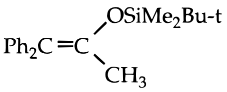


28

This dilemma was resolved, however, when we undertook a study of the deprotonation of silyl enol ethers, such as **29**, that contain bulky silyl groups.[24] It was found that the action of i-Pr_2NLi (LDA) in THF on such silyl enol ethers gives an unstable intermediate which rapidly eliminates t-$BuMe_2SiOLi$. The 1,1-diphenylallene which is formed undergoes lithiation to $Ph_2C{=}C{=}CLi_2$, and the final product, after a monochlorosilane has been added, is a 1,1-diphenyl-3,3-bis(silyl)allene. The reaction course is shown in Scheme 6. When **29** and LDA are allowed to react in a 1:1 molar ratio, the yield of $Ph_2C{=}C{=}C(SiMe_3)_2$ is low; very good yields are obtained with a stoichiometry of 3.3/1 LDA **29**.



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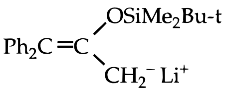

30

The product of the lithiation of the silyl enol ether can only be **30**. If in the reaction of the 1,1-diphenylacetone dianion with t-$BuMe_2SiCl$ the initial attack is at the oxygen terminus, giving **30**, then rapid elimination of t-$BuMe_2SiO^-$, as shown in Scheme 1, should have occurred. No $Ph_2C{=}C(CH_2SiMe_2$-t-Bu)($OSiMe_2H$) should have been formed, and $Ph_2C{=}C{=}C(SiMe_2H)_2$ should have been formed in a substantial yield. However, $Ph_2C{=}C{=}C(SiMe_2H)_2$ was formed in, at the most, a 2% yield (by GC) when Me_2HSiCl was added as the second chlorosilane. This leads us to conclude that the initial silylation product of the $[CH_2C(O)CPh_2]^{2-}$ anion is the stable anion **26**, which then reacts with the second added monochlorosilane at the oxygen terminus. It may be that the minor amount of allene formed is the result of a Peterson reaction[25] of anion **26**, i.e., elimination of R_3SiO^- (R = t-$BuMe_2Si$) to form $Ph_2C{=}C{=}CH_2$, which then is metalated to $Ph_2C{=}C{=}CLi_2$.

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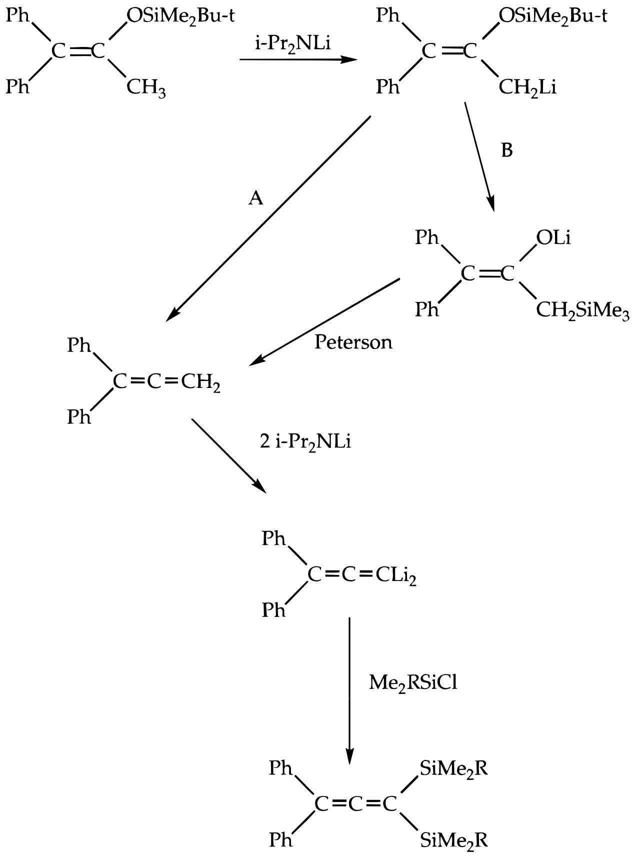
[22] Bates, R. B.; Kroposki, I. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560.

[23] Corey, E. J.; Rücker, C. *Tetrahedron Lett.* **1984**, *25*, 4345.

[24] Seyferth, D.; Langer, P.; Döring, M. *Organometallics* **1995**, *14*, 4457.

[25] Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780.

Scheme 6



This conclusion merits some comment in view of the fact that silylation of ketone monoanions, i.e., alkali-metal enolates, takes place at the oxygen atom giving silyl enol ethers. In the case of the acetone dianions, **1**, the three carbon atoms form a highly nucleophilic allyl anion system, more nucleophilic than the carbon atom in an enolate monoanion, in which much of the negative charge resides at the oxygen atom.

Experimental Section

General Comments. All reactions were performed under an inert atmosphere using standard Schlenk techniques. All solvents were distilled under nitrogen from the appropriate drying agents. Chlorosilanes were purchased from Hüls, Inc., and distilled from magnesium chips before use. *n*-Butyllithium in hexane was purchased from Aldrich and titrated for RLi content by the Gilman double-titration method.[26] Methyllithium in ether was purchased from Johnson and Matthey as a complex with lithium bromide. Potassium hydride was purified by washing with a THF solution of lithium aluminum hydride (approximately 4 mmol of lithium aluminum hydride in 10 mL of THF).[27] 1,1-Diphenylacetone was purchased from Aldrich and used without further purification.

Gas chromatography (GC) analyses were performed on a Hewlett-Packard 5890A gas chromatograph equipped with a 6 ft, 0.25 in. column packed with 10% SE-30 silicone rubber gum on Chromosorb P.

NMR spectra were obtained on either a Bruker AC-250 or a Varian XL-300 NMR spectrometer, and chemical shifts are listed in parts per million downfield from tetramethylsilane. ^{13}C NMR spectra, both proton-coupled and -decoupled, were obtained at 75.4 MHz in $CDCl_3$. ^{29}Si NMR spectra were recorded at 59.59 MHz in $CDCl_3$, using tetramethylsilane as the external standard at 0.00 ppm.

Electron impact mass spectra (MS) were obtained using a Finnigan-3200 mass spectrometer operating at 70 eV. Infrared spectra (KBr) were obtained using a Perkin-Elmer 1600 Fourier Transform infrared spectrophotometer. Melting points of analytically pure crystalline and solid products were determined in air, using a Büchi melting point apparatus. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Preparation of 1,1-Diphenylacetone Dianion $[Ph_2CC(O)CH_2]^{2-}$, 6. 1,1-Diphenylacetone dianion was prepared according to a literature procedure.[4a] A 100 mL round-bottomed Schlenk flask equipped with a magnetic stir bar and a rubber septum was charged with 0.5 g (12.5 mmol) of KH and 50 mL of THF. A solution of 1,1-diphenylacetone (2.62 g, 12.5 mmol) in 10 mL of THF was added slowly to the flask by cannula. Hydrogen gas evolution was observed. After the reaction mixture was stirred at room temperature for 15−20 min, a clear orange solution was obtained. To this was added, at 0 °C, 1 molar equiv of *n*-BuLi (4.93 mL of a 2.53 M solution). The resulting red mixture was stirred at 0 °C under argon for 5−7 min, at which point it was ready for further reaction.

Reactions of Dianion 6 with Dihalosilanes. 1. Preparation of 1,1,5,5-Tetramethyl-3,7-bis(diphenylmethylene)-1,5-disila-2,8-dioxacyclooctane, 10. A 250 mL round-bottomed Schlenk flask equipped with a magnetic stir bar and a rubber septum was charged with 1.61 g (12.5 mmol) of Me_2SiCl_2 and 100 mL of THF. To this solution at 0 °C was added slowly by cannula 12.5 mmol of 1,1-diphenylacetone dianion **6** in 50 mL of THF. The resulting mixture was stirred at room temperature for 5 h. A yellow suspension was obtained. All volatiles were removed by evaporation under reduced pressure, and the resulting residue was extracted with hexane (3 × 100 mL). Filtration under nitrogen through Celite gave a pale yellow filtrate. The filtrate was concentrated to about 30 mL under reduced pressure and stored at −23 °C for 2 days. Compound **10** was obtained as colorless, air-stable needles, 2.3 g (69%), after recrystallization from hexane, mp 145−147 °C.

^1H NMR (300 MHz, $CDCl_3$): δ −0.04 (s, 6 H, $CSi(CH_3)_2$), 0.14 (s, 6 H, $OSi(CH_3)_2$), 2.01 (s, 4 H, CH_2), 7.06−7.32 (m, 20 H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C −2.7 (q, J = 118.8 Hz, $CSi(CH_3)_2$), −2.3 (q, J = 119.7 Hz, $OSi(CH_3)_2$), 24.7 (t, J = 121.1 Hz, $\mathit{CH_2}Si(CH_3)_2$), 120.5 (s, $CH_2C{=}\mathit{C}Ph_2$), 125.3−146.2 (m, Ph), 146.9 (t, ^2J = 5.8 Hz, $CH_2\mathit{C}{=}CPh_2$). ^{29}Si NMR (59.59 MHz, $CDCl_3$): δ_{Si} −6.2 ($CSiMe_2$), 3.4 ($OSiMe_2$). MS (EI) *m/z* (fragment, relative intensity): 532 (M^+, 53), 503 ($M^+ - 2CH_3$, 2), 365 ($M^+ - CPh_2$, 11), 340 ($M^+ - Ph_2C{=}CCH_2$, 21), 282 ($M^+ - Ph_2C{=}CCH_2SiMe_2$, 6), 210 (18), 192 ($Ph_2C{=}CCH_2^+$, 100), 182 (96), 166 ($CPh_2$, 90), 152 (57), 77 (Ph, 83). IR (KBr, cm^{-1}): 2977 (s), 2932 (w), 2864 (s), 1580 (m), 1444 (m), 1382 (m), 1350 (m), 1123 (s), 1077 (s, Si−O), 1005 (w), 840 (w), 833 (w), 702 (m). Anal. Calcd for $C_{34}H_{36}Si_2O_2$: C, 76.64; H, 6.81. Found: C, 76.60; H, 7.03. Mol wt (VPO, $CHCl_3$): calcd for $C_{34}H_{36}Si_2O_2$ 532; found 545.

2. Preparation of 1,1,5,5-Tetraphenyl-3,7-bis(diphenylmethylene)-1,5-disila-2,8-dioxacyclooctane, 9. A THF solution containing 12.5 mmol of dianion **6** was added dropwise to Ph_2SiCl_2 (3.16 g, 12.5 mmol) in 100 mL of THF at 0 °C. During the addition, the red color of the dianion was discharged slowly. Upon completion of the dianion addition, the resulting mixture was stirred at room temperature overnight to give a yellow suspension. Workup as in 1 gave a colorless, air-stable solid, 2.0 g (40%), after recrystallization from dichloromethane and hexane at −23 °C for 1 week, mp 189−191 °C. Single crystals of X-ray quality were obtained by dissolving **9** in methylene chloride and allowing the solution to evaporate slowly.

^1H NMR (300 MHz, $CDCl_3$): δ 2.62 (s, 4 H, CH_2), 6.61−7.42 (m, 40 H, Ph). ^{13}C NMR (75.4MHz, $CDCl_3$): δ_C 22.8 (t, J

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= 122.0 Hz, CH$_2$SiPh$_2$), 122.5 (s, CH$_2$C=*C*Ph$_2$), 125.7−141.2 (m, Ph), 145.4 (t, ^2J = 5.8 Hz, CH$_2$*C*=CPh$_2$). ^{29}Si NMR (59.59 MHz, CDCl$_3$): δ_{Si} −36.6 (CSi), −9.4 (OSi). MS (EI) *m*/*z* (fragment, relative intensity): 780 (M$^+$, 18), 588 (M$^+$ − Ph$_2$C=CCH$_2$, 17), 493 (14), 397 (16), 319 (28), 259(15), 216 (23), 192 (Ph$_2$C=CCH$_2$$^+$, 100), 177 (5), 115 (4). IR (KBr, cm^{-1}): 3051 (w), 3026 (s), 2898 (w), 1643 (m), 1619 (m), 1598 (w), 1492 (w), 1426 (s), 13954 (w), 1218 (s), 1187 (w), 1146 (w), 1111 (s), 1077 (s, Si−O), 1070 (w), 1004 (s), 962 (w), 853 (w), 768 (m), 723 (w). Anal. Calcd for C$_{54}$H$_{44}$Si$_2$O$_2$: C, 83.03; H, 5.68. Found: C, 82.72; H, 5.76. Mol wt (VPO, CHCl$_3$): calcd for C$_{54}$H$_{44}$Si$_2$O$_2$ 780; found 830.

3. Preparation of 1,1,5,5-Tetraethyl-3,7-bis(diphenylmethylene)-1,5-disila-2,8-dioxacyclooctane. A THF solution containing 12.5 mmol of dianion **6** was added dropwise to Et$_2$SiCl$_2$ (1.96 g, 12.5 mmol) in 100 mL of THF at 0 °C. The resulting mixture was stirred at room temperature for 5 h. A yellow suspension was obtained. Workup as in 1 gave colorless, air-stable crystals, 2.1 g (56%), after recrystallization twice from hexane at −23 °C, mp 110−112 °C.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.43 (q, 4 H, *J* = 7.8 Hz, CSi*CH*$_2$CH$_3$), 0.57 (q, 4 H, *J* = 7.6 Hz, OSi*CH*$_2$CH$_3$), 0.68 (t, 6 H, *J* = 7.8 Hz, CSiCH$_2$*CH*$_3$), 0.79 (t, 6 H, *J* = 7.6 Hz, OSiCH$_2$*CH*$_3$), 2.09 (s, 4 H, CH$_2$), 7.06−7.33 (m, 20 H, Ph). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ_{C} 3.9 (m, Si*CH*$_2$CH$_3$), 4.9 (m, Si*CH*$_2$-CH$_3$), 5.9 (m, SiCH$_2$*CH*$_3$), 7.0 (m, SiCH$_2$*CH*$_3$), 21.3 (t, *J* = 120.5 Hz, *CH*$_2$SiCH$_2$CH$_3$), 120.4 (s, CH$_2$C=*C*Ph$_2$), 125.2−142.3 (m, Ph), 147.4 (t, ^2J = 5.9 Hz, CH$_2$*C*=CPh$_2$). ^{29}Si NMR (59.59 MHz, CDCl$_3$): δ_{Si} −7.46 (CSi), 7.25 (OSi). MS (EI) *m*/*z* (fragment, relative intensity): 588 (M$^+$, 31), 421 (M$^+$ − Ph$_2$C, 5), 396 (M$^+$ − Ph$_2$C=CCH$_2$, 15), 380 (M$^+$ − Ph$_2$C=C(O)CH$_2$, 3), 349 (3), 192 (Ph$_2$C=CCH$_2$$^+$, 100), 155 (8), 147 (20), 119 (16), 115 (6). IR (KBr, cm^{-1}): 3054 (w), 3024 (w), 2954 (m), 2876 (m), 1619 (m,), 1494 (w), 1457 (w), 1442 (w), 1221 (s), 1196 (m), 1150 (m), 1072 (w), 1004 (s, Si−O), 909 (m), 815 (w), 767 (s), 697(s). Anal. Calcd for C$_{38}$H$_{44}$Si$_2$O$_2$: C, 77.49; H, 7.55. Found: C, 77.40; H, 7.55. Mol wt (VPO, CHCl$_3$): calcd for C$_{38}$H$_{44}$Si$_2$O$_2$ 588; found 618.

4. Preparation of 1,5-Dihydrido-1,5-dimethyl-3,7 bis(diphenylmethylene)-1,5-disila-2,8-dioxacyclooctane. A THF solution containing 12.5 mmol of dianion **6** was added dropwise to MeHSiCl$_2$ (1.43 g, 12.5 mmol) in 100 mL of THF at 0 °C. The resulting mixture was stirred at room temperature for 5 h. A pale yellow suspension was obtained. Workup as in 1 gave a colorless, air-stable solid, 2.2 g (70%), after recrystallization from hexane, mp 180−182 °C.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.10 (d, 3 H, ^3J = 3.6, SiH*CH*$_3$), 0.16 (d, 3 H, ^3J = 1.5, OSiH*CH*$_3$), 2.05 (dd, 2 H, ^2J = 14.2 Hz, ^3J = 4.0 Hz, C*H*$_a$H$_b$SiHCH$_3$), 2.18 (d, 2 H, ^2J = 14.2 Hz, CH$_a$*H*$_b$SiHMe), 4.05 (m, 1 H, CH$_2$Si*H*CH$_3$), 4.65 (d, 1 H, ^3J = 1.5, OSi*H*CH$_3$), 7.09−7.34 (m, 20 H, Ph). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ_{C} −5.3 (dq, *J* = 122.2 Hz, ^2J = 18.7 Hz, CSiH*CH*$_3$), −2.6 (dq, *J* = 119.5 Hz, ^2J = 17.3 Hz, OSiH*CH*$_3$), 21.7 (t, *J* = 114.5 Hz, *CH*$_2$SiHCH$_3$), 121.4 (s, CH$_2$C=*C*Ph$_2$), 124.6−141.9 (m, Ph), 146.4 (s, CH$_2$*C*=CPh$_2$). ^{29}Si NMR (59.59 MHz, CDCl$_3$): δ_{Si} −21.2 (d, $J_{\mathrm{Si-H}}$ = 203 Hz, CSi), −10.4 (d, $J_{\mathrm{Si-H}}$ = 262 Hz, OSi). MS (EI) *m*/*z* (fragment, relative intensity): 504 (M$^+$, 34), 312 (M$^+$ − Ph$_2$C=CCH$_2$, 23), 293 (6), 233 (7), 192 (Ph$_2$C=CCH$_2$$^+$, 100), 166 (CPh$_2$, 20), 119 (57), 91 (17). IR (KBr, cm^{-1}): 3124 (w), 3005 (w), 2985 (w), 2916 (w), 2200 (m, Si-H), 2122 (m, Si-H), 1636 (m), 1492 (m), 1441 (m), 1243 (s), 1223 (s), 1207 (m), 1118 (s), 1072 (s, Si−O), 1033 (w), 930 (w), 916 (m), 864 (s), 784 (m), 761 (s), 742 (m), 698 (s). Anal. Calcd for C$_{32}$H$_{32}$Si$_2$O$_2$: C, 76.14; H, 6.39. Found: C, 75.99; H, 6.45. Mol. wt (VPO, CHCl$_3$): calcd for C$_{32}$H$_{32}$Si$_2$O$_2$ 504; found 534.

5. Preparation of 1,1,5,5-Tetraethyl-3,7-bis(diphenylmethylene)-1,5-disila-2,6-dioxacyclooctane. A THF solution containing 12.5 mmol of dianion **6** was added dropwise to Et$_2$SiF$_2$ (1.96 g, 12.5 mmol) in 100 mL of THF at 0 °C. The red color of the dianion was discharged quickly at the beginning of the reaction. As the addition progressed, the red color of the dianion was discharged very slowly. Upon completion of the dianion addition, the resulting mixture was stirred at room temperature overnight. A red suspension was obtained. All volatiles were removed by evaporation under reduced pressure, and the resulting residue was extracted with hexane (3 × 100 mL). Filtration under nitrogen through Celite gave a yellow filtrate. The filtrate was concentrated to about 10 mL under reduced pressure and stored at −23 °C. The product was obtained as colorless, air-stable crystals, 1.7 g (47%), after recrystallization twice from hexane at −23 °C, mp 84−86 °C.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.62 (m, 8 H, Si*CH*$_2$CH$_3$), 0.84 (t, 12 H, *J* = 7.8, SiCH$_2$*CH*$_3$), 2.10 (s, 4 H, CH$_2$), 7.23−7.38 (m, 20 H, Ph). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ_{C} 5.8 (m, Si*CH*$_2$CH$_3$), 6.1 (m, SiCH$_2$*CH*$_3$), 23.8 (t, *J* = 120.5 Hz, *CH*$_2$-SiCH$_2$CH$_3$), 120.3 (s, CH$_2$C=*C*Ph$_2$), 123.9−142.5 (m, Ph), 146.7 (t, ^2J = 5.9 Hz, CH$_2$*C*=CPh$_2$). ^{29}Si NMR (59.59 MHz, CDCl$_3$): δ_{Si} 13.6. MS (EI) *m*/*z* (fragment, relative intensity): 588 (M$^+$, 35), 486 (M$^+$ − Et$_2$SiO, 4), 396 (M$^+$ − Ph$_2$C=CCH$_2$, 30), 380 (M$^+$ − Ph$_2$C=C(O)CH$_2$, 18), 294 (0.5M$^+$, 18), 247 (5), 192 (Ph$_2$C=CCH$_2$$^+$, 100), 147 (18), 119 (10). IR (KBr, cm^{-1}): 3056 (w), 3028 (w), 2951 (m0, 2872 (m), 1622 (s), 1596 (m), 1574 (w), 1494 (m), 1458 (w), 1442 (m), 1407 (w), 1386 (w), 1231 (broad, s), 1196 (m), 1160 (w), 1126 (m), 1071 (w), 995 (s, Si−O), 907 (m), 866 (w), 845 (s), 794 (s). Anal. Calcd for C$_{38}$H$_{44}$Si$_2$O$_2$: C, 77.49; H, 7.55. Found: C, 77.39; H, 7.58. Mol wt (VPO, CHCl$_3$): calcd for C$_{38}$H$_{44}$Si$_2$O$_2$ 588; found 603.

6. Preparation of 1,1,5,5-Tetraphenyl-3,7-bis(diphenylmethylene)-1,5-disila-2,6-dioxacyclooctane. A THF solution containing 12.5 mmol of dianion **6** was added dropwise to Ph$_2$SiF$_2$ (2.75 g, 12.5 mmol) in 100 mL of THF at 0 °C. The red color of the dianion was discharged very slowly. Upon completion of the dianion addition, the resulting mixture was stirred at room temperature overnight. A red suspension was obtained. All volatiles were removed by evaporation under reduced pressure, and the resulting residue was first extracted with hexane (2 × 100 mL) and then with toluene (3 × 50 mL). Filtration of the hexane extracts under nitrogen through Celite gave an orange solution. A yellow polymeric mixture (2.5 g), which has a molecular weight range from 500 to 2400 by GPC, was obtained after removing hexane under reduced pressure. The ^{29}Si NMR of this mixture showed 4−5 signals, which were very weak and difficult to identify. Filtration of the toluene extracts under nitrogen through Celite gave a yellow filtrate. The filtrate was evaporated under reduced pressure. Compound **8** was obtained as colorless, air-stable crystals, 1.0 g (21%), after recrystallization from dichloromethane and hexane, mp 239−240 °C. Single crystals of X-ray quality were obtained by dissolving compound **8** in a minimum amount of methylene chloride, adding 2 volume equiv of hexane, and storing the resulting solution at −23 °C.

^{1}H NMR (300 MHz, CDCl$_3$): δ 2.56 (s, 4 H, CH$_2$), 6.71−7.38 (m, 40 H Ph). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ_{C} 24.4 (t, *J* = 120.4 Hz, *CH*$_2$SiPh$_2$), 122.3 (s, CH$_2$C=*C*Ph$_2$), 124.4−141.7 (m, Ph), 144.8 (t, ^2J = 5.8 Hz, CH$_2$*C*=CPh$_2$). ^{29}Si NMR (59.59 MHz, CDCl$_3$): δ_{Si} −10.7. MS (EI) *m*/*z* (fragment, relative intensity): 780 (M$^+$, 25), 588 (M$^+$ − Ph$_2$C=CCH$_2$, 8), 494 (20), 415 (7), 397 (14), 390 (0.5M$^+$, 9), 319 (31), 257 (5), 192 (Ph$_2$C=CCH$_2$$^+$, 100), 115 (5). IR (KBr, cm^{-1}): 3045 (w), 3030 (w), 3992 (w), 1629 (m), 1493 (m), 1427 (s), 1241 (s), 1156 (w), 1136 (w), 1121 (s), 1101 (w), 1050 (w), 1005 (s, Si−O), 910 (w), 763 (w), 731 (m), 714 (m), 697 (s), 529 (w). Anal. Calcd for C$_{54}$H$_{44}$Si$_2$O$_2$: C, 83.03; H, 5.68. Found: C, 82.79; H, 5.72. Mol wt (VPO, CHCl$_3$): calcd for C$_{54}$H$_{44}$Si$_2$O$_2$ 780; found 813.

Preparation of 1,1,2,2,6,6,7,7-Octamethyl-4,9-bis(diphenylmethylene)-1,2,6,7-tetrasila-3,10-dioxacyclodecane, 12. A THF solution containing 12.5 mmol of dianion **6** was added dropwise to ClSiMe$_2$Me$_2$SiCl (2.32 g, 12.5 mmol) in 100 mL of THF at 0 °C. The resulting mixture was stirred at room temperature overnight. A yellow suspension was obtained. All volatiles were removed by evaporation under reduced pressure, and the resulting residue was subsequently extracted with hexane (3 × 100 mL). Filtration under nitrogen through Celite gave a pale yellow filtrate. The filtrate was concentrated to about 40 mL under reduced pressure and stored at −23 °C. Compound **12** was obtained as colorless, air-stable crystals, 2.7 g (67%), after recrystallization from hexane, mp 132−134 °C Single crystals of X-ray quality were obtained by dissolving **12** in hexane and allowing the solution stand at room temperature for 2 days.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.02 (s, 12 H, $SiMe_2SiMe_2$), 0.05 (s, 12 H, $SiMe_2SiMe_2$), 1.99 (s, 4 H, CH_2), 7.01−7.35 (m, 20 H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C −3.2 (q, J = 119.8 Hz, $SiMe_2SiMe_2$), −3.1 (q, J = 119.9 Hz, $SiMe_2SiMe_2$), 24.9 (t, J = 122.0 Hz, CH_2), 121.5 (s, $CH_2C{=}\mathit{C}Ph_2$), 125.2−142.8 (m, Ph), 149.0 (t, ^2J = 6.0 Hz, $CH_2\mathit{C}{=}CPh_2$). ^{29}Si NMR (59.59 MHz, $CDCl_3$): δ_{Si} −14.7 (CSi), 10.0 (OSi). MS (EI) m/z (fragment, relative intensity): calcd 648; found: 648 (M^+, 42), 456 ($M^+ - Ph_2C{=}CCH_2$, 1), 324 ($0.5M^+$, 13), 233 ($PhC{=}COSiMe_2SiMe_2^+$, 31), 192 ($Ph_2C{=}CCH_2^+$, 100), 147 (35), 133 ($Me_2SiMe_2SiO^+$, 41), 117 ($Me_2SiSiMe_2^+$, 21), 73 (100). IR (KBr, cm^{-1}): 3075 (w), 3017 (w), 2950 (m), 2921 (m), 1615 (m), 1594 (m), 1492 (s), 1468 (w), 1441 (m), 1398 (w), 1247 (m), 1225 (s), 1189 (m), 1135 (m), 1108 (s), 1071 (w), 1032 (w), 971 (s, Si−O), 926 (w), 854 (m), 830 (s), 819 (s), 792 (s), 697 (s). Anal. Calcd for $C_{38}H_{48}Si_2O_4$: C, 70.31; H, 7.45. Found: C, 70.27; H, 7.46. Mol wt (VPO, $CHCl_3$) calcd for $C_{38}H_{48}Si_2O_4$ 648; found 672.

Preparation of 1,1,2,2,3,3-Hexamethyl-5-diphenylmethylene-1,2,3-trisila-4-oxacyclohexane, 16. A THF solution containing 12.5 mmol of dianion **6** was added dropwise to 1 equiv of 1,3-dichlorohexamethyltrisilane (3.05 g, 12.5 mmol) in 100 mL of THF at 0 °C. The resulting mixture was stirred at room temperature overnight. A pale yellow suspension was obtained. All volatiles were removed by evaporation under reduced pressure, and the resulting residue was subsequently extracted with hexane (3 × 100 mL). Filtration under nitrogen through Celite gave a pale yellow filtrate. All volatiles were removed under reduced pressure, and a yellow, viscous, oily mixture was obtained. A colorless, air-stable solid was obtained after Kugelrohr distillation of the oily mixture at 0.01 mmHg with heating to 103−130 °C. Compound **16** was obtained as colorless, air-stable crystals, 3.0 g (62%), after recrystallization from hexane at −23 °C, mp 94−96 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.08 (s, 6 H, $CH_2Si(\mathit{CH_3})_2$), 0.16 (s, 6 H, $Si(CH_3)_2$), 0.19 (s, 6 H, $OSi(CH_3)_2$), 1.82 (s, 2 H, CH_2), 7.03−7.29 (m, 10 H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C −7.8 (q, J = 120.0 Hz, $Si(CH_3)_2$), −3.1 (q, J = 117.0 Hz, $Si(CH_3)_2$), 1.0 (q, J = 120.0 Hz, $Si(CH_3)_2$), 24.3 (t, J = 121.4 Hz, CH_2), 119.5 (s, $CH_2C{=}\mathit{C}Ph_2$), 123.8−142.8 (m, Ph), 149.3 (t, ^2J = 6.0 Hz, $CH_2\mathit{C}{=}CPh_2$). ^{29}Si NMR (59.59 MHz, $CDCl_3$): δ_{Si} −56.1 (CH_2SiMe_2), −17.9 ($SiMe_2$), 19.4 ($OSiMe_2$). MS (EI) m/z (fragment, relative intensity): 382 (M^+, 49), 367 ($M^+ -$ Me, 9), 324 ($M^+ - SiMe_2$, 9), 233 ($PhC{=}COSiMe_2SiMe_2^+$, 27), 192 ($Ph_2C{=}CCH_2^+$, 100), 174 ($Me_2SiMe_2SiSiMe_2^+$, 55), 132 ($Me_2SiMe_2SiO^+$, 81), 116 ($Me_2SiSiMe_2^+$, 56), 73 (100). IR (KBr, cm^{-1}): 3054 (w), 3025 (w), 2950 (m), 2891 (w), 1614 (broad, m), 1584 (w), 1494 (m), 1400 (w), 1441 (m), 1400 (w), 1246 (s), 1225 (m), 1190 (w), 1115 (w), 1032 (w), 979 (m, Si−O), 899 (w), 829 (s), 779 (s), 699 (s), 649 (w). Anal. Calcd for $C_{21}H_{30}Si_3O$: C, 65.90; H, 7.90. Found: C, 66.03; H, 7.91. Mol wt (VPO, $CHCl_3$): calcd for $C_{21}H_{30}Si_3O$ 382; found 399.

Reaction of Compound 10 with Methyllithium. A 100 mL round-bottomed Schlenk flask equipped with a magnetic stir bar and a rubber septum was charged with 0.35 g of **10** (0.66 mmol) and 50 mL of Et_2O. To this solution at 0 °C was added, dropwise with stirring, 2 molar equiv of CH_3Li as a complex with LiBr (0.88 mL, 1.5 M in diethyl ether). The resulting mixture was stirred at 0 °C for 30 min and then at room temperature for approximately 1 h, and then a solution of saturated aqueous NH_4Cl was added. The organic layer was separated, the aqueous layer was extracted twice with Et_2O, and the combined organic layers were washed twice with water. The organic layer was dried over $MgSO_4$, and all volatiles were removed at reduced pressure to leave **11** as a colorless solid. Further purification by recrystallization from hexane at −23 °C yielded colorless, air-stable crystals of **11**, 0.25 g (80%), mp 79−81 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.16 (s, 6 H, $SiMe_2$), 2.33 (s, 4 H, CH_2), 5.11 (s, 2 H, $\mathit{CH}Ph_2$), 7.20−7.35 (m, 20 H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C −1.9 (q, J = 120.3 Hz, $SiMe_2$), 36.1 (t, J = 122.1 Hz, CH_2), 65.7 (d, J = 127.0 Hz, $CHPh_2$), 127.0−138.3 (m, Ph), 206.2 (s, C=O). ^{29}Si NMR (59.59 MHz, $CDCl_3$): δ_{Si} 2.68. MS (EI): 476 (M^+, 1), 309 ($M^+ - Ph_2C$, 19), 267 ($M^+ - Ph_2CHCOCH_2$, 100), 192 ($Ph_2C{=}CCH_2$, 55), 167 (Ph_2C^+, 100), 152 (35), 135 (82), 115 (60), 75 (70). IR (KBr, cm^{-1}): 3025 (w), 3008 (w), 2920 (w), 1693 (s, C=O), 1598 (w), 1493 (m), 1451 (w), 1403 (w), 1253 (w), 1186 (w), 1113 (w), 1040 (w), 843 (m), 745 (w), 699 (s), 599 (w). Anal. Calcd for $C_{32}H_{32}O_2Si$: C, 80.63; H, 6.77. Found: C, 80.63; H, 6.81.

Reaction of Compound 12 with Methyllithium. A 100 mL round-bottomed Schlenk flask equipped with a magnetic stir bar and a rubber septum was charged with 0.36 g of **13** (0.56 mmol) and 50 mL of Et_2O. To this solution at 0 °C was added dropwise with stirring 2 molar equiv of CH_3Li as a complex with LiBr (0.74 mL, 1.5 M in diethyl ether). The resulting mixture was stirred at 0 °C for 30 min and then stirred at room temperature for approximately 1 h. A solution of saturated aqueous NH_4Cl was added. Workup as in the previous experiment left a colorless solid. Recrystallization from hexane at −23 °C yielded colorless, air-stable crystals of **14**, 0.18 g (60%), mp 88−90 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.06 (s, 12 H, $SiMe_2$), 3.93 (d, 2 H, ^2J = 1.5 Hz, $\mathit{CH_a}H_b$), 4.14 (d, 2 H, ^2J = 1.5 Hz, $CH_a\mathit{H_b}$), 4.63 (s, 2 H, $CHPh_2$), 7.14−7.25 (m, 20 H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C −0.6 (q, J = 120.0 Hz, $SiMe_2$), 58.1 (d, J = 127.4 Hz, $CHPh_2$), 92.8 (t, J = 156.1 Hz, $C{=}\mathit{CH_2}$), 126.3−141.7 (m, Ph), 160.3 (t, ^2J = 3.6 Hz, $\mathit{C}{=}CH_2$). ^{29}Si NMR (59.59 MHz, $CDCl_3$): δ_{Si} 10.65. MS (EI): 534 (M^+, 3), 325 ($M^+ - Ph_2CHC{=}CH_2O$, 34), 267 ($0.5M^+$, 100), 209 ($Ph_2CHC{=}CH_2O^+$, 11), 192 ($Ph_2CHC{=}CH_2^+$, 94), 178 (21), 135 (80), 115 (65), 91 (42), 75 (38). IR (KBr, cm^{-1}): 3052 (w), 3025 (m), 2952 (w), 2901 (w), 1626 (s), 1598 (w), 1494 (s), 1449 (m), 1380 (w), 1290 (w), 1275 (s), 1248 (s), 1214 (s), 1090 (w), 1008 (s), 920 (w), 903 (w), 826 (w), 787 (w), 740 (w), 697 (s). Anal. Calcd for $C_{34}H_{38}O_2Si_2$: C, 76.35; H, 7.16. Found: C, 76.28; H, 7.22.

Reactions of the 1,1-Diphenylacetone Dianion with Two Molar Equivalents of a Monochlorosilane. A 100 mL Schlenk flask equipped with a magnetic stir bar and a rubber septum was charged with 0.5 g (12.5 mmol) of KH and 50 mL of THF. Subsequently, a solution of 2.62 g (12.5 mmol) of $Ph_2CHC(O)CH_3$ in 10 mL of THF was added dropwise by syringe with stirring. Gas evolution was observed. After the resulting orange solution had been stirred at room temperature for 40 min, it was cooled to 0 °C and 4.93 mL of 2.53 M n-BuLi (12.5 mmol) in hexane was added. The resulting red suspension was stirred at 0 °C for 5−7 min.[4a]

The $LiK[CH_2C(O)CPh_2]$ solution was then added at 0 °C to 25 mmol of the monochlorosilane (120 mL), slowly with stirring. The red color was discharged immediately in the case of the Me_3SiCl and Me_2HSiCl reactions, only slowly over 30 min in the case of $MePh_2SiCl$. The reaction mixture was stirred at room temperature for 12 h, and then the solvents were removed at reduced pressure. The residue was extracted with hexane, and the extracts were filtered through Celite and evaporated at reduced pressure, leaving the crude product. The only other compound present in the product was starting material (~15% recovery as estimated by ^{1}H NMR).

The following disilyl products were prepared.

$Ph_2C{=}C(CH_2SiMe_3)(OSiMe_3)$, 71%, colorless oil, purified by column chromatography (neutral alumina, activity 1, pentane). ^{1}H NMR (300 MHz): δ 0.09 (s, 9 H, $CSiMe_3$), −0.01 (s, 9 H, $OSiMe_3$), 1.68 (s, CH_2Si), 7.05 (m, 10 H, C_6H_5). ^{13}C NMR: δ_C 0.21 (q, J = 119.4 Hz, $CSiMe_3$), 0.85 (q, J = 118.1 Hz, $OSiMe_3$), 26.4 (t, J = 121.9 Hz, CH_2), 121.9 (s, $Ph_2C{=}$), 125.8, 126.4, 127.9, 128.6, 130.9, 131.4, 142.2, 143.5 (C_6H_5), 149.6 (${=}C{-}O$).

Table 6. Structure Determination of 9

Crystal Data	
empirical formula	$C_{54}H_{44}O_2Si_2$
color; habit	colorless block
cryst size (mm)	0.46 × 0.48 × 0.52
cryst syst	orthorhombic
space group	*Pbca*
unit-cell dimens	$a = 11.676(4)$ Å $b = 23.057(11)$ Å $c = 31.850(15)$ Å
volume	8575(7) Å^3
Z	8
fw	781.1
density (calcd)	1.210 g/cm^3
abs coeff	0.124 mm^{-1}
$F(000)$	3296
Data Collection	
diffractometer used	Siemens P4
radiation	Mo Kα ($\lambda = 0.710\,73$ Å)
temperature (K)	238
monochromator	highly oriented graphite crystal
2θ range	4.0−42.0°
scan tyupe	ω
scan speed	variable; 6.51−19.53°/min in ω
scan range (ω)	1.00°
background measurement	stationary crystal and counter at beginning and end of scan, each for 1.0% of total scan time
standard reflections	3 measured every 197 reflns
index ranges	$o \leq h \leq 11$, $0 \leq k \leq 23$, $0 \leq l \leq 32$
no. of reflns collected	4593
no. of independent reflns	4593 ($R_{int} = 0.00\%$)
no. of obsd reflns	2501 ($F > 4.0\sigma(F)$)
Structure Solution and Refinement	
syst used	Siemens SHELXTL PLUS (PC version)
solution	direct methods
refinement method	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$\omega^{-1} = \sigma^2(F) + 0.0010\text{F}^2$
no. of params refined	283
final R indices (obsd data)	$R = 7.39\%$, $R_w = 8.07\%$
goodness-of-fit	1.46
largest and mean Δ/s	0.010, 0.001
data-to-parameter ratio	8.8:1
largest diff peak	0.51 e Å^{-3}
largest diff hole	−0.39 e Å^{-3}

Table 7. Structure Determination of 8

Crystal Data	
empirical formula	$C_{54}H_{44}O_2Si_2$
color; habit	colorless block
cryst size (mm)	0.16 × 0.42 × 0.80
cryst syst	monoclinic
space group	$P2_1/n$
unit-cell dimens	$a = 10.384(2)$ Å $b = 19.762(4)$ Å $c = 21.513(5)$ Å $\beta = 96.65(2)°$
volume	4384.9(16) Å^3
Z	4
fw	781.1
density (calcd)	1.183 g/cm^3
abs coeff	0.122 mm^{-1}
$F(000)$	1648
Data Collection	
diffractometer used	Siemens P4
radiation	Mo Kα ($\lambda = 0.710\,73$ Å)
temperature (K)	296
monochromator	highly oriented graphite crystal
2θ range	4.0−42.0°
scan type	$\theta - 2\theta$
scan speed	variable; 7.00−20.00°/min in ω
scan range (ω)	1.00°
background measurement	stationary crystal and counter at beginning and end of scan, each for 50.0% of total scan time
standard reflections	3 measured every 100 reflns
index ranges	$-9 \leq h \leq 10$, $-19 \leq k \leq 0$, $-9 \leq l \leq 21$
no. of reflns collected	4889
no. of independent reflns	4740 ($R_{int} = 1.61\%$)
no. of obsd reflns	2022 ($F > 5.0\sigma(F)$)
Structure Solution and Refinement	
syst used	Siemens SHELXTL PLUS (PC version)
solution	direct methods
refinement method	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
no. of params refined	427
final R indices (obsd data)	$R = 5.49\%$, $R_w = 6.42\%$
R indices (all data)	$R = 12.21\%$, $R_w = 7.83\%$
goodness-of-fit	1.29
largest and mean Δ/s	0.011, 0.001
data-to-parameter ratio	4.7:1
largest diff peak	0.22 e Å^{-3}
largest diff hole	−0.25 e Å^{-3}

^{29}Si NMR: δ_{Si} 2.43 ($CSiMe_3$), 16.40 ($OSiMe_3$). Anal. Calcd for $C_{21}H_{30}OSi_2$: C, 71.12; H, 8.53. Found: C, 71.47; H, 8.70.

$Ph_2C{=}C(CH_2SiMe_2H)(OSiMe_2H)$, 82%, bp 95 °C/0.05 Torr. ^{1}H NMR (300 MHz): δ 0.09 (d, $J = 1.5$ Hz, 6 H, $CSiMe_2H$), 0.16 (d, $J = 1.5$ Hz, 6 H, $OSiMe_2H$), 1.88 (d, $J = 1.5$ Hz, 2 H, CH_2Si), 4.02 (nonet, $J = 1.5$ Hz, 1 H, CSiH), 4.57 (sept, $J = 1.5$ Hz, 1 H, OSiH), 7.26 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR: δ_C −3.9 ($CSiMe_2$), −1.3 ($OSiMe_2$), 22.6 (CH_2Si), 121.7, ($Ph_2C{=}$), 125.6, 126.09 *[126.1??]*, 127.5, 128.2, 130.2, 130.8, 141.2, 142.6 (C_6H_5), 148.9 (=C−O). ^{29}Si NMR: δ_{Si} −11.18 (CSi), 5.02 (OSi). Anal. Calcd for $C_{19}H_{26}OSi_2$: C, 69.88; H, 8.02. Found: C, 69.53; H, 7.96.

$Ph_2C{=}C(CH_2SiMePh_2)(OSiMePh_2)$, 56%, Kugelrohr bp 160 °C/0.03 Torr, contained a minor impurity that could not be separated. ^{1}H NMR (300 MHz): δ 0.32 (s, 3 H, CSiMe), 0.39 (s, 3 H, $OSiMe_3$), 1.62 (s, 2 H, CH_2Si), 7.15 (m, 30 H, C_6H_5). $^{13}C\{^1H\}$ NMR: δ_C −2.04 (CSiMe), −0.56 (OSiMe), 21.50 (CH_2Si), 123.6 ($Ph_2C{=}$), 125.8, 126.2, 127.7, 127.95, 128.0, 130.4, 130.5, 135.7, 137.6, 140.8, 141.9 (C_6H_5), 146.0 (=C−O).

Reaction of the 1,1-Diphenylacetone Dianion with 1 Molar Equiv Each of Two Different Monochlorosilanes Added in Succession. Essentially the same procedure was used. After the $LiK[CH_2C(O)CPh_2]$ solution had been prepared, 1 equiv of the first chlorosilane was added slowly over a 15−20 min period. The resulting orange solution was stirred for 10 min, and then 1 equiv of the second chlorosilane was added, which caused complete decolorization. A byproduct in all cases was the silyl enol ether formed by reaction of the 1,1-diphenylacetone dianion with 2 equiv of the first chlorosilane added (yields up to 20%). Because of this byproduct, vacuum distillation did not give a pure product and column chromatography or preparative GC had to be used.

Prepared by this procedure were the following:

$Ph_2C{=}C(CH_2SiMe_3)(OSiMe_2H)$ (Me_3SiCl added first), 72%, isolated by preparative GC. ^{1}H NMR (300 MHz): δ 0.03 (s, 9 H, Me_3Si), 0.07 (d, $J = 2.5$ Hz, 6 H, $OSiMe_2H$), 1.78 (s, 2 H, CH_2Si), 4.52 (sept, $J = 2.5$ Hz, 1 H, SiH), 7.25 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR: δ_C −0.10, −0.08 (Me_3Si, Me_2Si), 25.1 (CH_2Si), 120.8 ($Ph_2C{=}$), 125.2, 125.8, 126.4, 127.2, 129.7, 130.4, 141.2, 142.9 (C_6H_5), 149.50 (=C−O). ^{29}Si NMR: δ_{Si} 4.20 (CS), 4.75 (OSi). Anal. Calcd for $C_{20}H_{28}OSi_2$: C, 70.53; H, 8.29. Found: C, 70.97; H, 8.18.

$Ph_2C{=}C(CH_2SiMe_3)(OSiMePh_2)$ (Me_3SiCl added first), 71%, isolated by column chromatography (neutral alumina), preparative GC. ^{1}H NMR (300 MHz): δ −0.26 (s, 9 H, Me_3Si), 0.16 (s, 3 H, OSiMe), 1.43 (s, 2 H, CH_2Si), 7.05 (m, 20 H, C_6H_5). $^{13}C\{^1H\}$ NMR: δ_C −2.34 ($CSiMe_3$), −0.64 (OSiMe), 25.4 (CH_2Si), 121.8 ($Ph_2C{=}$), 125.4, 125.9, 127.6, 127.8, 128.1, 129.8, 130.6, 131.0, 134.5, 135.7, 141.7, 143.0 (C_6H_5), 149.5 (=C−O).

Table 8. Structure Determination of 12

Crystal Data	
empirical formular	$C_{41}H_{55}O_2Si_4$
color; habit	colorless block
cryst size (mm)	0.24 × 0.36 × 0.40
cryst syst	monoclinic
space group	$P2_1/n$
unit-cell dimens	$a = 29.901(6)$ Å $b = 9.926(1)$ Å $c = 14.221(4)$ Å $\beta = 97.78(2)°$
volume	4181.9(14) Å^3
Z	4
fw	692.2
density (calcd)	1.099 g/cm^3
abs coeff	0.173 mm^{-1}
F(000)	1492
Data Collection	
diffractometer used	Siemens P4
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)
temperature (K)	233
monochromator	highly oriented graphite crystal
2θ range	7.0−42.0°
scan type	ω
scan speed	variable; 2.00−29.30°/min in ω
scan range (ω)	0.06°
background measurement	stationary crystal and counter at beginning and end of scah, each for 0.5% of total scan time
standard reflections	3 measured every 100 reflns
index ranges	$-34 \leq h \leq 33$, $0 \leq k \leq 11$, $0 \leq l \leq 16$
no. of reflns collected	6879
no. of independent reflns	6567 ($R_{int} = 3.70\%$)
no. of obsd. reflns	4102 ($F > 5.0\sigma(F)$)
Structure Solution and Refinement	
syst used	Siemens SHELXTL PLUS (PC version)
solution	direct methods
refinement method	full-matrix least-sqares
quantity minimized	$\sum w(F_o - F_c)^2$
extinction correction	c = 0.00016(8), where $F^* = F\,[1 + 0.0002\chi F^2/\sin(2\theta)]^{-1/4}$
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010\mathrm{F}^2$
no. of params refined	426
final R indices (obsd data)	$R = 4.96\%$, $R_w = 6.29\%$
R indices (all data)	$R = 8.72\%$, $R_w = 7.48\%$
goodness-of-fit	1.26
largest and mean Δ/s	0.138, 0.014
data-to-parameter ratio	9.7:1
largest diff peak	0.28 e Å^{-3}
largest diff hole	−0.24 e Å^{-3}

^{29}Si NMR: δ_{Si} −4.22 (CSi), 2.85 (OSi). Anal. Calcd for $C_{31}H_{34}OSi_2$: C, 70.77; H, 7.16. Found: C, 70.83; H, 7.28.

$Ph_2C{=}C(CH_2SiMe_3)(OSiMe_2\text{-t-Bu})$ (Me_3SiCl added first), 82%, isolated by column chromatography (neutral alumina). ^{1}H NMR (300 MHz): δ −0.08 (s, 6 H, CSiMe), 0.08 (s, 9 H, OMe_3Si), 0.86 (s, 9 H, CMe_3), 1.88 (s, 2 H, CH_2Si), 7.23 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR: δ_C −4.2 (Me_3Si), −0.1 ($OSiMe_2$), 18.2 (CMe_3), 25.8 (CH_2Si), 26.1 (CMe_3), 121.2 ($Ph_2C{=}$), 125.3, 125.8, 127.1, 127.8, 130.4, 130.9, 142.2, 143.5 (C_6H_5), 149.8 (${=}C{-}O$). ^{29}Si NMR: δ_{Si} 6.85 (CSi), 22.87 (OSi). Anal. Calcd for $C_{24}H_{36}OSi_2$: C, 72.66; H, 9.15. Found: C, 72.54; H, 9.13.

$Ph_2C{=}C(CH_2SiMe_2H)(OSiMe_2\text{-t-Bu})$ (Me_2HSiCl added first), 72%, isolated by column chromatography on neutral alumina and preparative GC. ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.38 (d, $^3J = 2.4$ Hz, 6 H, $CH_2Si(CH_3)_2$), −0.17 (s, 6 H, $OSiMe_2$), 0.56 (s, 9 H, $SiCMe_3$), 1.59 (d, $^3J = 2.4$ Hz, 2 H, CH_2Si), 3.72 (m, $^3J = 2.4$ Hz, 1 H, SiH), 6.88 (m, 10 H, Ph). $^{13}C\{^1H\}$ NMR: δ_C −4.3 and −3.9 ($CSiMe_2$ and $OSiMe_2$), 18.1 (CMe_3), 23.2 (CH_2Si), 25.8 (CMe_3), 121.7 ($Ph_2C{=}$), 125.4, 125.9, 127.5, 128.1, 130.7, 131.0, 141.8, 143.2 (C_6H_5), 148.9 (${=}C{-}O$). ^{29}Si NMR: δ_{Si} −11.78 (CSi), 21.18 (OSi). Anal. Calcd for $C_{23}\ H_{34}OSi_2$: C, 72.19; H, 8.95. Found: C, 72.06; H, 8.91.

Table 9. Structure Determination of 17

Crystal Data	
empirical formula	$C_{54}H_{44}Ge_2O_2$
color; habit	colorless block
cryst size (mm)	0.2 × 0.2 × 0.3
cryst syst	monoclinic
space group	$P2_1/n$
unit-cell dimens	$a = 15.044(8)$ Å $b = 17.048(7)$ Å $c = 17.19(8)$ Å $\beta = 93.1(1)°$
volume	4402(3) Å^3
Z	4
fw	870.1
density (calcd)	1.310 g/cm^3
abs coeff	0.403 mm^{-1}
F(000)	1792
Data Collection	
diffractometer used	Siemens P4
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)
temperature (K)	296
monochromator	highly oriented graphite crystal
2θ range	4.0−41.0°
scan type	ω
scan speed	variable; 5.33−19.53°/min in ω
scan range (ω)	1.00°
background measurement	stationary crystal and counter at beginning and end of scan, each for 50.0% of total scan time
standard reflns	3 measured every 197 reflections
index ranges	$-14 \leq h \leq 13$, $0 \leq k \leq 16$, $0 \leq l \leq 16$
no. of reflns collected	4424
no. of independent reflns	4252 ($R_{int} = 2.54\%$)
no. of obsd reflns	1996 ($F > 5.0\sigma(F)$)
Structure Solution and Refinement	
syst used	Siemens SHELXTL PLUS (PC version)
solution	direct methods
refinement method	full-matrix least-sqares
quantity minimized	$\sum w(F_o - F_c)^2$
hydrogen atoms	riding model, fixed isotropic U
weigting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
no. of parameters refined	187
final R indices (obsd data)	$R = 6.14\%$, $R_w = 7.69\%$
R indices (all data)	$R = 11.03\%$, $R_w = 8.40\%$
goodness-of-fit	1.60
largest and mean Δ/s	0.011, 0.002
data-to-parameter ratio	10.7:1
largest diff peak	0.61 e Å^{-3}
largest diff hole	−0.46 e Å^{-3}

Reaction of the 1,1-Diphenylacetone Dianion with 1 Molar Equiv Each of t-BuMe$_2$SiCl and Me$_2$HSiCl in Succession. Using the general procedure described above, a solution of $LiK[CH_2C(O)CPh_2]$ was prepared from 1.31 g (6.25 mmol) of 1,1-diphenylacetone, 0.27 g (6.75 mmol) of KH, and 4.0 mL of 1.6 M *n*-BuLi in 60 mL of THF. To the resulting red solution was added, at 0 °C with stirring, 1.0 g (6.75 mmol) of $t\text{-}BuMe_2SiCl$ in 10 mL of THF. The mixture was stirred at 0 °C for 10 min, and then 1.2 mL (7.5 mmol) of Me_2HSiCl was added by syringe. The reaction mixture was stirred at room temperature for 12 h. Subsequently, the solvent was removed *in vacuo*, and the residue was extracted with 70 mL of hexane. The extracts were filtered through Celite, and the hexane was removed from the filtrate *in vacuo*. A light yellow oil remained (1.72 g). The ^{1}H NMR spectrum of the oil showed the main product to be $Ph_2C{=}C(CH_2SiMe_2H)(OSiMe_2H)$. GC/MS analysis showed this compound as well as $Ph_2C{=}C(CH_2SiMe_2\text{-t-Bu})(OSiMe_2H)$ to be present. GC yield determination (naphthalene internal standard) gave yields of 61% and 22%, respectively.

$Ph_2C{=}C(CH_2SiMe_2\text{-t-Bu})(OSiMe_2H)$ isolated by preparative GC. ^{1}H NMR (300 MHz): δ −0.30 (s, 6 H, $CSiMe_2$), −0.29 (d, $J = 2.5$ Hz, 6 H, $OSiMe_2H$), 0.41 (s, 9 H, CMe_3), 1.43 (s, 2 H, CH_2Si), 4.16 (sept, $J = 2.5$, 1 H, SiH), 6.92 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR: δ_C −5.2 ($CSiMe_2$), −1.4 ($OSiMe_2$), 16.7 (CMe_3), 21.0 (CH_2Si), 26.2 (CMe_3), 121.1 ($Ph_2C{=}$), 125.4, 126.0, 127.6, 128.2, 130.3, 131.0, 141.5, 142.9 (C_6H_5), 150.0 (=C—O). ^{29}Si NMR: δ_{Si} −3.85 (CSi), 11.54 (OSi). Anal. Calcd for $C_{23}H_{34}OSi_2$: C, 72.19; H, 8.95. Found: C, 72.48; H, 8.95.

In a similar experiment using 2.52 mmol of 1,1-diphenylacetone dianion and 2.70 mmol of t-$BuMe_2SiCl$, 3.3 mmol of Me_2HSiCl was added 3 h after the t-$BuMe_2SiCl$ had been added. After a reaction time of 10 h at room temperature, similar workup and GC/MS analysis and GC yield determination showed the products to be $Ph_2C{=}C(CH_2SiMe_2\text{-t-Bu})(OSiMe_2H)$, 39.7%, $Ph_2C{=}C(CH_3)(OSiMe_2H)$, 29.8%, and $Ph_2C{=}C{=}C(SiMe_2H)_2$,[24] 2.4%.

In a reaction in which the time interval between the addition of t-$BuMe_2SiCl$ and Me_2HSiCl was increased to 12 h, these yields were 40.5, 30.2, and 2.2%, respectively.

$Ph_2C{=}C(CH_3)(OSiMe_2H)$: ^{1}H NMR (300 MHz) δ −0.04 (d, J = 3.0 Hz, 6 H, Me_2Si), 1.84 (s, 3 H, CH_3), 4.54 (sept, J = 3 Hz, 1 H, SiH), 7.15 (m, 10 H, C_6H_5).

X-ray Crystallography. Structure of Compound 9. Colorless crystals of **9** were obtained by dissolving **9** in methylene chloride and allowing the solution to evaporate slowly. Data were collected at 238 K using Mo Kα radiation on a Siemens P4 diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares techniques. The non-hydrogen atoms were refined anisotropically. An absorption correction was not applied. Final R = 0.0739 and R_w = 0.0807 values for 2501 observed reflections ($F > 4.0\sigma(F)$) and 283 variables. The largest peak on the final difference Fourier map was 0.51 e Å^{-3}. A summary of data collection details and crystal data appear in Table 6.

Structure of Compound 8. Colorless crystals of **8** were obtained by dissolving **8** in a minimum amount of methylene chloride, adding 2 equiv of hexane, and storing the solution at −23 °C. Data were collected at 296 K using Mo Kα radiation on a Siemens P4 diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares techniques. The limited available data required the use of rigid-body constraints on the phenyl rings and prevented anisotropic refinement of their carbon atoms. The non-hydrogen atoms were refined anisotropically. An absorption correction was not applied. Final R = 0.0549 and R_w = 0.0642 values for 2022 observed reflections ($F > 5.0\sigma(F)$) and 427 variables. The largest peak on the final difference Fourier map was 0.22 e Å^{-3}. A summary of data collection details and crystal data appear in Table 7.

Structure of Compound 12. Colorless crystals of **12** were obtained by dissolving **12** in hexane and allowing the solution stand at room temperature for 2 days. Data were collected at 233 K using Mo Kα radiation on a Siemens P4 diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares techniques. The non-hydrogen atoms were refined anisotropically. An absorption correction was not applied. Final R = 0.0496 and R_w = 0.0629 values for 4102 observed reflections ($F > 5.0\sigma(F)$) and 425 variables. The largest peak on the final difference Fourier map was 0.28 e Å^{-3}. A summary of data collection details and crystal data appear in Table 8.

Structure of Compound 17. Colorless crystals of **17** were obtained by dissolving **17** in methylene chloride and allowing the solution to evaporate slowly. A colorless block was mounted on a glass fiber and found to possess 2/m Laue symmetry. Data were collected at 296 K using Mo Kα radiation on a Siemens P4 diffractometer. All specimens studied diffracted weakly and somewhat broadly; as a consequence, data were not available beyond $2\theta = 42°$. No correction for absorption was required; azimuthal scans showed <10% variation. The structure was solved by direct methods and refined by full-matrix least-squares techniques. The limited available data required the use of rigid-body constraints on the phenyl rings and prevented anisotropic refinement of their carbon atoms. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were idealized. Final R = 0.0614 and R_w = 0.0769 values for 1996 observed reflections ($F > 5.0\sigma(F)$) and 187 variables. A summary of data collection details and crystal data appear in Table 9.

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Supporting Information Available: Tables of the atomic coordinates and equivalent isotropic displacement coefficients, anisotropic displacement coefficients, H-atom coordinates, and bond distances and bond angles for **12** and **17** (11 pages). These data for **8** and **9** were deposited as Supporting Information for our preliminary communication (Seyferth, D.; Wang, T.; Ostrander, R. L.; Rheingold, A. L. *Organometallics* **1995**, *14*, 2136). Ordering information is given on any current masthead page.

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