Synthesis and structure of pentacoordinated monoorganosilane derivatives of pyridine ligands

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Abstract

The reaction of 2,6-disubstituted pyridines with bis(dimethylamine)dimethylsilane, dichlorophenylmethylsilane and dichlorodiphenylsilane yielded the monomeric silanes: 2,6-pyridinebis(1,1-di-*p*-bromophenylmethoxy)dimethylsilane (9a), 2,6-pyridinebis(1,1-di-*p-tert*-butylphenylmethoxy)dimethylsilane (9b), 2,6-pyridinebis(1,1-diphenylethoxy)methylphenylsilane (12a) and 2,6-pyridinebis(1,1-adamantylethoxy)diphenylsilane (12b). The ^{29}Si-NMR data for these compounds confirmed the presence of N→Si bonds and the variable temperature NMR study of 12a and 12b showed the existence of a fluxional behavior for the 2,6-diethoxypyridine derivatives, additionally the X-ray diffraction study of 9a showed that in this compound the silicon atom adopts a square pyramidal geometry. Moreover, 1,3,10,12-tetraoxo-2,11-(dimethylsilylene)[5.5]paracyclophane (10) was synthesized from 1,4-benzenedimethanol and its structure established by X-ray crystallographic analysis showing that the aromatic rings are not perfectly eclipsed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silane; Pyridinediols; Pentacoordinated; 1,4-Benzenedimethanol; ^{29}Si-NMR

1. Introduction

Compounds with pentacoordinated silicon atoms have attracted great interest from both the structural and reactivity point of view [1–3]. In previous studies on organosilicon compounds it has been described that the reaction of 2,6-pyridinedimethanol with dimethyldichlorosilane affords dimeric compound 1 [4]. Subsequent studies showed that cyclophane type structures (1–4) can also be obtained by reacting 2,6-pyridine or 1,3-benzenedimethanol with dichlorosilanes [5]. It should be noted, however, that the ^{29}Si-NMR chemical shift for compound 1 in both reports differed by 8.1 ppm [4,5] (Fig. 1).

More recently we reported the synthesis and X-ray structure of a cyclodisiloxane from the reaction of 2,6-pyridinedimethanol with diphenyldichlorosilane [6] as well as the synthesis of dimer 2 which showed the same ^{29}Si-NMR chemical shift as that reported by

Grignon-Dubois [5]. On the other hand it has been reported that treatment of 2,6-diethoxypyridine type ligands with chlorosilanes yields monomeric compounds (5–7) (Fig. 2) in which the N→Si bond is present [4,6,7].

Our interest in the study of compounds containing silicon led us to the preparation of 1,3,10,12-tetraoxo-2,11-(diphenylsilylene)[5.5]paracyclo-phane, which was achieved by reacting 1,4-benzenedimethanol with diphenyldichlorosilane [8]. Thus, in continuation of our
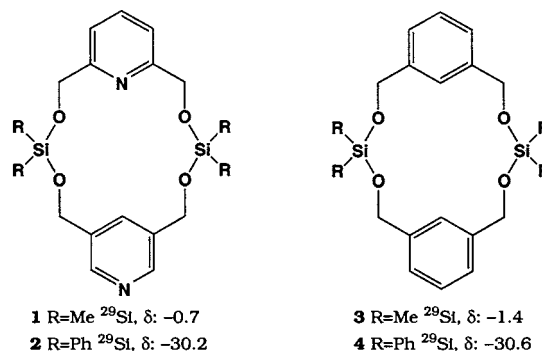

1 R=Me ^{29}Si, δ: −0.7
2 R=Ph ^{29}Si, δ: −30.2
3 R=Me ^{29}Si, δ: −1.4
4 R=Ph ^{29}Si, δ: −30.6

Fig. 1.

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5 Ad=adamantyl ^{29}Si, δ: -41.6   **6** ^{29}Si, δ: -32.4   **7** ^{29}Si, δ: -61.9
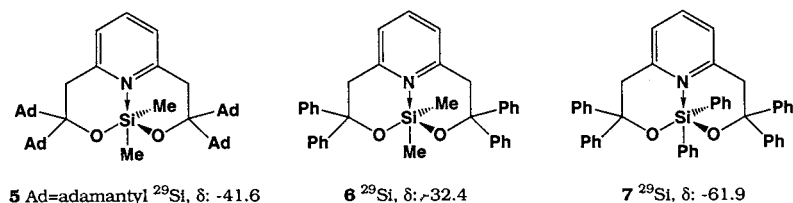
Fig. 2.

studies we describe herein the synthesis of four pentaco-ordinated monoorganosilanes (**9a**, **9b**, **12a**, **12b**) and the [5.5]parasilacyclophane (**10**).

2. Results and discussion

Pyridinediols **8a** and **8b** were synthesized by treating dimethyl 2,6-pyridinedicarboxylate with the appropriate Grignard reagent followed by reaction with bis(-dimethylamine)dimethylsilane to afford silanes **9a** and **9b** (Scheme 1). For both derivatives mass spectrometric analysis showed the molecular ion with loss of the methyl group $[M^+ - CH_3]$ [9–11] indicating formation of the monomeric species. The ^{29}Si-NMR spectra showed signals at -56.5 and -58.0 ppm for **9a** and **9b**, respectively, which are shifted to higher frequencies compared with the uncoordinated dimeric compound (δ, -0.7) suggesting the presence of a N→Si bond [5]. Examination of the ^{13}C-NMR data of **9a** and **9b** revealed that C-2 is shifted to lower frequencies ($\Delta\delta = 3.3$ and 3.0) with respect to the free ligands while C-4 shifts in the opposite direction ($\Delta\delta = 3.9$ and 4.0) this behavior can be attributed to the presence of N→Si bonds.
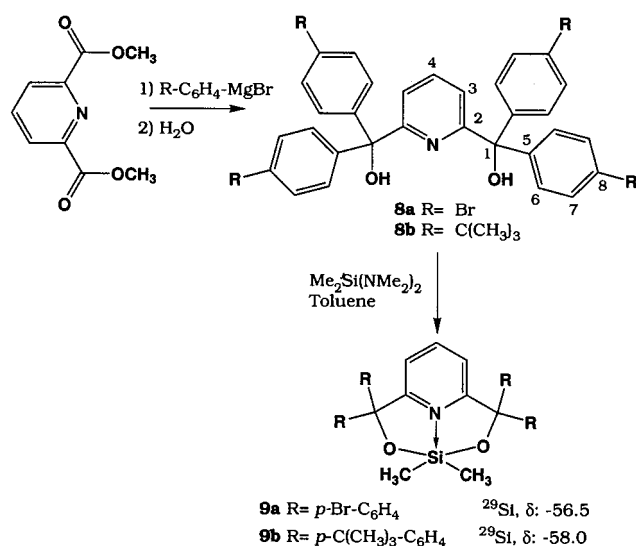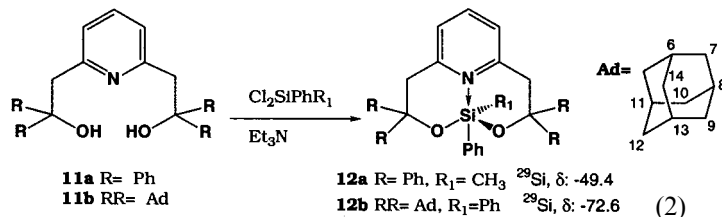
The molecular structure of **9a** was established by single-crystal X-ray diffraction analysis (Table 1), selected bond lengths and angles are given in Table 2. The structure of **9a** shows that the Si(1)–O(1) and Si(1)–O(2) bond lengths are similar and the N–Si distance (1.950(8) Å) is shorter than the sum of the van der Waals radii (3.65 Å) [12] but slightly longer than the sum of covalent radii (1.93 Å). Moreover, this distance is shorter than that observed for cyclic silanes **5**–**7**. The bond angles at the silicon atom have values from 142.8(3) to 151.8(4)° corresponding to a square pyramidal geometry (Fig. 3) and the silicon atom is deviated 0.496 Å from the base of the pyramid plane.

Compound **10** was prepared by reacting bis(dimethyl-amine)dimethylsilane with 1,4-benzenedimethanol as shown in Eq. (1). The formation of this compound was confirmed by ^{1}H-, ^{13}C- and ^{29}Si-NMR spectral analysis and mass spectrometry. In this case, the ^{29}Si signal appeared at -2.3 ppm and is shifted to lower frequencies compared with **9a** (-56.5 ppm) and **9b** (-58.0 ppm) which exhibit a N→Si bond, but similar to that reported for dimer **3** [5]. It is important to notice that the difference in chemical shifts between pentacoordi-

nated and tetracoordinated species containing methyl substituents at the silicon atom is fairly large and can be very useful for their structural analysis.

$$(1)$$

10 ^{29}Si, δ: -2.3
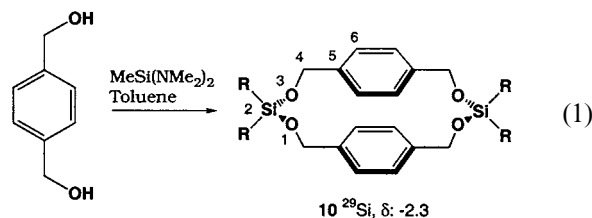
Examination of compound **10** by single-crystal X-ray analysis (Tables 1 and 3) showed that the bond angles at the silicon atom vary from 104.8(1) to 111.1(1)°. The aromatic rings are not perfectly eclipsed (Fig. 4) showing an interplanar distance of 4.174 Å, which is slightly longer than that observed for the parasilacyclophane containing phenyl substituents (3.909 Å) [8]. The distance between the silicon atoms is 8.638 Å whereas the Si(1)–O(1), Si(1)–O(2) bond lengths showed no significant differences.

11a R= Ph   **12a** R= Ph, R$_1$= CH$_3$ ^{29}Si, δ: -49.4
11b RR= Ad   **12b** RR= Ad, R$_1$=Ph ^{29}Si, δ: -72.6   (2)

8a R= Br
8b R= C(CH$_3$)$_3$

9a R= p-Br-C$_6$H$_4$ ^{29}Si, δ: -56.5
9b R= p-C(CH$_3$)$_3$-C$_6$H$_4$ ^{29}Si, δ: -58.0

Scheme 1.

Table 1
Crystallographic data for **9a** and **10**

	9a	**10**
Formula	$C_{33}H_{25}Br_4NO_2Si \cdot 1.5\ C_6H_6$	$C_{20}H_{28}O_4Si_2$
Formula weight (g mol^{-1})	932.43	388.6
Crystal size (mm)	$0.7 \times 0.45 \times 0.28$	$0.3 \times 0.24 \times 0.24$
Color	Colorless	Colorless
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.462(2)	7.714(2)
b (Å)	13.414(3)	8.443(2)
c (Å)	14.578(3)	9.859(2)
α (°)	106.84(2)	66.57(3)
β (°)	101.79(2)	68.79(3)
γ (°)	103.73(3)	66.83(3)
V (Å^3)	1992.0(7)	525.4(2)
Z	2	1
D_{calc} (g cm^{-3})	1.555	1.228
No. of collected reflections	7371	1987
No. of independent reflections	6997($R_{int} = 0.062$)	1836 ($R_{int} = 0.0301$)
No. of observed reflections [a]	1956	1437
No. of parameters	406	118
R [b]	0.064	0.040
R_w [c]	0.156	0.108
GOF	0.811	1.066

[a] $F > 4\sigma(F)$.
[b] $R = \Sigma \left\| F_o \right| - \left| F_c \right\| / \Sigma \left| F_o \right|$.
[c] $R_w(F_o)^2 = [\Sigma_w(F_o^2 - F_c^2)^2 / \Sigma_w\ F_o^4]^{1/2}$.

Silanes **12a** and **12b** were prepared by reaction of PhMeSiCl$_2$ or Ph$_2$SiCl$_2$ with the corresponding pyridinediol in the presence of Et$_3$N (Eq. (2)). Evidence for the formation of these compounds was obtained from mass spectrometry which showed the molecular ion corresponding to the monomeric compounds. In the ^{1}H-NMR spectrum of **12a** the diastereotopic protons for the methylene groups give rise to a broad AB system at 3.63 and 3.79 ppm ($J_{AB} = 13.9$ Hz) while the methyl group attached to the silicon atom is shifted to 0.70 ppm suggesting fluxional behavior. The variable temperature ^{1}H-NMR of compound **12a** shows that at -60°C, two overlapping AB systems are observed, and the methyl singlet splits into two signals at 0.49 and 0.87 ppm in a 3.6:1 ratio. In addition, the ^{29}Si-NMR spectrum measured at -60°C showed two singlets at -44.5 and -56.1 ppm, the latter corresponding to the major component. The spectral data indicate the presence of two possible conformers where the methyl and phenyl substituents are interchanging from the axial to the equatorial positions (Scheme 2). Assignment of the signals for the individual conformers was carried out using a 2D NOESY experiment which showed that the AB system of the major compound correlates with the

methyl singlet at 0.87 ppm, therefore the major compound corresponds to the derivative where the methyl is in the equatorial site and the phenyl is axial. From the isomer ratio the energy for this process was calculated to be ΔG (213 K) = -9.95 kcal mol^{-1}, favoring the conformer having an axial phenyl group. These results are in agreement with the preference of electronegative groups for the axial position on the TBP (trigonal bipyramidal) [13–15].

The ^{1}H-NMR of **12b** at room temperature showed a broad singlet at 3.28 ppm for the methylene protons, however, at -60°C these protons give rise to an AB system at 3.15 and 3.40 ppm ($J_{AB} = 14.8$ Hz) and two different signals for the *ortho* protons corresponding to the axial and equatorial phenyl groups attached to the silicon atom. The low temperature ^{1}H-NMR data [16] gave $\Delta G^{\neq} = 13.5$ kcal mol^{-1} for the dynamic process, a value similar to that found for **7** (13.2 kcal mol^{-1}). On the other hand, the ^{29}Si-NMR signal of **12b** appeared at -72.6 ppm which is shifted 30 ppm to higher frequencies compared to monomer **5** containing methyl substituents (-41.6 ppm).

3. Conclusions

The present study shows that the reaction of 2,6-bis-disubstituted pyridine derivatives with silanes produces monomeric compounds which exhibit N → Si bond even

Table 2
Selected bond lengths (Å) and bond angles (°) for **9a**

Bond lengths

Br(1)–C(23)	1.891(11)	Br(2)–C(17)	1.873(11)
Br(3)–C(11)	1.891(11)	Br(4)–C(29)	1.885(12)
O(1)–Si(1)	1.732(8)	O(2)–Si(1)	1.728(7)
O(1)–C(1)	1.418(10)	O(2)–C(7)	1.433(10)
N(1)–C(6)	1.308(11)	N(1)–C(2)	1.308(11)
N(1)–Si(1)	1.950(8)	Si(1)–C(33)	1.868(10)
Si(1)–C(32)	1.896(9)	C(1)–C(2)	1.492(12)
C(1)–C(20)	1.519(12)	C(1)–C(26)	1.540(12)
C(2)–C(3)	1.368(13)	C(3)–C(4)	1.380(13)
C(4)–C(5)	1.369(12)	C(5)–C(6)	1.407(12)
C(6)–C(7)	1.490(12)	C(7)–C(14)	1.536(13)
C(7)–C(8)	1.530(12)		

Bond angles

C(1)–O(1)–Si(1)	121.9(5)	C(7)–O(2)–Si(1)	119.6(5)
C(6)–N(1)–C(2)	128.6(8)	C(6)–N(1)–Si(1)	115.3(6)
C(2)–N(1)–Si(1)	116.1(7)	O(2)–Si(1)–O(1)	142.8(3)
O(1)–Si(1)–C(33)	105.9(4)	O(2)–Si(1)–C(33)	108.5(4)
O(1)–Si(1)–C(32)	90.8(3)	O(2)–Si(1)–C(32)	91.4(4)
C(33)–Si(1)–C(32)	108.6(5)	O(2)–Si(1)–N(1)	81.2(3)
O(1)–Si(1)–N(1)	79.6(3)	C(32)–Si(1)–N(1)	151.8(4)
C(33)–Si(1)–N(1)	99.9(3)	O(1)–C(1)–C(2)	104.7(7)
O(1)–C(1)–C(20)	110.0(7)	C(2)–C(1)–C(20)	109.9(8)
O(1)–C(1)–C(26)	108.7(7)	C(2)–C(1)–C(26)	113.9(8)
O(2)–C(7)–C(8)	106.5(7)	O(2)–C(7)–C(14)	108.2(8)
C(8)–C(7)–C(14)	110.8(8)	C(20)–C(1)–C(26)	109.5(7)
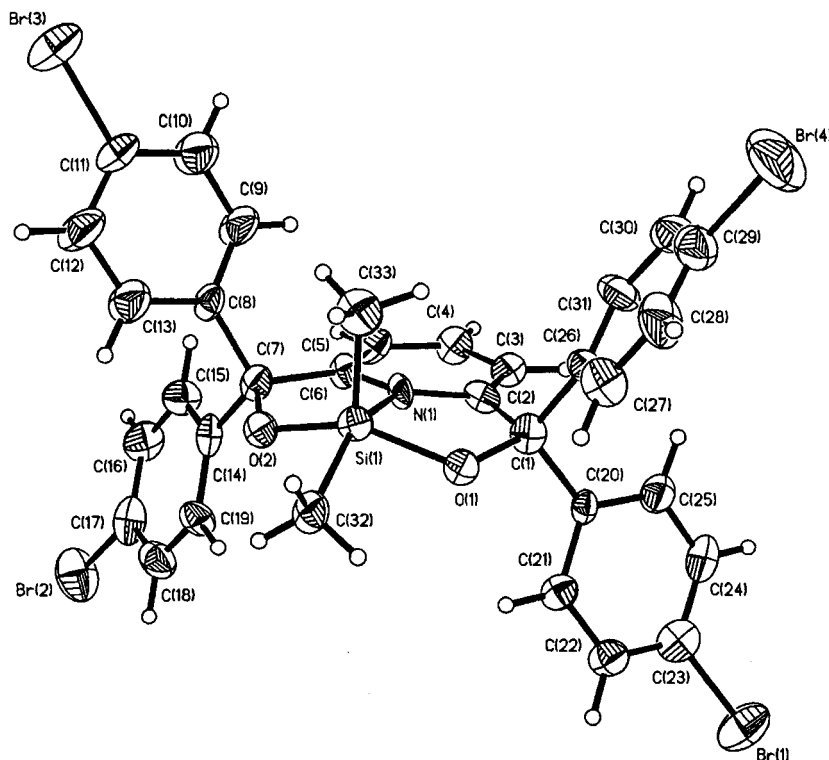
Fig. 3. Molecular structure of **9a**.

in the case of small ring sizes. The formation of monoorganosilanes **9a** and **9b** could be associated with an increasing steric factor on the α-pyridine carbons. Additionally we have shown that compounds **12a** and **12b** exhibit a fluxional behavior.

4. Experimental

Phenylmethyldichlorosilane, bis(dimethylamine)-dimethylsilane and 1,4-benzenedimethanol were purchased from Aldrich, 2,6-bis(2,2-hydroxyethyl)pyridine and 2,6-bis(2,2-adamantyl-2-hydroxyethyl)pyridine were prepared according to the procedure described in the literature [17].

^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were recorded using JEOL GSX270 and JEOL eclipse + 400 spectrometers. The ^{29}Si spectra were performed with the INEPT pulse sequence [18]. Chemical shifts (ppm) are relative to $(CH_3)_4Si$, coupling constants are reported in Hertz. Mass spectra were obtained on a HP 5989A spectrometer. Melting points were measured on a Gallenkamp MFB-595 apparatus and are uncorrected. Elemental microanalyses were performed by Oneida Research Services, Whitesboro, NY. X-ray crystallographic studies were done on an Enraf Nonius CAD4 diffractometer, $\lambda_{Mo-K_\alpha} = 0.71069$ Å, graphite monochromator, $T = 293$ K, $\omega/2\theta$ scan, range $2 < \theta < 25°$. Corrections were made for Lorentz and polarization effects. The struc-

tures were solved by direct methods (SHELXS-86). All nonhydrogen atoms were refined anisotropically by full-matrix least squares using SHELXS-93 [19] and hydrogen atoms were included in fixed positions. Compound **9a** crystallized with 1.5 molecules of benzene and these molecules were refined isotropically.

4.1. 2,6-Pyridinebis(di-4-bromophenylmethanol) (8a)

To a solution of the Grignard reagent prepared from 9.65 g (40.8 mmol) of 1,4-dibromobenzene and 0.99 g (40.8 mmol) of magnesium, 2.0 g (10.2 mmol) of dimethyl 2,6-pyridinedicarboxylate in 20 ml of THF were added and the reaction mixture was stirred for 6 h. After addition of H_2O, the mixture was filtered

Table 3
Selected bond lengths (Å) and bond angles (°) for **10**

Bond lengths		Bond angles	
Si(1)–O(2)	1.634(2)	O(2)–Si(1)–O(1)	111.1(1)
Si(1)–O(1)	1.636(2)	O(2)–Si(1)–C(8)	110.7(1)
Si(1)–C(8)	1.843(3)	O(2)–Si(1)–C(9)	104.7(1)
Si(1)–C(14)	1.836(3)	O(1)–Si(1)–C(9)	112.5(1)
O(2)–C(10)	1.419(3)	O(1)–Si(1)–C(8)	104.8(1)
O(1)–C(1)	1.428(3)	C(9)–Si(1)–C(8)	113.3(1)
C(1)–C(2)	1.511(3)	C(1)–O(1)–Si(1)	126.7(2)
C(2)–C(3)	1.381(3)	C(9)–Si(1)–C(8)	113.3(2)
C(2)–C(7)	1.383(3)	C(10)–O(2)–Si(1)	125.1(2)
		O(1)–C(1)–C(2)	113.6(2)
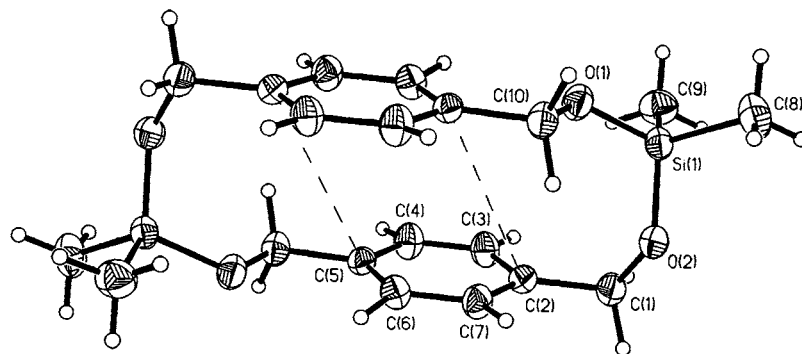
Fig. 4. Molecular structure of **10**.

through Celite under reduced pressure. The organic layer was evaporated, dried over Na$_2$SO$_4$, and the resulting product was purified by cromatography on silica gel (hexane/EtOAc = 8:2) affording 2.5 g (32%) of a white solid, m.p. 82–86°C. ^{1}H-NMR (CDCl$_3$, 399.78 MHz) δ: 4.92 (2H, s, OH), 7.20–7.42 (16H, AA′BB′, J = 8.8 Hz, H-6, H-7; 2H, H-3), 7.65 (1H, t, J = 7.7 Hz, H-4); ^{13}C-NMR (CDCl$_3$, 100.53 MHz) δ: 80.8 (C-1), 121.5 (C-3), 122.1 (C-8), 129.8 (C-6), 131.3 (C-7), 137.6 (C-4), 144.2 (C-5), 162.0 (C-2); MS, m/z (%): 763 [M$^+$ + 8, (1)], 762 [M$^+$ + 7, (2)], 761 [M$^+$ + 6, (8)], 760 [M$^+$ + 5, (4)], 759 [M$^+$ + 4, (12)], 758 [M$^+$ + 3, (4)], 757 [M$^+$ + 2, (8)], 755 [M$^+$, (2)], 662 (6), 568 (14), 401 (7), 341 (16), 332 (26), 263 (6), 183 (100), 155 (47), 76 (35); IRν_{max} (KBr): 3450, 2850, 1588, 1574, 1484, 1448, 1394, 1160, 1156, 1072, 1036, 1008, 994, 992, 826, 804, 752 cm^{-1}.

### 4.2. 2,6-Pyridine-bis(di-4-tert-butylphenylmethanol) (8b)

The title compound was prepared following the procedure described for **8a** from 8.69 g (40.8 mmol) of 1-bromo-4-*tert*-butylbenzene, 0.99 g (40.8 mmol) of magnesium and 2.0 g (10.2 mmol) of 2,6-dimethylpyridinedicarboxylate. The resulting product was washed with EtOAc giving 2.14 g (32%) of a white solid, m.p. 253–255°C; ^{1}H-NMR (CDCl$_3$, 399.78 MHz) δ:1.31 (36H, s, CH$_3$– 10), 5.12 (2H, s, OH), 7.16 and 7.30 (16H, AA′BB′, J = 8.8 Hz, H-6, H-7), 7.49 (2H, d, J = 7.7 Hz, H-3), 7.58 (1H, t, J = 7.7 Hz, H-4); ^{13}C-NMR (CDCl$_3$, 100.53 MHz) δ: 31.4 ((CH$_3$)$_3$), 34.5 (C(CH$_3$)$_3$), 81.0 (C-1), 121.3 (C-3), 124.8 (C-7), 127.8 (C-6), 136.7 (C-4), 143.0 (C-5), 150.1 (C-8), 162.6 (C-2); MS, m/z (%): 667 [M$^+$, (28)], 592 (100), 500 (83), 460 (21), 404 (24), 295 (50), 161 (79), 105 (14), 57 (39); IRν_{max} (KBr): 3088, 2962, 2904, 2866, 1576, 1508, 1474, 1458, 1448, 1400, 1362, 1268, 830 cm^{-1}; Anal. Calc. for C$_{47}$H$_{57}$NO$_2$: C, 84.55; H, 8.54; N, 2.09. Found: C, 84.64; H, 8.35; N, 2.30%.

4.3. 2,6-Pyridine-bis(1,1-di-p-bromophenylmethoxy)-dimethylsilane (9a)

To a solution of **8a** (0.5 g, 0.65 mmol) in 30 ml of toluene, 0.096 g (65 mol) of bis(dimethylamine)dimethylsilane) were added dropwise, and the reaction mixture was refluxed for 24 h. The solvent was removed under vacuum to give a yellow oil, which crystallized from benzene affording 0.1 g (19%) of colorless crystals; m.p. 133–135°C, ^{1}H-NMR (CDCl$_3$, 399.78 MHz) δ: − 0.14 (6H, s, CH$_3$–Si), 7.20 and 7.43 (16H, AA′BB′, J = 8.4 Hz, H-6, H-7), 7.49 (2H, d, J = 7.7 Hz, H-3), 7.98 (1H, t, J = 7.7 Hz, H-4); ^{13}C-NMR (CDCl$_3$, 100.53 MHz) δ: 4.1 (CH$_3$–Si), 80.8 (C-1), 122.0 (C-3), 122.1 (C-8), 129.0 (C-6), 131.5 (C-7), 141.5 (C-4), 144.4 (C-5), 158.7 (C-2); ^{29}Si-NMR (CDCl$_3$, 79.42 MHz) δ: − 56.5; MS, m/z (%): 804 [M$^+$ + 8 −CH$_3$, (10)], 803 [M$^+$ + 7 −CH$_3$, (12)], 802 [M$^+$ + 6 −CH$_3$, (2)], 801 [M$^+$ + 5 −CH$_3$, (19)], 800 [M$^+$ + 4 −CH$_3$, (46)], 799 [M$^+$ + 3 −CH$_3$, (14)], 798 [M$^+$ + 2 −CH$_3$, (31)], 796 [M$^+$ −CH$_3$, (7)], 720 (16), 584 (7), 567 (46), 490 (20), 400 (19), 320 (40), 183 (100), 155 (49); Anal. Calc. for C$_{33}$H$_{25}$NO$_2$SiBr$_4$: C, 47.05; H, 3.16; N, 1.77. Found: C, 47.06; H, 3.17; N, 1.83%.

4.4. 2,6-Pyridine-bis(1,1-di-p-tert-butylphenylmethoxy)-dimethylsilane (9b)

The title compound was prepared following the procedure described for **9a**: from 0.4 g (6.7 mmol) of **8b** and 0.098 ml (6.7 mmol) of bis(dimethylamine)dimethylsilane. After the solvent was removed 0.33 g (68%) of a white solid was isolated, m.p. 253–
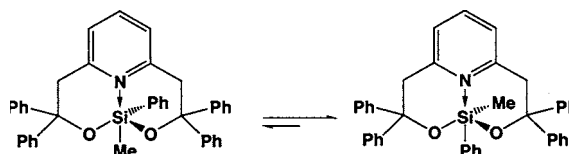
Scheme 2.

255°C. ^{1}H-NMR (CDCl$_3$, 270.16 MHz) δ: -0.07 (6H, s, CH$_3$–Si), 1.27 (36H, s, H-10), 7.24 and 7.29 (16H, AA′BB′, $J = 8.8$ Hz, H-6, H-7), 7.47 (2H, d, $J = 7.7$ Hz, H-3), 7.87 (1H, t, $J = 7.7$ Hz, H-4); ^{13}C-NMR (CDCl$_3$, 67.94 MHz) δ: 4.4 (CH$_3$–Si), 31.4 (C-10), 34.5 (C-9), 81.0 (C-1), 121.8 (C-3), 125.0 (C-7), 127.1 (C-6), 140.7 (C-4), 142.9 (C-5), 150.0 (C-8), 159.6 (C-2); ^{29}Si-NMR (CDCl$_3$, 53.67 MHz) δ: -58.0; MS, m/z (%): 708 [M$^+$ $-$ CH$_3$, (100)], 636 (18), 560 (5), 503 (4), 429 (7), 354 (8); Anal. Calc. for C$_{49}$H$_{61}$NO$_2$Si: C, 81.32; H, 8.43; N, 1.93. Found: C, 81.21; H, 8.31; N, 2.07%.

4.5. 1,3,10,12-Tetraoxo-2,11-(dimethylsilylene)[5.5]-paracyclophane (10)

To a solution of 0.1 g (0.72 mmol) of 1,4-benzenedimethanol in 30 ml of toluene at room temperature (r.t.), 0.1 g (0.72 mmol) of bis(dimethylamine)-dimethylsilane was added and the solution was refluxed for 24 h. The solvent was removed under vacuum to give a yellow oil and after addition of 10 ml of Et$_2$O, 0.1 g (35%) of colorless crystals were obtained; m.p. 156–157°C; ^{1}H-NMR (CDCl$_3$, 399.78 MHz) δ: 0.29 (3H, s, CH$_3$–Si), 4.59 (2H, s, CH$_2$), 6.90 (2H, s, H-6); ^{13}C-NMR (CDCl$_3$, 100.53 MHz) δ: -3.4 (CH$_3$–Si), 64.5 (C-4), 125.9 (C-6), 138.7 (C-5); ^{29}Si-NMR (CDCl$_3$, 79.42 MHz) δ: -2.3; MS, m/z (%): 388 [M$^+$, (100)], 373 (10), 284 (25), 194 (25), 179 (26), 149 (38), 104 (26), 91 (19), 75 (18); Anal. Calc. for C$_{20}$H$_{28}$O$_4$Si$_2$: C, 61.85; H, 7.21. Found: C, 61.58; H, 7.18%.

4.6. 2,6-Pyridine-bis(1,1-diphenylethoxy)-methylphenylsilane (12a)

To a solution of 0.5 g (1.06 mmol) of 11a and 0.21 g (2.12 mmol) of Et$_3$N in 30 ml of toluene, 0.20 g (1.06 mmol) of dichlorophenylmethylsilane was added dropwise and refluxed for 24 h. The solvent was removed under vacuum and the resulting white solid was treated with water to remove Et$_3$NHCl and extracted with chloroform giving 0.366 g (61%) of 12a, m.p. 227–229°C; ^{1}H-NMR (CDCl$_3$, 399.78 MHz) δ: 0.70 (3H, s, CH$_3$–Si), 3.63 and 3.79 (4H, AB, $J = 13.9$ Hz, H-2), 6.65 (2H, d, $J = 7.7$ Hz, H-4), 7.11–7.22 (24H, m, arom), 7.24 (2H, d, $J = 6.6$ Hz, H-o, Si–Ph); ^{13}C-NMR (CDCl$_3$, 100.53 MHz) δ: 5.1 (CH$_3$), 46.0 (CH$_2$), 83.2 (C-1), 121.8 (C-4), 126.3, 126.5, 126.6, 126.9. 127.6, 127.7, 127.9, 131.1, 136.1, 144.2, 147.1, 148.2, 155.6 (C-arom); ^{29}Si-NMR (CDCl$_3$, 79.42 MHz, 60°C) δ: -49.4; MS, m/z (%): 574 [M$^+$ $-$CH$_3$, (17)], 512 (100), 436 (5), 407 (70), 330 (21), 296 (2); Anal. Calc. for C$_{40}$H$_{35}$NO$_2$Si: C, 81.49; H, 5.94; N, 2.37. Found: C, 81.07; H, 5.99; N, 2.56%.

4.7. 2,6-pyridinebis(1,1-adamantylethoxy)diphenylsilane (12b)

To a solution of 0.33 g (0.8 mmol) of 11b and 0.16 g (1.6 mmol) of Et$_3$N in 30 ml of CH$_2$Cl$_2$, 0.20 g (1.06 mmol) of dichlorodiphenylsilane was added dropwise and refluxed for 36 h. The solvent was removed under vacuum and the resulting white solid was treated with water to remove Et$_3$NHCl, the organic layer extracted with chloroform (3 × 10 ml) and evaporated to yield a yellow oil which precipitated in ethyl ether. Recrystallization from methylene chloride gave 0.40 g (82%) of 12b, m.p. 224–227°C; ^{1}H-NMR (CDCl$_3$, 270.16 MHz) δ: 1.40 (4H, d, $J = 11.9$ Hz, H-12a, H-14a), 1.51–2.00 (20H, m, ad), 2.43 (4H, d, $J = 11.9$ Hz, H-14b, H-12b), 3.28 (4H, s, H-2), 6.90 (2H, d, $J = 7.7$ Hz, H-4), 7.14–7.20 (6H, m, H-p, H-m), 7.44 (1H, t, $J = 7.7$ Hz, H-5), 7.62 (4H, dd, $J = 2.7$, 7.0 Hz, H-o); ^{13}C-NMR (CDCl$_3$, 67.94 MHz) δ: 27.4 (C-8), 27.5 (C-13), 33.2 (C-14, C-12), 34.8 (C-7, C-10, C-6, C-11), 38.9 (C-9), 41.4 (C-2), 81.4 (C-1), 121.8 (C-4), 126.7 (C-m), 127.0 (C-p), 134.1 (C-o), 136.7 (C-5), 157.0 (C-3); ^{29}Si-NMR (CDCl$_3$, 53.67 MHz) δ: -72.6; MS, m/z (%): 587 [M$^+$, (0.3)], 510 [M$^+$ $-$C$_6$H$_5$ 100], 436 (4), 372 (10), 360 (12), 264 (1), 239 (2), 199 (3), 91 (2) 77 (8); Anal. Calc. for C$_{39}$H$_{45}$NO$_2$Si: C, 79.72; H, 7.66; N, 2.38. Found: C, 79.27; H, 7.52; N, 2.63%.

5. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 146364 for compound 9a and CCDC no. 146365 for compound 10. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; email: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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