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Platinum-Catalyzed Dehydrogenative Double Silylation of Carbonyl Compounds with *o*-Bis(dimethylsilyl)benzene

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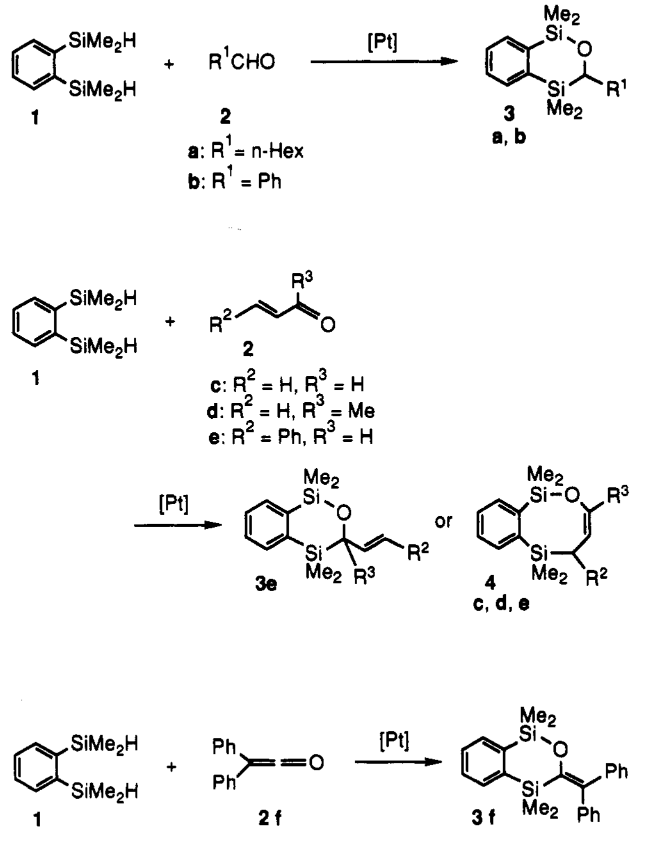
Heptanal, benzaldehyde, (*E*)-3-phenyl-2-propenal, and diphenylketene underwent dehydrogenative 1,2 double silylation with *o*-bis(dimethylsilyl)benzene (1) in the presence of a catalytic amount of (ethylene)bis(triphenylphosphine)platinum or bis(dibenzylideneacetone)platinum to afford 5,6-benzo-1,4-disila-2-oxa-5-cyclohexene (3). Dehydrogenative 1,4 double silylation of prop-2-enal and but-3-en-2-one with 1 also took place under similar conditions. The compound **3b** obtained from the $Pt(CH_2{=}CH_2)(PPh_3)_2$-catalyzed reaction of benzaldehyde **2b** with *o*-bis(deuteriodimethylsilyl)benzene did not show deuterium incorporation. The cyclic bis(silyl)platinum complex $\overline{\mathrm{Me_2Si(\textit{o}\text{-}C_6H_4)SiMe_2Pt}}(PPh_3)_2$ (7) prepared separately from 1 and $Pt(CH_2{=}CH_2)(PPh_3)_2$ readily reacted with **2b** in the presence of 1 to give **3b**. These observations suggest that the present reaction proceeds via 7 as a key intermediate. The structure of 5,6-benzo-1,1,4,4-tetramethyl-3-(diphenylmethylidene)-1,4-disila-2-oxa-5-cyclohexene **3f**, the 1,2-adduct of diphenylketene, was confirmed by X-ray crystallography. Compound **3f** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.400$ (2) Å, $b = 9.756$ (3) Å, $c = 20.341$ (3) Å, $\beta = 96.03$ (1)°, $V = 2249.8$ (4) Å^3, and $Z = 4$.

Transition-metal-complex-catalyzed double silylation of carbon unsaturated compounds such as olefins, dienes, acetylenes, and isocyanides with disilanes is of use to synthesize bis(silyl) compounds.[1] α,β-Unsaturated ketones also undergo double silylation to give 1,4-adducts.[2] To the best of our knowledge, however, metal-complex-catalyzed 1,2 double silylation of carbonyl groups with disilanes has never been reported although the fluoride ion is known to promote the reaction of aldehydes.[3,4] On the other hand, double silylation is expected to be accomplished using hydrosilanes under dehydrogenative conditions. Indeed, the nickel-catalyzed reaction of internal acetylenes with chlorohydrosilanes[5a] and the rhodium-catalyzed reaction of nitriles with bis(hydrosilane) compounds[5b] have been already reported. Recently, we have also reported that the dehydrogenative double silylation of acetylenes, olefins, dienes,[6,7] and nitriles[8] with *o*-bis(dimethylsilyl)benzene (1) or other bis(hydrosilane) species is effectively catalyzed by platinum complexes to form disila cyclic compounds. We report here the first successful examples of dehydrogenative 1,2 and 1,4 double silylation of aldehydes, α,β-unsaturated aldehydes, an α,β-unsaturated ketone, and a ketene with bis(hydrosilane) species.

Results and Discussion

Catalytic Reactions. Dehydrogenative double silylation of carbonyl compounds 2 with 1 was found to be catalyzed by $Pt(CH_2{=}CH_2)(PPh_3)_2$ or $Pt(dba)_2$ (dba = dibenzylideneacetone) to give 1,2- and/or 1,4-adducts (3 and/or 4) in good yields (Scheme I). The latter complex usually showed higher catalytic activity. In some cases, however, the reaction with this catalyst was less selective (vide infra). The results are summarized in Table I.

Scheme I



Heptanal (**2a**) readily reacted at 110 °C with 1 in the presence of $Pt(CH_2{=}CH_2)(PPh_3)_2$ to give the 1,2-adduct **3a** in 81% yield. Although 54% yield was obtained within 1 h, heating was continued for 20 h to complete the reaction. The reaction also proceeded at 80 °C but very slowly; after 12 h, **3a** was formed only in 4% yield. When $Pt(dba)_2$ was used at 80 °C, however, 91% of **3a** was

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(1) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991**, 241. Hayashi, T.; Kobayashi, T.-a.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280 and references cited therein.

(2) Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87. Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 4147; *J. Am. Chem. Soc.* **1988**, *110*, 5579.

(3) Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 914. Hiyama, T.; Obayashi, M. *Tetrahedron Lett.* **1983**, *24*, 4109.

(4) Very recently Ishikawa et al. reported the thermal double silylation of acetylenes, aldehydes, and an α,β-unsaturated carbonyl compound with a benzodisilacyclobutene. See: Ishikawa, M.; Sakamoto, H.; Tabuchi, T. *Organometallics* **1991**, *10*, 3173.

(5) (a) Tamao, K.; Miyake, N.; Kiso, Y.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5603. (b) Corriu, R. J. P.; Moreau, J. J. E.; Padaud-Sat, M. *J. Organomet. Chem.* **1982**, *228*, 301.

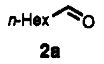
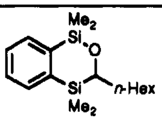
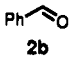
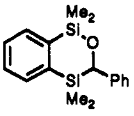
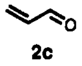
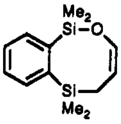
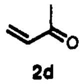
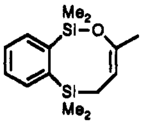
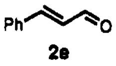
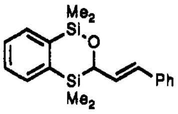
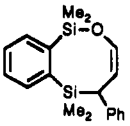
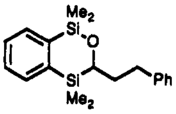
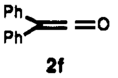
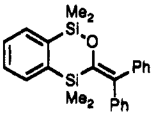
(6) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16.

(7) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992**, *428*, 1.

(8) Reddy, N. P.; Uchimaru, Y.; Lautenschlager, H.-J.; Tanaka, M. *Chem. Lett.* **1992**, 45.

0276-7333/92/2311-2639$03.00/0

Table I. Platinum-Catalyzed Reactions of Carbonyl Compounds with *o*-Bis(dimethylsilyl)benzene

carbonyl compd	catalyst[a]	temp, °C	time, h	product/yield[d]		
 **2a**	A	110	20	 **3a** 81%		
	B	80[c]	12	91%		
 **2b**	A	110	6	 **3b** 74%		
	B	80[c]	1	91%		
 **2c**	A	52	24		 **4c** 58%	
	B	52	6		51%	
 **2d**	A	40[c]	48		 **4d** 88%	
 **2e**	A	110	19	 **3e** 86%	 **4e** 9%	
	B	110	1	22%	16%	 **5e** 39%
 **2f**	A	30[c]	24	 **3f** 100%		

[a] A = $Pt(CH_2{=}CH_2)(PPh_3)_2$; B = $Pt(dba)_2$. [b] GC yields. [c] Effected in benzene (4 mL).

yielded within 12 h. Benzaldehyde (**2b**) also underwent 1,2 double silylation to produce **3b** under similar conditions. The rate of the reaction of **2b** was higher than that of **2a** with both catalysts. There was less than 7% of the five-membered cyclic disiloxane **6**[9] formed, and hydrosilylation products were not detected in each case.

6

When prop-2-enal (**2c**) was employed, 1,4 double silylation took place at 52 °C to form **4c** as the major product. The product that appeared to have come from 1,1 or 1,2 double silylation across the C=C double bond or from 1,2 double silylation across the C=O double bond was observed only in <2% yield. But-3-en-2-one (**2d**) similarly underwent 1,4 double silylation in 88% yield.

The $Pt(CH_2{=}CH_2)(PPh_3)_2$-catalyzed double silylation of (*E*)-3-phenyl-2-propenal (**2e**) needed a high reaction temperature (110 °C) and gave the 1,2-adduct across the C=O double bond **3e**. Unlike the reaction of prop-2-enal or but-3-en-2-one, the 1,4-adduct **4e** was a minor product. This is presumably associated with the steric hindrance of the phenyl group bound to the terminal carbon of the C=C—C=O moiety. When $Pt(dba)_2$ was used as catalyst for the reaction of **2e**, however, the main product was neither **3** nor **4**, but was **5e** (39%). As to the formation of **5e**, three routes may be conceivable: (1) the double hydrosilylation (1,4-hydrosilylation[10] with one of the two Si—H bonds of **1** followed by intramolecular 1,2-hydrosilylation of the resulting C=C bond with the other Si—H bond), (2) hydrogenation of **3e**, and (3) hydrogenation of the C=C bond of **2e** followed by dehydrogenative double

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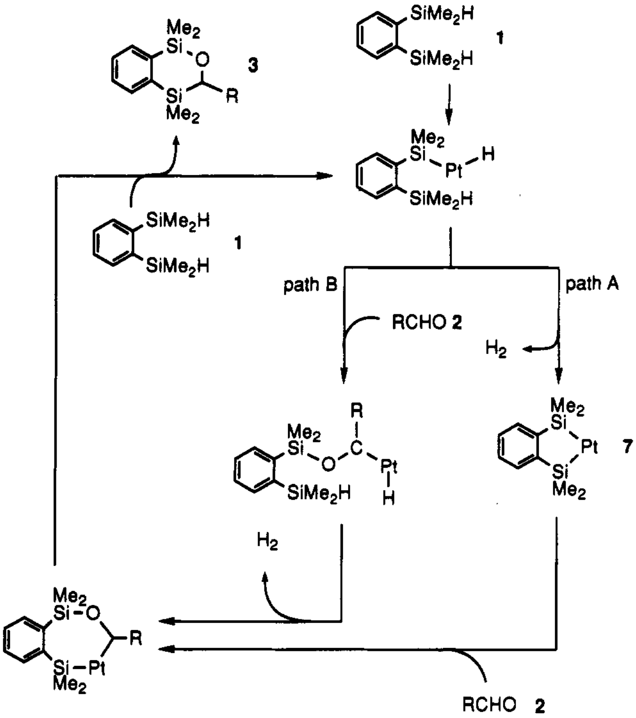
[9] Gladysz et al. reported almost quantitative formation of a cyclic disiloxane accompanied by a small amount of stilbene from a cyclic bis(silyl)iron complex with benzaldehyde. See: Johnson, D. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6433.

[10] 1,4-Hydrosilylation of cinnamaldehyde has been reported to be catalyzed by dichlorobis(2,4,6-collidine)platinum. See: Rumin, R. *J. Organomet. Chem.* **1983**, *247*, 351.

Scheme II



Pt = $Pt(PPh_3)_2$

silylation of the C=O bond of the resulting 3-phenylpropanal. When the reaction of **2b** (0.25 mmol, in refluxing toluene, 1 h, 0.005 mmol of $Pt(dba)_2$) with **1** was effected in the presence of **3e** (0.13 mmol, contaminated with 10% of **4e**), **3b** was normally formed with evolution of hydrogen gas, and hydrogenation of **3e** into **5e** took place only in 7% yield based on the charged amount of **3e**. In another experiment, hydrogen gas was bubbled into a refluxing toluene solution of **3e** (0.162 mmol), $Pt(dba)_2$ (0.005 mmol), **1** (0.025 mmol), and **2b** (0.025 mmol) for 1 h. However, the yield of **5e** was only 25% even though the reaction was carried out under the forcing conditions for hydrogenation. These results indicate that while the reaction of **2e** with **1** is in progress, the subsequent hydrogenation of **3e** takes place but that this is not the dominant route to **5e**. On the other hand, **2e** was hydrogenated to give 3-phenylpropanal in 32% yield when **2e** (0.25 mmol) in refluxing toluene was treated with hydrogen bubbling for 1 h in the presence of the same complex (0.005 mmol) and **1** (0.025 mmol). This suggests that route 3 is likely to be involved. However, this observation cannot be considered to be totally against route 1 since experimental conditions were set advantageously for hydrogenation. Indeed, dehydrogenative double silylation of **2e** effected under the standard conditions but with nitrogen bubbling into the solution ended up with nearly the same result as the foregoing standard experiment in which the top of the refluxing condenser was connected to the nitrogen stream. Combining all of these observations together, we consider that route 1 and/or 3 can be the provenance of **5e** and that route 2 plays only a minor role if any.

Diphenylketene (**2f**) also underwent dehydrogenative double silylation with **1**, and the 1,2-adduct across the carbonyl group **3f** was obtained quantitatively. The structure of **3f** was confirmed by X-ray crystallography (vide infra). Attempted reactions of acetophenone with **1** in the presence of either $Pt(CH_2{=}CH_2)(PPh_3)_2$ (150 °C, 18 h) or $Pt(dba)_2$ (150 °C, 18 h) failed, presumably because of the increased steric hindrance as compared with the foregoing carbonyl compounds.

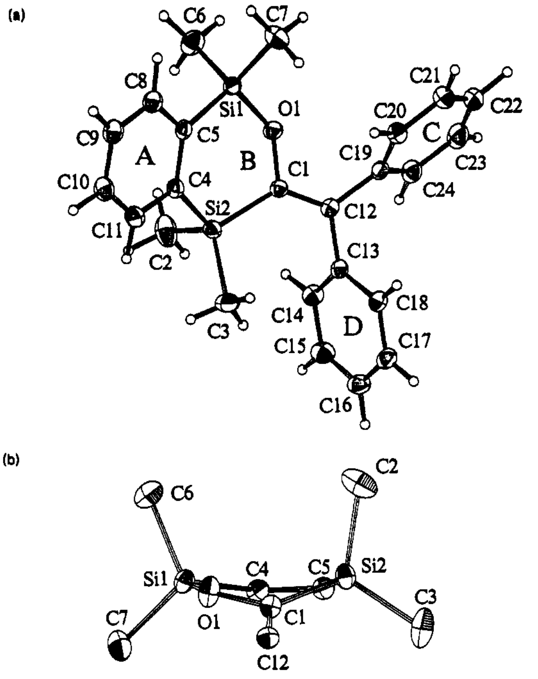
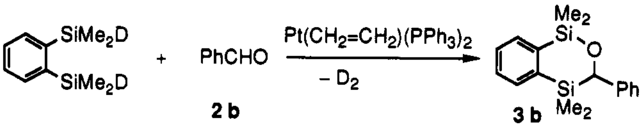


Figure 1. Perspective views of the molecule **3f** with the numbering scheme: (a, top) top view; (b, bottom) side view (only the 1,4-disila-2-oxa-5-cyclohexene ring is drawn for clarity).

Reaction Mechanism. The reaction of carbonyl groups is best explained by Scheme II. Treatment of **2b** with *o*-bis(deuteriodimethylsilyl)benzene in the presence of $Pt(CH_2{=}CH_2)(PPh_3)_2$ afforded only **3b**; deuterium incorporation was not observed in the product. This is in agreement with paths A and B. In addition, when compound **7**, which was separately prepared from **1** and $Pt(CH_2{=}CH_2)(PPh_3)_2$, was heated with **1** (1.0 equiv) and **2b** (1.6 equiv) at 110 °C for 30 min in an NMR tube, **3b** was formed in 73% yield and **7** was regenerated quantitatively. On the other hand, the reaction of **2b** (0.25 mmol) with phenyldimethylsilane (0.25 mmol) catalyzed by $Pt(CH_2{=}CH_2)(PPh_3)_2$ (0.005 mol) in toluene (4 mL) (a model reaction for path B) did not give (benzyloxy)phenyldimethylsilane in a detectable yield (the limit of detection ≈0.4%) even under forcing conditions (110 °C, 54 h), although traces of diphenyldimethylsilane and other unknown byproducts were formed. Accordingly, path A appears the more likely route.



(1)

Crystal Structure of 3f. Two ORTEP[11] drawings are shown in Figure 1. Details of the data collection, positional and thermal parameters, and selected bond distances and angles are summarized in Tables II–IV, respectively. All bond lengths are unexceptional. The heterocyclic ring (ring B) is best described as a flattened boat conformation. (Figure 1b and Table V). The phenyl ring A and the best-fit plane for ring B have a small dihedral angle of 9.8°. The C1-C12 double bond is slightly twisted. The torsion angles Si2–C1-C12-C13 and O1-C1-C12-C19 are 7.3 and 7.4°, respectively, and the dihedral angle between the two

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[11] Johnson, C. K. ORTEP, Report ORNL-3794. Oak Ridge National Laboratory: Oak Ridge, TN.

Table II. Crystallographic Data for 3f

formula	$C_{24}H_{26}Si_2O_1$
fw	386.65
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	11.400 (2)
b, Å	9.756 (3)
c, Å	20.341 (3)
β, deg	96.03 (1)
V, Å^3	2249.8 (4)
Z	4
calcd density, g cm^{-1}	1.14
cryst size, mm	1.0 × 0.7 × 0.2
diffractometer	Enraf-Nonius CAD4
λ(Cu Kα radiation), Å	1.5418
scan type	ω-scan
scan rate, deg min^{-1}	1–4 (in ω)
2θ range, deg	4–120
no. of reflcns measd	3786
no. of indep reflcns	3242
no. of indep reflcns used ($\lvert F_o\rvert \geq 3\sigma\lvert F_o\rvert$)	3036
transm factor[a]	0.678–1.00
decay	no
μ(Cu Kα), cm^{-1}	14.820
R	0.051
R_w[b]	0.072
S	1.628
differential Fourier map max/min, e Å^{-3}	+0.25/−0.34

[a] Correction: empirical ψ scan method. [b] $w = 1/(0.0040\lvert F_o\rvert^2 - 0.048\lvert F_o\rvert + 0.865)$.

Table III. Positional and Thermal Parameters for Non-Hydrogen Atoms of 3f[a]

atom	x	y	z	B(eq), Å^2
Si1	0.42376 (6)	0.13616 (6)	0.65761 (3)	3.49 (2)
Si2	0.46524 (6)	−0.20833 (7)	0.63583 (3)	3.80 (2)
O1	0.4967 (2)	0.0297 (2)	0.7094 (1)	4.7 (1)
C1	0.5006 (2)	−0.1119 (2)	0.7161 (1)	3.5 (1)
C2	0.5976 (3)	−0.2135 (6)	0.5899 (2)	7.4 (1)
C3	0.4042 (4)	−0.3836 (3)	0.6480 (2)	7.0 (1)
C4	0.3474 (2)	−0.1064 (3)	0.5856 (1)	3.7 (1)
C5	0.3297 (2)	0.0352 (2)	0.5945 (1)	3.6 (1)
C6	0.5354 (3)	0.2376 (4)	0.6189 (2)	6.1 (1)
C7	0.3319 (3)	0.2492 (4)	0.7047 (2)	5.6 (1)
C8	0.2414 (2)	0.1022 (3)	0.5539 (1)	4.5 (1)
C9	0.1723 (3)	0.0338 (3)	0.5045 (1)	5.2 (1)
C10	0.1894 (3)	−0.1038 (3)	0.4949 (1)	5.3 (1)
C11	0.2764 (3)	−0.1729 (3)	0.5349 (1)	4.7 (1)
C12	0.5316 (2)	−0.1603 (2)	0.7772 (1)	3.4 (1)
C13	0.5568 (2)	−0.3088 (2)	0.7891 (1)	3.5 (1)
C14	0.6522 (2)	−0.3731 (3)	0.7643 (1)	4.5 (1)
C15	0.6738 (3)	−0.5118 (3)	0.7766 (2)	5.4 (1)
C16	0.6017 (3)	−0.5868 (3)	0.8134 (2)	5.3 (1)
C17	0.5084 (3)	−0.5234 (3)	0.8393 (1)	4.7 (1)
C18	0.4878 (2)	−0.3853 (3)	0.8283 (1)	4.1 (1)
C19	0.5466 (2)	−0.0700 (3)	0.8364 (1)	3.7 (1)
C20	0.4578 (3)	0.0206 (3)	0.8504 (1)	4.9 (1)
C21	0.4723 (4)	0.1044 (4)	0.9060 (2)	6.7 (1)
C22	0.5735 (4)	0.0993 (4)	0.9479 (2)	7.1 (1)
C23	0.6618 (4)	0.0107 (4)	0.9352 (2)	6.7 (1)
C24	0.6500 (3)	−0.0754 (3)	0.8800 (1)	5.1 (1)

[a] $B_{eq} = {}^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + 2abB_{12}\cos\gamma + 2bcB_{23}\cos\alpha + 2caB_{13}\cos\beta]$.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for 3f

Bond Distances			
Si1–O1	1.642 (2)	C4–C5	1.410 (3)
C1–O1	1.388 (3)	C5–C8	1.395 (3)
Si1–C6	1.866 (2)	C8–C9	1.382 (4)
Si1–C6	1.851 (4)	C9–C10	1.373 (5)
Si1–C7	1.855 (4)	C10–C11	1.390 (4)
Si2–C1	1.891 (2)	C11–C4	1.403 (4)
Si2–C2	1.857 (4)	C1–C12	1.342 (3)
Si2–C3	1.873 (4)	C12–C13	1.491 (3)
Si2–C4	1.884 (2)	C12–C19	1.487 (3)
Bond Angles			
O1–Si1–C5	108.9 (1)	Si2–C1–C12	129.5 (2)
O1–Si1–C6	106.7 (1)	Si2–C4–C5	123.5 (2)
O1–Si1–C7	108.7 (1)	Si2–C4–C11	118.6 (2)
C5–Si1–C6	111.1 (1)	Si1–C5–C4	121.7 (2)
C5–Si1–C7	111.0 (1)	Si1–C5–C8	119.1 (2)
C6–Si1–C7	110.6 (2)	C4–C5–C8	119.2 (2)
C1–Si2–C2	109.7 (2)	C5–C8–C9	121.7 (3)
C1–Si2–C3	112.9 (2)	C8–C9–C10	119.8 (3)
C1–Si2–C4	106.3 (1)	C9–C10–C11	119.6 (3)
C2–Si2–C3	112.0 (2)	C10–C11–C4	121.9 (3)
C2–Si2–C4	108.2 (2)	C11–C4–C5	117.9 (2)
C3–Si2–C4	107.5 (1)	C1–C12–C13	121.4 (2)
Si1–O1–C1	134.5 (1)	C1–C12–C19	122.5 (2)
Si2–C1–O1	114.2 (2)	C13–C12–C19	116.0 (2)
O1–C1–C12	116.3 (2)		

Table V. Distances (Å) of Atoms from Best Fit Least-Squares Plane of 1,4-Disila-2-oxa-5-cyclohexene Ring in Compound 3f

Least-Squares Plane for Si1, C5, C4, Si2, C1, and O1 $(-0.83834X - 0.19436Y + 0.59457Z = 3.69)$[a]					
Si1	−0.044	C5	0.282	C4	0.275
Si2	−0.051	C1	0.399	O1	0.087
Least-Squares Plane for Si2, C1, O1, C12, C13, and C19 $(-0.98340X - 0.06054Y + 0.27341Z = 1.56)$[a]					
Si2	0.008	C1	0.001	O1	−0.075
C12	0.022	C13	−0.107	C19	0.129

[a] X, Y, and Z (in Å) are along a, b, and c, respectively.

planes defined by Si2, C1, O1 and C13, C12, C19 is 8.3°. Both of the two phenyl rings C and D attached to C12 are rotated relative to the best-fit plane for Si2, C1, O1, C12, C13, and C19 by 67.9 and 54.0°, respectively, and are nearly perpendicular to one another with a dihedral angle of 87.8°. The phenyl ring D is also nearly perpendicular to ring B with a dihedral angle of 86.9° (cf. dihedral angle between the rings B and C = 37.2°). The exocyclic Si2–C1–C12 angle (129.5°) is larger than theoretical value for the sp^2-carbon (120°), but the endocyclic Si2–C1–O1 angle (114.2°) is smaller. Additionally, the C2–Si2–C3 and C1–Si2–C3 angles (112.0 and 112.9°, respectively) are slightly larger than the conventional sp^3-silicon bond angle (109.8°). The deviations of these angles and the rotation of the phenyl ring D around the C12–C13 bond suggest that there is steric repulsion between the phenyl ring D and one of the methyl groups (C3) attached to Si2.

Experimental Section

General Comments. All manipulations were carried out under nitrogen. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with tetramethylsilane or chloroform standard on Hitachi R-40 (90 MHz) and/or Bruker AC-200 (200 MHz) instruments. Infrared spectra were measured on a JASCO A-302 spectrometer. Mass spectra (EI) were recorded on Shimadzu QP-1000 and JEOL JMS-DX303 GC-MS spectrometers. Solvents were appropriately dried, and distilled under nitrogen. Other liquid materials were also distilled before use. *o*-Bis(dimethylsilyl)benzene (1),[12] diphenylketene,[13] $Pt(CH_2{=}CH_2)(PPh_3)_2$,[14] $Pt(dba)_2$,[15] and $Me_2\overline{Si(o\text{-}C_6H_4)SiMe_2Pt}(PPh_3)_2$ (7)[16] were prepared by literature methods. *o*-Bis(deuteriodimethylsilyl)benzene was prepared by chlorination of 1 with the $PdCl_2$–CCl_4 system followed by reduction with $LiAlD_4$.[7]

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Typical Procedure for Catalytic Reactions: Reaction of Heptanal (2a) with *o*-Bis(dimethylsilyl)benzene (1). A toluene solution (2 mL) of heptanal (**2a**, 0.25 mmol) was added to a mixture of 1 (0.25 mmol), $Pt(CH_2{=}CH_2)(PPh_3)_2$ (0.005 mmol), 2-methylnaphthalene (an internal standard for GC analysis, 10 mg), and toluene (2 mL). GC analysis after heating at 110 °C for 20 h revealed the formation of the 1,2-adduct **3a** in 81% yield. The product was isolated by preparative TLC on silica gel eluting with benzene and distillation as a pale yellow oil in 75% yield. Bp: 95–105 °C C/0.5 Torr (Kugelrohr). IR (neat, cm^{-1}): 1246, 1121, 1050, 822. ^{1}H NMR: δ 7.55–7.35 (m, 4 H, aromatic), 3.8–3.7 (m, 1 H, Si—CH—O), 1.8–1.5 (m, 4 H, CH_2), 1.5–1.15 (br s, 6 H, CH_2), 0.90 (t, 3 H, *J* = 7, $\mathrm{CH_2C}H_3$), 0.35 (s, 3 H, SiMe), 0.31 (s, 3 H, SiMe), 0.28 (s, 3 H, SiMe), 0.25 (s, 3 H, SiMe). ^{13}C NMR: δ 144.9, 144.1, 133.2, 132.3, 128.44, 128.38, 66.6, 33.2, 31.9, 29.1, 26.6, 22.7, 14.1, 0.2, –0.7, –4.1, –4.8. MS: *m/z* 306 (M^{+}, 0.1), 291 (M^{+} – Me, 0.1), 193 (100). HRMS Calcd for $C_{17}H_{30}OSi_2$: 306.1835. Found: 306.1827.

Compound 3b. Recrystallized from ethanol after distillation. Bp: 123 °C/0.8 Torr (Kugelrohr). Mp: 80.5–81.0 °C. IR (Nujol, cm^{-1}): 1255, 1250, 1020, 780. ^{1}H NMR: δ 7.6–7.1 (m, 9 H, aromatic), 5.00 (s, 1 H, Si–CH–O), 0.43 (s, 3 H, SiMe), 0.38 (s, 3 H, SiMe), 0.29 (s, 3 H, SiMe), 0.00 (s, 3 H, SiMe). ^{13}C NMR: δ 144.6, 143.7, 142.6, 133.4, 132.5, 128.64, 128.60, 128.1 (2 C), 125.5, 124.5 (2 C), 69.8, 0.2, –0.6, –4.98, –5.03. MS: *m/z* 298 (M^{+}, 39), 283 (M^{+} – Me, 16), 193 (100). Anal. Calcd for $C_{17}H_{22}OSi_2$: C, 68.40; H, 7.43. Found: C, 68.09; H, 7.48.

Compound 4c. Bp: 120 °C/56 Torr (Kugelrohr). IR (neat, cm^{-1}): 1657, 1260, 1250, 1119, 1074, 830. ^{1}H NMR: δ 7.75–7.3 (m, 4 H, aromatic), 6.17 (dt, *J* = 6.0, 2.0, 1 H, =CH—O), 4.86 (q, *J* = 6.0, 1 H, =C*H*—CH_2), 1.47 (dd, *J* = 6.0, 2.0, 2 H, Si—CH_2), 0.46 (s, 6 H, SiMe), 0.39 (s, 6 H, SiMe). ^{13}C NMR: δ 144.6, 143.9, 138.8, 134.9, 133.7, 128.8, 128.1, 110.4, 14.5, 0.8 (2 C), 0.1 (2 C). MS: *m/z* 248 (M^{+}, 10), 233 (M^{+} – Me, 8), 193 (100). HRMS calcd for $C_{13}H_{20}OSi_2$: 248.1053. Found: 248.1055.

Compound 4d. Bp: 65 °C/0.5 Torr (Kugelrohr). IR (neat, cm^{-1}): 1260, 1250, 1160, 940, 830. ^{1}H NMR: δ 7.7–7.3 (m, 4 H, aromatic), 4.71 (t, *J* = 6.6, 1 H, =CH), 1.73 (s, 3 H, =C—Me), 1.53 (d, *J* = 6.6, 2 H, CH_2), 0.47 (s, 6 H, SiMe), 0.32 (s, 6 H, SiMe). ^{13}C NMR: δ 146.8, 146.0, 143.4, 134.9, 133.8, 128.7, 127.9, 103.9, 22.1, 14.7, 1.3 (2 C), 0.35 (2 C). MS: *m/z* 262 (M^{+}, 45), 247 (M^{+} – Me, 8), 194 (100). HRMS calcd for $C_{14}H_{22}OSi_2$: 262.1269. Found: 262.1238.

Compound 3e. Bp: 143–150 °C/0.4 Torr (Kugelrohr). IR (neat, cm^{-1}): 1420, 1249, 1118, 1087, 829. ^{1}H NMR: δ 7.45–7.1 (m, 9 H, aromatic), 6.53 (dd, *J* = 15.8, 1.4, 1 H, Ph—C*H*=), 6.25 (dd, *J* = 15.8, 5.5, 1 H, =CH—C—O), 4.56 (dd, *J* = 5.5, 1.4, 1 H, Si—CH—O), 0.34 (s, 3 H, SiMe), 0.30 (s, 3 H, SiMe), 0.27 (s, 3 H, SiMe), 0.13 (s, 3 H, SiMe). ^{13}C NMR: δ 144.5, 143.5, 137.7, 133.2, 132.5, 129.7, 128.7, 128.6, 128.4 (2 C), 126.7, 126.1, 126.0 (2 C), 68.9, 0.2, –0.5, –4.8 (2 C). MS: *m/z* 324 (M^{+}, 41), 309 (M^{+} – Me, 3), 193 (32), 115 (100). HRMS calcd for $C_{19}H_{24}OSi_2$: 324.1365. Found: 324.1370.

Compound 4e. ^{1}H MMR: δ 7.45–7.0 (m, 9 H, aromatic), 6.21 (dd, *J* = 5.5, 1.6, 1 H, O—CH=), 4.88 (dd, *J* = 5.6, 5.5, 1 H, O—CH=C*H*), 2.81 (dd, *J* = 5.6, 1.6, 1 H, C*H*—Ph), 0.45 (s, 3 H, SiMe), 0.42 (s, 3 H, SiMe), 0.28 (s, 3 H, SiMe), 0.10 (s, 3 H, SiMe). ^{13}C NMR: δ 143.5, 143.3, 138.6, 135.6, 133.7, 131.0, 129.0 (2 C), 128.3 (2 C), 127.9 (2 C), 124.8, 116.5, 36.4, 1.0, 0.3, 0.0, –0.8. MS: *m/z* 324 (M^{+}, 66), 309 (M^{+} – Me, 12), 193 (45), 115 (100). HRMS Calcd for $C_{19}H_{24}OSi_2$: 324.1365. Found: 324.1367.

Compound 5e. Bp: 90–110 °C/0.3 Torr (Kugelrohr). IR (neat, cm^{-1}): 1420, 1248, 1120, 1025, 828. ^{1}H NMR: δ 7.6–7.1 (m, 9 H, aromatic), 3.75 (dd, *J* = 11.5, 2.9, 1 H, O–CH), 3.2–2.9 (m, 1 H), 2.8–2.6 (m, 1 H), 2.2–2.0 (m, 1 H), 2.0–1.8 (m, 1 H), 0.39 (s, 3 H, SiMe), 0.32 (s, 3 H, SiMe), 0.24 (s, 6 H, SiMe). ^{13}C NMR: δ 144.7, 143.8, 142.3, 133.2, 132.4, 128.6 (2 C), 128.4 (2 C), 128.2 (2 C), 125.6, 65.4, 34.8, 32.7, 0.4, –0.5, –4.4, –4.8. MS: *m/z* 326 (M^{+}, 1), 235 (M^{+} – CH_2Ph, 100), 193 (62). HRMS Calcd for $C_{19}H_{26}OSi_2$: 326.1522. Found: 326.1523.

Compound 3f. Recrystallized from diethyl ether/hexane after distillation. Bp: 150 °C/0.8 Torr (Kugelrohr). Mp: 65–65 °C. IR (neat, cm^{-1}): 1260, 1250, 1195, 1120, 830. ^{1}H NMR: δ 7.45–7.05 (m, 14 H, aromatic), 0.39 (s, 6 H, SiMe), 0.01 (s, 6 H, SiMe). ^{13}C NMR: δ 152.6, 144.6, 143.6, 140.7, 139.7, 137.9, 133.2, 131.9, 131.6 (2 C), 129.6 (2 C), 128.9, 128.3, 128.0 (2 C), 127.5 (2 C), 127.3, 126.3, 0.4 (2 C), –0.6 (2 C). MS: *m/z* 386 (M^{+}, 96), 371 (M^{+} – Me, 10), 193 (100). Anal. Calcd for $C_{24}H_{26}OSi_2$: C, 74.56; H 6.78. Found: C, 74.33; H 6.69.

X-ray Structure Determination of 3f. Absorption corrections were empirical, based upon ψ scans. Cell constants were obtained from 25 high-angle ($30 < 2\theta < 40°$) reflections. The structure was solved by direct methods using MULTAN78.[17] Sixteen hydrogen atoms were introduced from the difference Fourier map, and the remainder were placed at calculated positions. The structural parameters were refined by a full-matrix least-squares methods with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms. Scattering factors for atoms were taken from ref. 18. Calculations were carried out on a FACOM M-780 computer with UNICS III.[19]

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Supplementary Material Available: Tables of hydrogen parameters, anisotropic thermal parameters, bond distances and angles, and torsion angles and a unit cell and packing diagram for **3f** (7 pages). Ordering information is given on any current masthead page.

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