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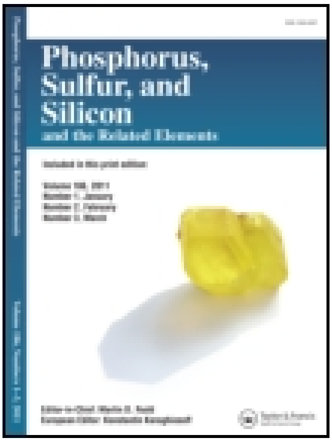

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Synthesis and Properties of Pentacoordinated Phenoxysilane and Carboxysilanes with Intramolecular Nitrogen-Silicon Coordination

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SYNTHESIS AND PROPERTIES OF PENTACOORDINATED PHENOXYSILANE AND CARBOXYSILANES WITH INTRAMOLECULAR NITROGEN–SILICON COORDINATION

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Reactions of a neutral pentacoordinated monohydrosilane bearing a dative N—Si bond with phenol and benzoic acid derivatives gave the corresponding pentacoordinated phenoxysilane and carboxysilanes, respectively. X-ray crystallographic analyses of these silanes revealed that the distance of the N—Si dative bond is shortened and the pentacoordination character of the silicon center becomes greater with the increase in the electron-withdrawing character of the apical substituent on silicon.

Keywords Carboxysilanes; intramolecular coordination; pentacoordinated silicon compounds; phenoxysilanes

INTRODUCTION

Highly coordinated silicon compounds are known to exhibit distinct difference in reactivities, structures, and properties from their tetracoordinated counterparts.[1] Among them, much attention has been paid to neutral pentacoordinated silicon compounds with an intramolecular N—Si dative bond for examination of their intriguing structures and reactivities that originate from the characteristics of the dative bond.[2] In this class of compounds,

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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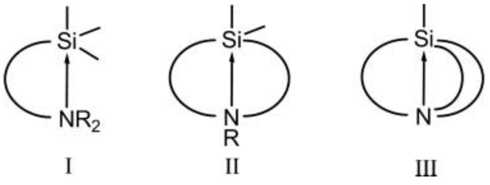


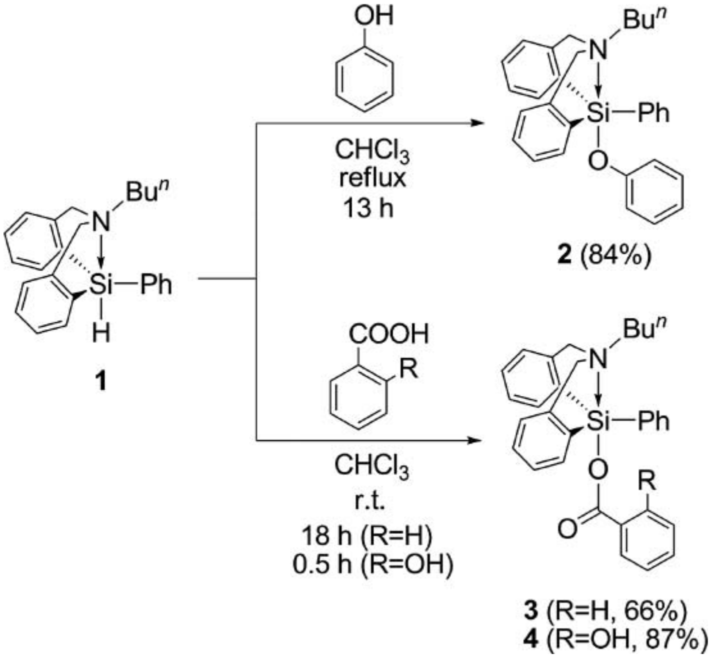
Figure 1 Schematic representation of pentacoordinated silanes with monocyclic (I), bicyclic (II), and tricyclic (III) motifs.

monocyclic,[2a,b] bicyclic,[2c,d] or tricyclic frameworks,[2e,f] have been utilized to hold the nitrogen and silicon atoms in proximity (Figure 1), and it was found that the N—Si interaction is sensitive to the electronic character of the substituents on the silicon atom. To date, extensive structural investigations concerning pentacoordinated silicon compounds with a tricyclic motif such as silatranes have been undertaken, which have revealed that electron-withdrawing substituents on the silicon shorten the N—Si distance.[3] For pentacoordinated silanes with the mono- and bicyclic frameworks, however, systematic study from this viewpoint is still missing in spite of extensive exploration of their reactivities. Recently, we have reported the synthesis of neutral pentacoordinated hydrosilanes with a bicyclic motif based on the dibenzosilazocine framework[4a] and application to the construction of a tweezer-type cavitand.[4b] This type of bicyclic motif has been successfully utilized for the investigation of the substituent effects on highly coordinated main group elements.[5] Several compounds bearing the dibenzosilazocine framework have been reported by Carré et al.,[2c] although crystallographic analysis has been performed only for dimethyl- and difluoro-substituted derivatives. In this article, we report the synthesis of neutral pentacoordinated phenoxy- and carboxysilanes by the reaction of a pentacoordinated hydrosilane with phenol and benzoic acid derivatives, respectively, along with their structural characterization.

RESULTS AND DISCUSSION

Treatment of neutral pentacoordinated hydrosilane **1**[4a] with phenol in chloroform under reflux for 13 h gave the corresponding phenoxysilane **2** in 84% yield. The reaction of **1** with benzoic acid proceeded under milder conditions, and silyl benzoate **3** was formed after 18 h at room temperature, which was isolated in 66% yield. It is of note that salicylic acid reacts with **1** much faster than benzoic acid. The reaction was completed within 10 min at room temperature, affording silyl salicylate **4** in 87% yield. Compounds **2**–**4** (Scheme 1) were unambiguously characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si) and elemental analyses. The ^{29}Si NMR (CDCl$_3$) resonances of **2–4** appear at −40.3, −44.1, and −46.1 ppm, respectively, the high-field shifts of which are typical for pentacoordinated silicon compounds.[6]

While there have been extensive studies on pentacoordinated aryloxy- and carboxysilanes with intramolecular coordination of an amine unit, their structural properties have been hardly explored, and crystallographic analyses of the compounds bearing a monodentate aryloxy or carboxy ligand have been performed only for silatrane derivatives.[7] The structures of phenoxysilane **2** and carboxysilanes **3** and **4** were established by X-ray crystallographic analyses. Figure 2 shows the ORTEP drawing of **2**. The selected bond lengths and angles of **2** are given in Table I.



Scheme 1

In the crystal structure of phenoxysilane **2**, there are two independent molecules in the asymmetric unit. The silicon atoms of both fragments adopt slightly distorted trigonal bipyramidal structures with the nitrogen and oxygen atoms at apical positions and three carbon atoms at equatorial positions. The N—Si distances of **2** [2.439(4) and 2.419(4) Å for

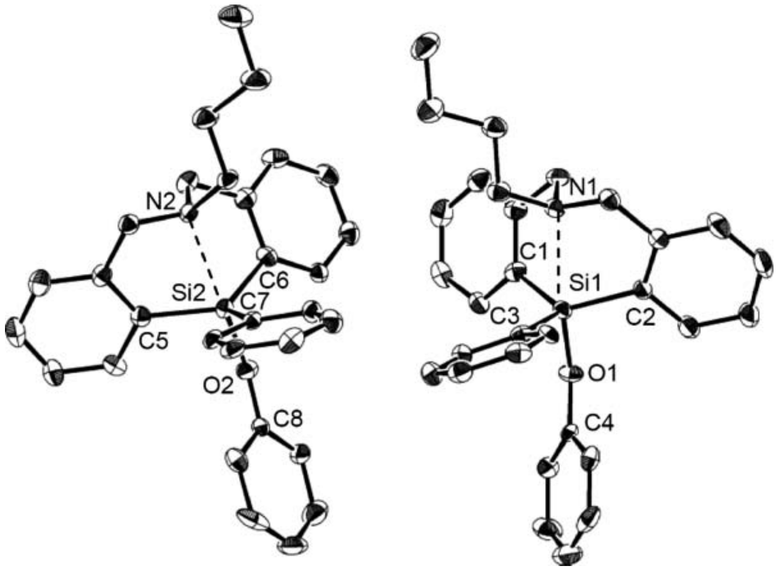


Figure 2 ORTEP drawing of **2** (50% probability). Hydrogen atoms are omitted for clarity.

Table I Selected bond lengths (Å) and angles (deg) for **2**

Bond lengths		Bond angles			
Si(1)—N(1)	2.439(4)	N(1)—Si(1)—O(1)	167.72(14)	N(2)—Si(2)—O(2)	168.02(15)
Si(1)—O(1)	1.696(3)	N(1)—Si(1)—C(1)	77.19(17)	N(2)—Si(2)—C(5)	77.46(16)
Si(1)—C(1)	1.880(5)	N(1)—Si(1)—C(2)	76.64(16)	N(2)—Si(2)—C(6)	76.82(17)
Si(1)—C(2)	1.890(5)	N(1)—Si(1)—C(3)	88.03(15)	N(2)—Si(2)—C(7)	87.33(16)
Si(1)—C(3)	1.873(4)	O(1)—Si(1)—C(1)	100.83(19)	O(2)—Si(2)—C(5)	94.08(18)
O(1)—C(4)	1.360(5)	O(1)—Si(1)—C(2)	94.71(18)	O(2)—Si(2)—C(6)	101.10(18)
Si(2)—N(2)	2.419(4)	O(1)—Si(1)—C(3)	103.73(16)	O(2)—Si(2)—C(7)	104.29(17)
Si(2)—O(2)	1.692(3)	C(1)—Si(1)—C(3)	113.3(2)	C(5)—Si(2)—C(7)	118.73(19)
Si(2)—C(5)	1.882(4)	C(1)—Si(1)—C(2)	122.22(19)	C(5)—Si(2)—C(6)	121.7(2)
Si(2)—C(6)	1.884(5)	C(2)—Si(1)—C(3)	116.2(2)	C(6)—Si(2)—C(7)	111.29(19)
Si(2)—C(7)	1.885(4)	Si(1)—O(1)—C(4)	138.0(3)	Si(2)—O(2)—C(8)	140.2(3)
O(2)—C(8)	1.352(5)				

each fragment] are much shorter than the sum of van der Waals radii of silicon and nitrogen (3.65 Å),[8] proving strong interaction between the two atoms in the crystalline state, although they are longer than the values observed for silatranes bearing an aryloxy ligand (2.07–2.11 Å).[7a,b] Carré et al. reported the crystal structure of a pentacoordinated difluorosilane with the same type of dibenzosilazocine framework,[2c] the N—Si distance of which [2.430 Å (average)] is close to those of **2**. The Si—O bond lengths of **2** [1.696(3) and 1.692(3) Å for each fragment] are slightly longer than that of (2-bromophenoxy)triphenylsilane (1.645(4) Å),[9] indicating the hypervalent character of the Si—O bond of **2**.

The ORTEP drawings of carboxysilanes **3** and **4** are shown in Figures 3 and 4, respectively. The selected bond lengths and angles of **3** and **4** are given in Table II. In silyl benzoate **3**, the N—Si distance is 2.315(2) Å, which is much shorter than that of **2**. Silyl salicylate **4** showed even shorter N—Si distance (2.2865(17) Å), although it is still longer than those of silatranes bearing an carboxy ligand (2.05–2.07 Å).[7c,d] There have been several examples of pentacoordinated silanes with a salicylate ligand,[10] but in all cases the salicylate serves as an *O*,*O*-bidentate ligand to form a cyclic structure. In contrast, a monodentate coordination of the salicylate ligand is clearly shown in the crystal structure of **4**, where the *o*-OH group is located in the far side of the silicon atom.

The pentacoordination characters (%TBP$_a$/%TBP$_e$)[11] and the N—Si bond distances of **2**–**4** are summarized in Table III along with their ^{29}Si NMR chemical shifts. The geometry around the silicon center becomes closer to the ideal TBP as the electron-withdrawing ability of the substituent at the apical position is higher.[12] The N—Si bond distance also depends on the electronic nature of the apical substituent and is shortened as the pentacoordination character becomes greater, as has been observed for the analogues with other main group element bearing the same type of framework.[5] In the ^{29}Si NMR spectra, small but apparent high-field shifts were observed as the apical substituent becomes electron-withdrawing, showing the increase in the degree of pentacoordination. These results indicate that the correlation between pentacoordination character and electronic nature of the apical substituent is preserved also in solution.

In summary, we have synthesized neutral pentacoordinated phenoxy- and carboxysilanes with a N—Si dative bond bearing a bicyclic framework. We have also performed a systematic structural analysis of the phenoxy- and carboxysilanes and revealed that, in analogy with neutral pentacoordinated organosilanes with a tricyclic motif such as silatranes,

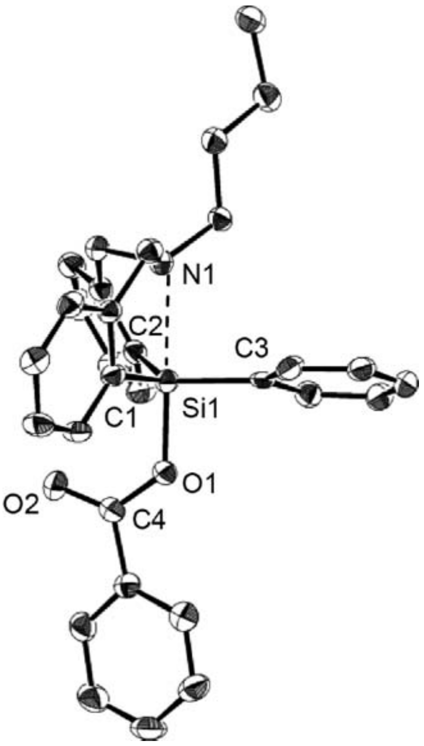


Figure 3 ORTEP drawing of **3** (50% probability). Hydrogen atoms are omitted for clarity.

Table II Selected bond lengths (Å) and angles (deg) for **3** and **4**

3		4	
	Bond lengths		
Si(1)−N(1)	2.315(2)	Si(1)−N(1)	2.2865(17)
Si(1)−O(1)	1.768(2)	Si(1)−O(1)	1.7772(14)
Si(1)−C(1)	1.886(3)	Si(1)−C(1)	1.880(2)
Si(1)−C(2)	1.881(3)	Si(1)−C(2)	1.880(2)
Si(1)−C(3)	1.878(2)	Si(1)−C(3)	1.868(2)
O(1)−C(4)	1.335(3)	O(1)−C(4)	1.314(2)
C(4)−O(2)	1.219(3)	C(4)−O(2)	1.236(2)
	Bond angles		
N(1)−Si(1)−O(1)	175.86(7)	N(1)−Si(1)−O(1)	171.25(7)
N(1)−Si(1)−C(1)	79.07(10)	N(1)−Si(1)−C(1)	79.49(8)
N(1)−Si(1)−C(2)	78.74(10)	N(1)−Si(1)−C(2)	79.61(8)
N(1)−Si(1)−C(3)	90.73(10)	N(1)−Si(1)−C(3)	89.37(8)
O(1)−Si(1)−C(1)	99.70(11)	O(1)−Si(1)−C(1)	93.45(8)
O(1)−Si(1)−C(2)	98.84(11)	O(1)−Si(1)−C(2)	100.03(8)
O(1)−Si(1)−C(3)	93.37(10)	O(1)−Si(1)−C(3)	98.55(8)
C(1)−Si(1)−C(3)	114.05(11)	C(1)−Si(1)−C(3)	117.64(10)
C(1)−Si(1)−C(2)	123.46(10)	C(1)−Si(1)−C(2)	121.50(9)
C(2)−Si(1)−C(3)	117.53(12)	C(2)−Si(1)−C(3)	116.07(9)
Si(1)−O(1)−C(4)	127.18(16)	Si(1)−O(1)−C(4)	127.82(13)
O(1)−C(4)−O(2)	123.3(3)	O(1)−C(4)−O(2)	123.07(18)

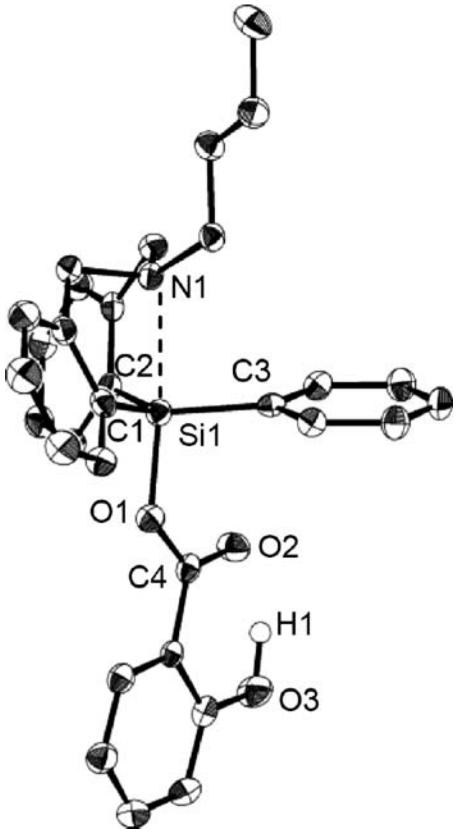


Figure 4 ORTEP drawing of **4** (50% probability). Hydrogen atoms, except for that of the hydroxy group, are omitted for clarity.

the dative N—Si bond distance is shortened with the increase in the electron-withdrawing character of the substituent at the apical position, and the pentacoordination character at the silicon center concomitantly becomes greater.

EXPERIMENTAL

All reactions were carried out under an argon atmosphere. Melting points were determined on a Yanaco micro melting point apparatus. All melting points were uncorrected. Chloroform was distilled from calcium hydride under an Ar atmosphere before use. ^{1}H,^{13}C, and^{29}Si NMR spectra were recorded on a Bruker DRX-500 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced using a residual peak of $CDCl_3$ (^{1}H, δ_H 7.25, ^{13}C, δ_C 77.0) as an

Table III Selected structural parameters and ^{29}Si NMR (99 MHz, $CDCl_3$) data of **2**, **3**, and **4**

	N—Si/Å	%TBP$_e$/%TBP$_a$	δ_{Si}
2	2.439(4)	74/50	−40.3
3	2.315(2)	84/63	−44.1
4	2.2865(17)	85/62	−46.1

internal standard. ^{29}Si NMR chemical shifts are reported relative to Me_4Si (0 ppm) in ppm. IR spectra were recorded on JASCO V-650. Gel permeation liquid chromatography (GPLC) was performed by LC-918 and LC-9204 with JAIGEL 1H+2H columns (Japan Analytical Industry) with chloroform as solvent. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, the University of Tokyo, or on a Perkin-Elmer PE2400 Series II CHNS/O Analyzer. Pentacoordinated hydrosilane **1** was prepared according to the reported procedure.[4a]

Synthesis of Phenoxysilane 2

To the mixture of monohydrosilane **1** (116 mg, 0.325 mmol) and phenol (31 mg, 0.33 mmol), $CHCl_3$ (3 mL) was added. After stirring for 13 h at reflux temperature, the solvent was removed, and the residue was purified by GPLC to give phenoxysilane **2** as a colorless solid (123 mg, 0.272 mmol, 84%). Mp 78–80°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.65 (t, $^3J_{HH} = 7.3$ Hz, 3H), 0.83–0.87 (m, 2H), 1.17–1.23 (m,2H), 1.44–1.46 (m, 2H), 3.68 (d, $^2J_{HH} = 14.7$ Hz, 2H), 3.74 (d, $^2J_{HH} = 14.7$ Hz, 2H), 6.70 (tt, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.1$ Hz, 1H), 6.75 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 1.1$ Hz, 2H), 6.98–7.02 (m, 2H), 7.14–7.21 (m, 5H), 7.26–7.28 (m, 2H), 7.34–7.40 (m, 4H), 8.24–8.26 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.6 (q), 20.5 (t), 24.5 (t), 52.3 (t), 55.6 (t), 119.2 (d), 120.1 (d), 125.6 (d), 127.3 (d), 127.4 (d), 128.1 (d), 128.7 (d), 129.9 (d), 132.3 (d), 133.0 (s), 136.7 (s), 138.5 (d), 146.5 (s), 157.6 (s); ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$) δ –40.3. Anal. Calcd. For $C_{30}H_{31}NOSi$: C, 80.13; H, 6.95; N 3.11. Found: C, 80.07; H, 6.97; N, 2.88.

Synthesis of Carboxysilane 3

To the mixture of monohydrosilane **1** (288 mg, 0.806 mmol) and benzoic acid (99 mg, 0.81 mmol), $CHCl_3$ (4 mL) was added. After stirring for 18 h at room temperature, the solvent was removed and the residue was purified by GPLC to give carboxysilane **3** as colorless solid (253 mg, 0.529 mmol, 66%). Mp 65–67°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.67 (t, $^3J_{HH} = 7.3$ Hz, 3H), 0.84–0.90 (m, 2H), 1.21–1.28 (m, 2H), 1.48–1.51 (m, 2H), 3.72 (d, $^2J_{HH} = 14.6$ Hz, 2H), 3.76 (d, $^2J_{HH} = 14.6$ Hz, 2H), 7.18–7.26 (m, 7H), 7.36–7.43 (m, 7H), 7.51 (tt, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.4$ Hz, 1H), 8.10–8.15 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.6 (q), 20.5 (t), 24.4 (t), 52.6 (t), 55.5 (t), 125.5 (d), 127.3 (d), 127.5 (d), 128.1 (d), 128.3 (d), 130.1 (d), 130.1 (d), 131.6 (s), 132.0 (d), 132.3 (d), 133.5 (s), 136.5 (s), 137.8 (d), 145.8 (s), 166.7 (s); ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$) δ –44.1; IR (KBr) $\nu_{C=O}$ 1687 cm^{-1}. Anal. Calcd. For $C_{31}H_{31}NO_2Si$: C, 77.95; H, 6.54; N 2.93, Found: C, 77.74; H, 6.83; N, 2.66.

Synthesis of Carboxysilane 4

The carboxysilane **4** (374 mg, 0.758 mmol, 87%) was prepared from monohydrosilane **1** (312 mg, 0.873 mmol) and salicylic acid (122 mg, 0.883 mmol) by the same procedure as the synthesis of **3**, while the reaction time was 0.5 h. Mp 123–125°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.66 (t, $^3J_{HH} = 7.3$ Hz, 3H), 0.85–0.90 (m, 2H), 1.23–1.29 (m, 2H), 1.53–1.56 (m, 2H), 3.76 (d, $^2J_{HH} = 14.7$ Hz, 2H), 3.80 (d, $^2J_{HH} = 14.7$ Hz, 2H), 6.88 (dt, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 1.0$ Hz, 1H), 6.92 (dd, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 1.0$ Hz, 1H), 7.20–7.29 (m, 5H), 7.37–7.44 (m, 7H), 8.05–8.07 (m, 3H), 11.48 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.5 (q), 20.4 (t), 24.5 (t), 52.7 (t), 55.6 (t), 115.4 (s), 117.2 (d), 118.6 (d), 125.6 (d), 127.5 (d), 127.7 (d), 128.5 (d), 130.3 (d), 130.8 (d), 131.2 (s), 132.2 (d), 134.7 (d), 136.2 (s), 137.6 (d), 145.5 (s), 162.2 (s), 171.0 (s); ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$) δ –46.1; IR (KBr) $\nu_{C=O}$ 1606, 1647 cm^{-1}. Anal. Calcd. For $C_{31}H_{31}NO_3Si$: C, 75.42; H, 6.33; N 2.84, Found C, 75.58; H, 6.57; N, 2.64.

X-Ray Crystallographic Analysis of 2, 3, and 4

Single crystals of **2**, **3**, and **4** were grown in their chloroform/hexane solutions. The intensity data were collected at 120 K on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å). Crystallographic and experimental data are listed in Table IV. The structures were solved by the direct method and refined by full-matrix least squares on F^2 using SHELXL 97.[13] The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were idealized by using the riding models except for the OH hydrogen of **4**, which was located in the difference Fourier map and refined isotropically. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 721463, 721464, and 721465 for **2**, **3**, and **4** respectively. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44–1223-336-033; e-mail: deposit@ccdc.cam.ac.jk or www: http://www.ccdc.cam.ac.uk).

Table IV Crystallographic data for **2**, **3**, and **4**

	2	3	4
Formula	$C_{30}H_{31}NOSi$	$C_{31}H_{31}NO_2Si$	$C_{31}H_{31}NO_3Si$
Temperature/K	120(2)	123(2)	120(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P1$	$P2_1/c$	$P2_1/c$
a/Å	9.628(5)	9.081(6)	8.6593(18)
b/Å	10.143(4)	18.032(10)	17.938(4)
c/Å	13.930(6)	15.749(10)	17.321(4)
α/deg	66.272(14)		
β/deg	82.83(2)	95.935(13)	102.809(3)
γ/deg	88.67(2)		
V/Å^3	1235.2(10)	2565(3)	2623.4(9)
Z	2	4	4
Calculated density/g cm^{-3}	1.209	1.237	1.250
Reflections collected	8093	10995	17116
Unique	6056	3720	4614
R_{int}	0.0326	0.0447	0.0703
F_{000}	480	1016	1048
Limiting indices	$-11 \le h \le 11$	$-7 \le h \le 10$	$-10 \le h \le 7$
	$-12 \le k \le 11$	$-19 \le k \le 20$	$-21 \le k \le 21$
	$-16 \le l \le 15$	$-18 \le l \le 16$	$-20 \le l \le 20$
Restraints/parameters	3/597	0/317	0/330
Goodness of fit (F^2)	1.080	1.079	1.001
R indices ($I > 2\sigma(I)$)	$R1 = 0.0566$	$R1 = 0.0467$	$R1 = 0.0478$
	$wR2 = 0.1298$	$wR2 = 0.1084$	$wR2 = 0.1132$
R indices (all data)	$R1 = 0.0613$	$R1 = 0.0711$	$R1 = 0.0594$
	$wR2 = 0.1336$	$wR2 = 0.1243$	$wR2 = 0.1270$

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