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Synthesis and characterization of two cyclic organosiloxanes by multinuclear NMR spectroscopy and X-ray crystallography

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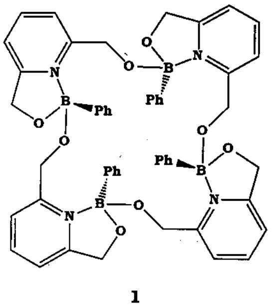
Abstract

1,3-[2′,6′-Pyridinebis(methyleneoxy)]-1,3-bis(diphenyl)cyclodisiloxane (**9**) and 2,6-pyridinebis(1,1-diphenylethoxy)diphenylsilane (**11**) were obtained from 2,6-pyridinediol derivatives with dichlorodiphenylsilane. An N → Si interaction is present in 2,6-pyridinebis(1,1-diphenylethoxy)diphenylsilane, which also shows fluxional behavior. The activation energy of 13.2 kcal mol^{-1} for **11** was obtained for the intramolecular exchange between the phenyl groups from a variable-temperature ^{1}H-NMR study. The compounds were characterized by ^{1}H-, ^{13}C- and ^{29}Si-NMR and their structures were established by X-ray crystallographic studies.

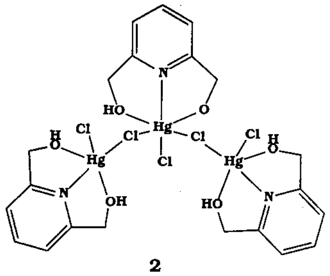
Keywords: Siloxane; 2,6-Pyridinediol; X-ray structure; NMR spectroscopy

1. Introduction

In recent studies, we reported the formation of a new macrocyclic oligoboronate **1** by reaction of 2,6-pyridinedimethanol with phenylboronic acid [1]. A subsequent study showed that 2,6-pyridinedimethanol also reacts with mercury (II) chloride to give a trimeric chlorine bridged molecule **2** [2]. In this case the X-ray structure showed that the coordination geometry around the central mercury atom is distorted octahedral, while around the lateral metal atoms it is distorted square-pyramidal.



1



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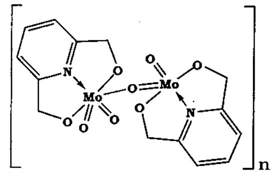
The same ligand with $MoO_2(acac)_2$ gives a linear polymeric oxygen-bridged structure **3** [3], while the reaction with various R_2SnO gives monomeric structures **4** [4,5]. When 2,6-pyridinedimethanol is reacted with dimethyl or diphenyldichlorosilane the dimeric compounds **5a** and **5b** [6,7] are obtained.



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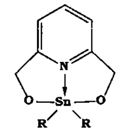
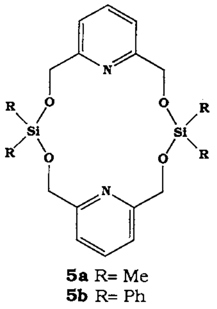
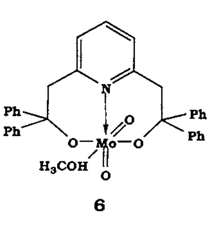


4 R= Et, Ph, t-Bu, n-Bu

Subsequent studies showed that increasing the lateral chain in the pyridinediol derivative affords a monomeric octahedral complex **6** in the reaction with $Mo_2(acac)_2$ [8]. It is interesting to note that, when the substituent at the carbon bearing the hydroxyl group is bulky, the monomeric silicon compounds **7a** and **7b** are obtained [6,9].



5a R= Me
5b R= Ph



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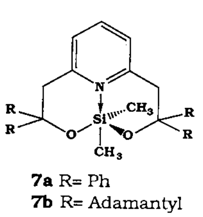

7a R= Ph
7b R= Adamantyl

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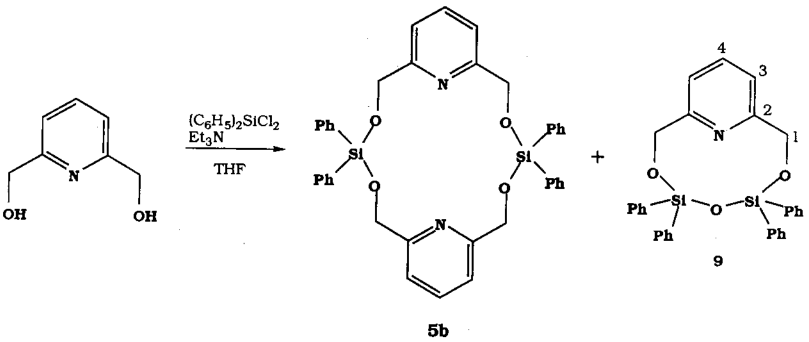
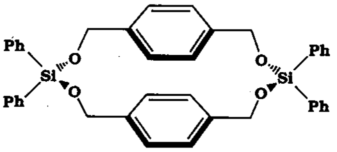


Scheme 1.

Recently, we reported the synthesis and study of 1,3,10,12-tetraoxo-2,11-(diphenylsilylene)[5.5]paracyclophane (**8**) from the reaction of 1,4-benzenedimethanol with dichlorodiphenylsilane [10].



8

In this work we report the synthesis and study of 1,3–[2′,6′-pyridinebis(methyleneoxy)]-1,3-bis(diphenyl)-cyclodisiloxane (**9**) and 2,6-pyridinebis(1,1-diphenylethoxy)diphenylsilane (**11**) from the reaction of diphenyldichlorosilane with the corresponding pyridinediol.

2. Results and discussion

The reaction of dichlorodiphenylsilane with 2,6-pyridinedimethanol in the presence of Et_3N and THF yielded a mixture of 2,6-pyridinebis(methyleneoxy)-diphenylsilane (**5b**) and 1,3-[2′,6′-pyridinebis(methyleneoxy)]-1,3-bis(diphenyl)cyclodisiloxane (**9**) (Scheme 1). The ^{1}H-NMR spectrum shows two different signals for the methylene groups. In the ^{29}Si-NMR spectrum two singlets are observed at −30.2 and −41.6 ppm, the first one corresponding to dimer **5b** previously reported [7] and the second one to disiloxane **9**, formed because of the presence of traces of water in the reaction mixture.

Compound **9** was characterized by ^{1}H- and ^{13}C-NMR spectra and complete spectral assignment was achieved by a 2D HETCOR experiment. The ^{1}H-NMR spectrum of **9** shows a signal at 5.11 ppm for the methylene groups, which correlates with the corresponding signal at 67.4 ppm in the ^{13}C-NMR spectrum. In the ^{29}Si-NMR spectrum a singlet appears at −41.6 ppm.

The molecular structure of **9** was established by a single-crystal X-ray diffraction analysis (Table 1). Selected bond lengths and angles are summarized in Table 2. The Si(1)–N(1) and Si(2)–N(1) distances are 2.882 (2) and 2.938 (2) Å, respectively, therefore an N → Si interaction can be excluded. These distances are shorter than the sum of the van der Waals radii (3.65 Å), but significantly larger than the sum of the covalent radii (1.93 Å). The bond angles at the silicon atom have values from 107.8 to 114.5° corresponding to a tetrahedral geometry and for the Si–O–Si moiety the bond angle is 146.3° (Fig. 1). It is worth noting that Si(1) and Si(2) are 1.0 and −0.74 Å deviated from the pyridine ring mean plane while the oxygen atoms deviate by

Table 1
Crystallographic data for **9** and **11**

	9	**11**
Formula	$C_{31}H_{27}NO_3Si_2$	$C_{45}H_{37}NO_2Si$
Formula weight (g mol^{-1})	517.72	651.85
Crystal size (mm)	0.48 × 0.45 × 0.33	0.51 × 0.36 × 0.18
Color	Colorless	Colorless
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	11.974(2)	10.100(2)
b (Å)	16.804(3)	12.669(3)
c (Å)	14.318(3)	16.108(3)
α (°)	90	84.94(3)
β (°)	109.68(3)	75.14(3)
γ (°)	90	68.12(3)
V (Å^3)	2712.7(9)	1848.6(7)
Z	4	2
$D_{\text{calc.}}$ (g cm^{-3})	1.268	1.171
No. of collected reflections	6806	3710
No. of independent reflections (R_{int})	6509 (0.03)	3566 (0.03)
No. of observed reflections	3129	2168
No. of parameters	334	444
R [a]	0.040	0.044
R_w [b]	0.105	0.115
GOF	0.984	0.982

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w(F_o)^2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

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

Bond lengths			
O(1)–Si(1)	1.629(2)	N(1)–C(6)	1.335(3)
O(2)–Si(2)	1.628(2)	Si(1)–C(20)	1.867(2)
O(3)–Si(1)	1.625(2)	Si(1)–C(26)	1.863(2)
O(3)–Si(2)	1.616(2)	Si(2)–C(14)	1.855(3)
O(1)–C(1)	1.408(3)	Si(2)–C(8)	1.862(2)
O(2)–C(7)	1.399(3)	C(1)–C(2)	1.497(4)
N(1)–C(2)	1.329(4)	C(6)–C(7)	1.498(4)
Bond angles			
O(3)–Si(1)–O(1)	112.7(1)	O(1)–C(1)–C(2)	115.5(2)
O(3)–Si(1)–C(26)	112.6(1)	O(2)–C(7)–C(6)	116.8(2)
O(1)–Si(1)–C(26)	112.8(1)	Si(2)–O(3)–Si(1)	146.3(1)
O(3)–Si(1)–C(20)	105.6(1)	C(1)–O(1)–Si(1)	130.4(2)
O(1)–Si(1)–C(20)	104.6(1)	C(7)–O(2)–Si(2)	130.6(2)
O(3)–Si(2)–O(2)	114.5(1)	C(2)–N(1)–C(6)	118.4(2)
O(3)–Si(2)–C(14)	104.5(1)	N(1)–C(2)–C(1)	118.4(2)
O(2)–Si(2)–C(14)	103.6(1)	N(1)–C(6)–C(7)	117.8(2)
O(3)–Si(2)–C(8)	113.6(1)	C(14)–Si(2)–C(8)	113.6(1)
O(2)–Si(2)–C(8)	109.3(1)	C(26)–Si(1)–C(20)	107.8(1)

0.142, 0.026 and 0.110 Å for O(1), O(2), O(3), respectively.

The reaction of compound **10** with dichlorodiphenylsilane in toluene in the presence of Et_3N led to the formation of monomer **11** whose molecular ion, $m/z = 651$, was observed in the mass spectrum (Scheme 2).

The examination of **11** by a single-crystal X-ray crystallographic analysis (Tables 1 and 3) confirmed the structure (Fig. 2). The molecule exhibits a trigonal bypiramidal geometry around the silicon atom with angles of 119.4(2), 115.8(2) and 111.7(2)° for O(1)–Si–O(2), O(1)–Si–C(10) and O(2)–Si–C(10), respectively. The N–Si–C(16) bond angle is 170(3)° showing a TBP distorted geometry. A $T_d \rightarrow TBP$ displacement of 50.6% for **11** from a tetrahedron towards a trigonal bipyramid was calculated according to a method reported by Holmes and co-workers [11]. On the other hand the correlation between the $N \rightarrow Si$ distance and the displacement percent $T_d \rightarrow TBP$ is noticeable [12]. The equatorial Si–C(10) bond (1.871(4) Å) is significantly shorter than the axial Si–C(16) bond (1.970(4) Å), as expected for this type of geometry. The $N \rightarrow Si$ distance for **11** of 2.790(3) Å is slightly longer than those of the monomeric compounds **7a** and **7b**, 2.703(2) and 2.727(2) Å, respectively [6,9]. Although it could be expected that the presence of phenyl groups at the silicon atom would increase the Lewis acidity leading to a shorter $N \rightarrow Si$ distance, the presence of steric effects between the phenyl groups at the silicon atom and those of the ligand could account for the longer $N \rightarrow Si$ length found in **11**.

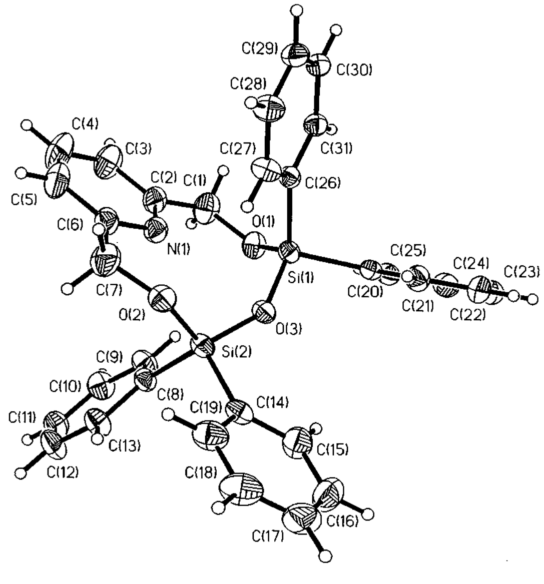
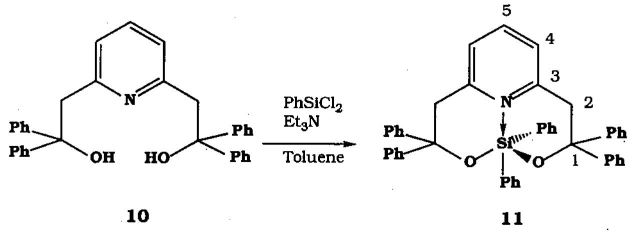


Fig. 1. Molecular structure of compound **9**.



Scheme 2.

The ^{29}Si-NMR signal for **11** is shifted to − 63.8 ppm, which suggests a $N \rightarrow Si$ interaction, in contrast to the dimer **5b** and the disiloxane **9** for which the signals appeared at − 30.2 and − 40.1 ppm, respectively. It is interesting to note that the monomer **7a** reported by Holmes and co-workers [6] shows a ^{29}Si-NMR signal at − 32.4 ppm, probably due to the difference of Lewis acidity at the silicon atom. The ^{1}H-NMR spectrum at

Table 3
Selected bond lengths (Å) and angles (°) for **11**

Bond lengths			
Si(1)–O(2)	1.622(3)	C(2)–C(3)	1.529(6)
Si(1)–O(1)	1.631(3)	C(1)–C(28)	1.539(5)
Si(1)–N(1)	2.790(3)	C(1)–C(22)	1.565(6)
Si(1)–C(10)	1.871(4)	C(7)–C(8)	1.490(5)
Si(1)–C(16)	1.970(4)	C(8)–C(9)	1.620(6)
O(1)–C(1)	1.428(4)	C(9)–C(34)	1.528(5)
O(2)–C(9)	1.451(4)	C(9)–C(40)	1.544(6)
C(1)–C(2)	1.612(5)	N(1)–C(3)	1.327(5)
Bond angles			
O(2)–Si(1)–O(1)	119.4(2)	C(1)–O(1)–Si(1)	141.0(2)
O(2)–Si(1)–C(10)	111.7(2)	C(9)–O(2)–Si(1)	151.7(2)
O(2)–Si(1)–C(16)	102.2(2)	O(1)–C(1)–C(22)	106.7(3)
O(1)–Si(1)–C(10)	115.8(2)	O(1)–C(1)–C(2	111.1(3)
O(1)–Si(1)–C(16)	98.0(2)	O(2)–C(9)–C(8)	113.4(3)
C(10)–Si(1)–C(16)	106.7(2)	N(1)–Si(1)–C(16)	170.0(3)

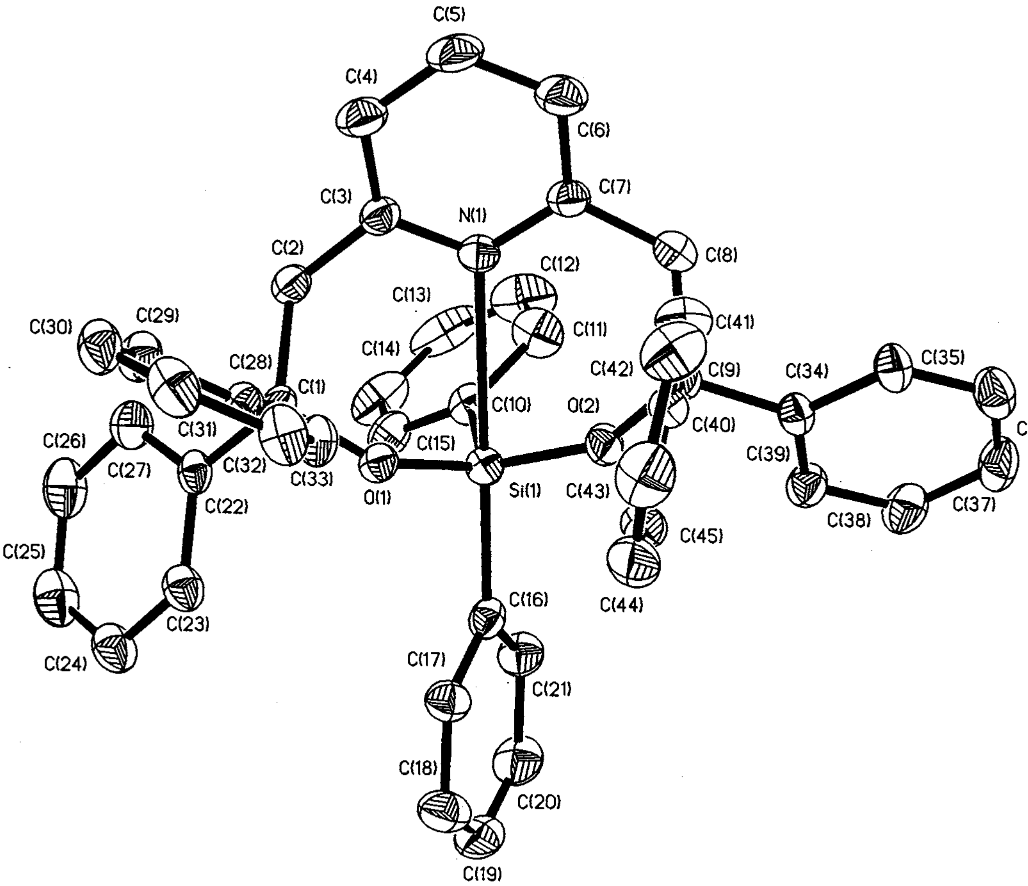


Fig. 2. Molecular structure of compound **11**.

20°C shows a broad signal at 3.72 ppm for the methylene groups and the *ortho* protons of the Si–Ph show a broad doublet at 7.56 ppm, suggesting a fluxional behavior where the phenyl groups attached to the silicon atom are interchanging (Scheme 3). Thus upon cooling to −90°C the methylene signal splits into an AB system ($J_{HaHb} = 14.4$ Hz) for the two nonequivalent hydrogens, while the *ortho* protons of Si–Ph split into two doublets shifted at 7.51 and 7.58 ppm. Coalescence was achieved at 0°C, and a $\Delta G^{\neq}$ value of 13.2 kcal mol^{-1} was calculated for this process [13]. This value is similar to those reported by Holmes and co-workers [14].

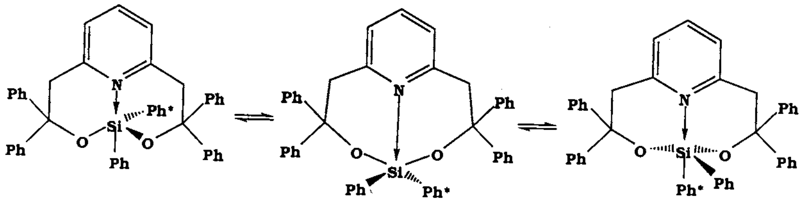
3. Conclusions

The reaction of 2,6-pyridenedimethanol and dichlorodiphenylsilane afforded the dimer **5b** and siloxane **9**. The ^{29}Si-NMR and the X-ray diffraction study show that the N → Si coordination bond is not present in compound **9**. On the other hand, the N → Si interaction is present in compound **11** as shown by the X-ray crystallographic analysis and NMR spectroscopy. A $\Delta G^{\neq}$ value of 13.2 kcal mol^{-1} was obtained for the interchange of phenyl groups attached to the silicon atom from a variable-temperature ^{1}H-NMR study. Additionally a $T_d \rightarrow TBP$ value of 50.6% was calculated.

4. Experimental

Diphenyldichlorosilane and 2,6-pyridinedimethanol were purchased from Aldrich; 2,6-bis(2,2-diphenyl-2-hydroxyethyl)pyridine (**10**) was prepared according to a procedure described in the literature [8].

^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were recorded on a Jeol GSX270 equipment. The ^{29}Si-NMR spectra were recorded with the INEPT pulse sequence [15]. Chemical shifts (ppm) are relative to $(CH_3)_4Si$. The mass spectra were obtained on an HP 5989A spectrometer. Melting points were obtained on a Gallenkamp MFB-595 apparatus and are uncorrected. Elemental microanalyses were performed by Oneida Research Services, Whitesboro, NY 13492. The X-ray crystallographic studies were done on an Enraf Nonius CAD4 diffractometer, $\lambda_{(\mathrm{Mo-K_\alpha})} = 0.71073$ Å, graphite monochromator, $T = 293$ K, $\omega/2\theta$ scan, range $2 < \theta < 25°$. Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS-86). Using



Scheme 3.

SHELXS-93 [16] all nonhydrogen atoms were refined anisotropically by full-matrix least squares, the hydrogen atoms being included as fixed isotropic scatterers in ideal positions.

*4.1. 1,3-[2′,6′-pyridinebis(methyleneoxy)]-1,3-bis-(diphenyl)cyclodisiloxane (**9**)*

To a solution of 0.5 g (3.6 mmol) of 2,6-pyridinedimethanol and 0.725 g (7.2 mmol) of Et_3N in 30 ml of THF, 0.91 g (3.6 mmol) of dichlorodiphenylsilane was added dropwise and the mixture was then refluxed for 24 h. The solvent was removed under vacuum and the resulting white solid was treated with water to remove Et_3NHCl. After extraction with chloroform and slow evaporation of the solvent 0.792 g (42.8%) of crystalline **9** was obtained; m.p. 146–147°C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 5.11 (4H, s, CH_2), 6.76 (2H, d, $J = 7$ Hz, H-3), 7.25–7.76 (21H, m, arom) ppm; ^{29}Si-NMR (53.7 MHz, $CDCl_3$) δ: -41.6 ppm; ^{13}C-NMR (67.9 MHz, $CDCl_3$) δ: 67.37 (CH_2), 118.06 (C-3), 127.65 (C-*m*), 129.56 (C-*p*), 134.64 (C-*o*), 135.80 (C-4), 136.60 (C-*i*), 157.5 (C-2) ppm; MS *m/z* (%): [$M^+ - C_6H_5$, 440 (100)], 362 (7), 284 (2), 264 (3), 234 (4), 180 (4), 142 (2) 77 (13), 51 (7); IR ν_{max} (KBr): 3068, 3050, 3022, 1590, 1428, 1128, 1118, 1062, 1036, 1012, 994, 744, 724, 698, 678, 526, 488 cm^{-1}; Anal. Calc. for $C_{31}H_{27}NO_3Si_2$: C, 71.91; H, 5.25; N, 2.70. Found: C, 71.88; H, 5.29; N, 2.84.

*4.2. 2,6-pyridinebis(1,1-diphenylethoxy)diphenylsilane (**11**)*

To a solution of 0.25 g (0.53 mmol) of **10** and 0.15 g (1.06 mmol) of Et_3N in 30 ml of toluene, 0.13 g (5.3 mmol) of dichlorodiphenylsilane was added dropwise and the mixture was refluxed for 24 h. The solvent was removed under vacuum and the resulting white solid was treated with water to remove Et_3NHCl and extracted with chloroform. Slow evaporation of the solvent afforded 0.195 g (56.5%) of crystalline **10**; m.p. 248–249°C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 3.72 (2H, s, CH_2), 6.72 (1H, d, $J = 7.8$ Hz, H-4), 7.14-7.31 (14H, m, arom), 7.56 (2H, d, $J = 7.7$ Hz, H-*o* Si–Ph) ppm; ^{29}Si-NMR (53.7 MHz, $CDCl_3$) δ: -61.9 ppm; ^{13}C-NMR (67.9 MHz, $CDCl_3$) δ: 45.67 (CH_2), 83.81 (C-1), 122.0 (C-4), 126.1, 126.5, 126.7, 126.9, 127.9, 128.1, 134.4, 134.9 (C-arom), 136.2 (C-*o* Si–Ph), 156.0 (C-3 Py) ppm; MS *m/z* (%): 651 [M^+, (0.1)], 574 (100), 469 (26), 436 (5), 392 (10), 296 (3); Anal. Calc. for $C_{45}H_{37}NO_2Si$: C, 82.95; H, 5.68; N, 2.15. Found: C, 82.77; H, 5.80; N, 2.14.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 117963 for **9** and CCDC 117962 for **11**. 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.uk].

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