

# Multinuclear NMR and X-ray diffraction study of pentacoordinated siloxane structures derived of pyridine diols

Elizabeth Gómez <sup>a,\*</sup>, Zulema Hernández <sup>a</sup>, Cecilio Alvarez-Toledano <sup>a</sup>,  
Rubén A. Toscano <sup>a</sup>, Víctor Santes <sup>b</sup>, Pankaj Sharma <sup>a</sup>

<sup>a</sup> Instituto de Química-UNAM, Circuito Exterior, Ciudad Universitaria, Coyoacán, C.P. 04510 México D.F., Mexico

<sup>b</sup> Instituto Mexicano del Petróleo, Programa de Tratamiento de Crudo Maya, Eje central Lázaro Cárdenas # 152, Col. San Bartolo Atepehuacan, C. P. 07730 México D. F., Mexico

Received 3 October 2001; received in revised form 20 November 2001; accepted 20 November 2001

## Abstract

Synthesis and characterization of hypervalent pentacoordinated organosilicon complexes obtained from the reaction of disubstituted pyridine ligands with dichlorodiphenylsilane, dichloromethylphenylsilane and bis(dimethylamino)dimethylsilane are reported. The monomeric complexes obtained were characterized by mass spectrometry and multinuclear NMR spectroscopy; additionally their structures were established by X-ray diffraction analysis. The structural parameters indicated Si–N interaction with pentacoordinated geometries displaced towards trigonal bipyramid (TBP); the <sup>29</sup>Si-NMR data for these compounds are in agreement with the presence of N→Si bond. In addition to a variable temperature <sup>1</sup>H-NMR study was carried out showing a dynamic behavior for these compounds. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Siloxane; Pentacoordinated; Pyridinediols; <sup>29</sup>Si-NMR; X-ray diffraction; Hypervalency

## 1. Introduction

Hypervalent silicon compounds have attracted much interest in view of their diverse structure and reactivity, which include studies of nucleophilic substitution at the silicon center atom in halofunctionalized silanes [1–3], Lewis acidity of silacyclobutane derivatives [4], silanes with potential pesticide activity [5], optically active organosilanes [6] and silicon-bridged ferrocenophane type structure [7]; all of these investigations involve hypervalent silicon.

On the other hand, pyridine diol ligands are of interest as complexing agents, for example, the reaction of 2,6 dimethanopyridine with Sn, Si, Hg, Mo affords monomeric, dimeric, trimeric and polymeric compounds [7–11].

In the course of our research concerning the synthesis and structural characterization of pentacoordinated monoorganosilanes from 2,6-disubstituted pyridine lig-

ands we were interested in studying the effect of substituents around the silicon atom in the formation of dimeric or monomeric organosilanes, likewise the dynamic behavior experimented by these kind of compounds. The aim of this work is to describe the synthesis and characterization by multinuclear NMR spectroscopy and X-ray examination of monomeric systems containing silicon **2a–2c**, to establish the influence of the substituents present at the beta carbon on the N→Si coordination, which has not been undertaken in earlier investigations [12–15].

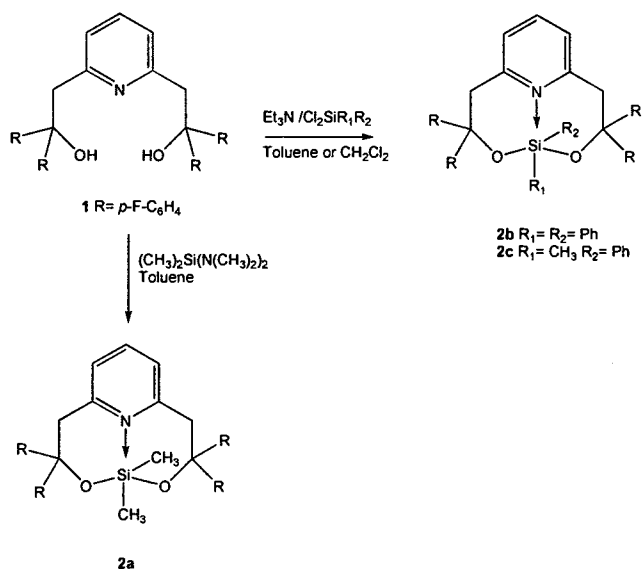
## 2. Results and discussion

The reaction of ligand **1** with bisdimethylaminodimethylsilane gave the compound **2a**, whereas reaction with dichloromethylphenylsilane or dichlorodiphenylsilane, in the presence of triethylamine afforded the compounds **2b** and **2c** (Scheme 1).

The proton NMR spectrum of **2a** showed a singlet at  $\delta$  0.27 corresponding to the protons of equivalent methyl groups; likewise the <sup>13</sup>C-NMR of **2a** showed the

\* Corresponding author. Fax: +52-5-616-2217.

E-mail address: [elgomez@correo.unam.mx](mailto:elgomez@correo.unam.mx) (E. Gómez).



Scheme 1.

methyl signal at  $\delta$  5.3. On cooling to  $-90$  °C in the <sup>1</sup>H-NMR spectrum the signal for methylene protons did not show any change, but methyl singlet turned into two signals shifted to  $\delta$  0.11 and 0.35 which coalesced at  $-50$  °C. On the other hand, for organosiloxane **2b** the <sup>1</sup>H spectrum showed a broad singlet at  $\delta$  3.61 which was assigned to the methylene protons. However, in contrast to compound **2a**, the <sup>1</sup>H spectrum at  $-90$  °C showed an AB system at  $\delta$  3.78 and 3.48 ( $J = 14.7$  Hz); as the temperature was increased the coalescence temperature was achieved at  $0$  °C. This dynamic behavior is consistent with the existence of a mixture of conformational isomers of identical energy in both cases (Scheme 2). The activation energy calculated for the exchange ( $\Delta G^\ddagger$ ) is 10.71 and 13.04 kcal mol<sup>-1</sup> for **2a** and **2b**, respectively [16]. These results are in agreement with similar silane type structures earlier reported, which also present pseudorotational behavior, with energy values of 9–13 kcal mol<sup>-1</sup> for the process [17–19].

The silicon NMR showed signals at  $-31.7$  and  $-60.9$  ppm for **2a** and **2b**, respectively. This result is in agreement with the presence of the N→Si bond as reported previously [14,15]. On the other hand, due to the nature of the substituents on the silicon atom of compound **2c**, the <sup>1</sup>H spectrum at room temperature

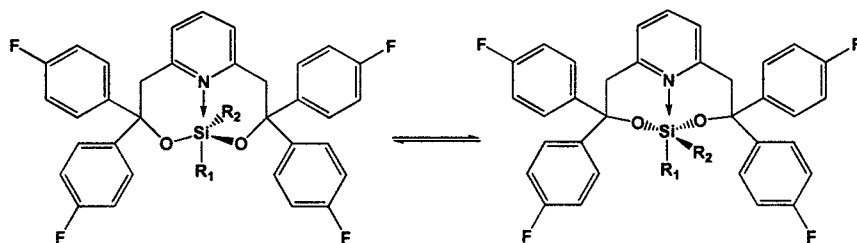
showed a broad AB system at  $\delta$  3.73 and 3.55  $J_{AB} = 14.0$  Hz which corresponds to methylene protons. However, when the spectrum was obtained at  $-60$  °C, a new AB system was observed. Additionally, the methyl singlet split into two singlets located at 0.75 and 0.38 ppm in a 4:1 ratio which was determined from the integration of peak areas; this fact evidences the presence of two isomers of different energy. It should be noted that the methyl singlet for the major isomer is shifted to downfield suggesting that this methyl occupies an equatorial position in the TBP. Additional evidence for the assignment of the individual spectral resonances was supported by 2D NOESY experiment which was obtained at  $-60$  °C where it was observed that the singlet at  $\delta$  0.75 correlates with the AB system at  $\delta$  3.81 and 3.54. It is important to mention that this correlation can only be observed if the methyl group is in equatorial, which is in agreement with its chemical shift previously discussed. Furthermore, from this experiment it was also possible to observe the interchange of methyl group from axial to the equatorial position. As expected, the <sup>29</sup>Si-NMR at  $-60$  °C for **2c** showed two different silicon resonances shifted to  $-43.6$  and  $-54.7$  ppm, this last being the most intense; it therefore corresponds to the major isomer. It is worth noting that no signal was observed when the spectrum was acquired at room temperature, and this fact can be rationalized by the coalescence, however, on heating to  $45$  °C a singlet shifted to  $-48.9$  ppm was observed. The major apical phenyl isomer can be explained by the electronegativity differences between phenyl and methyl groups.

The <sup>13</sup>C-NMR spectra of **2a**, **2b** and **2c** showed that the C-1 is shifted to higher frequencies in comparison to **1**  $\Delta\delta = 4, 5$  and  $5$  for **2a–2c**, respectively. Furthermore, C-2 and C-3 carbons are to lower frequencies  $\Delta\delta = 2$  (see Table 1).

The <sup>29</sup>Si chemical shifts for **2a**, **3a** and **4a** are compared with related five member rings siloxanes in the range  $\Delta\delta = 15–25$  (Chart 1).

The mass spectrometry for **2a–2c** showed the ion  $m/z = 584, 643, 643$  corresponding to the loss of methyl or phenyl group attached to the silicon atom.

The X-ray diffraction structures of **1**, **2a** and **2c** were established at room temperature. Crystallographic data and selected bond lengths and angles are summarized in

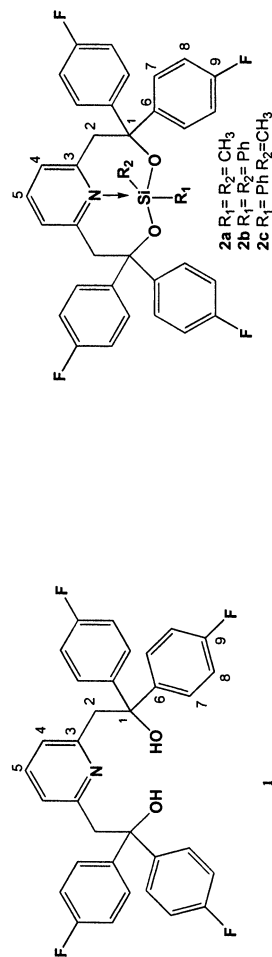


Scheme 2.

Table 1  
<sup>1</sup>H- and <sup>13</sup>C-NMR data for **1**, **2a–2c**

	H-2	H-4	H-5	H-7	H-8	CH <sub>3</sub> -Si	C-6	C-7	C-8	C-9	CH <sub>3</sub> Si
<b>1</b>	3.59 (4H, s)	6.72 (2H, d, <i>J</i> = 7.8)	7.31 (1H, t, <i>J</i> = 7.8)	7.23–7.29 (4H, m)	6.89–6.95 (4H, m)						
<b>2</b>	3.62 (4H, s)	6.57 (2H, d, <i>J</i> = 7.7)	7.22 (1H, t, <i>J</i> = 7.7)	7.17–7.23 (4H, m)	6.83–6.91 (4H, m)	0.27 (6H, s)					
<b>2b</b>	3.61 (4H, s)	6.71 (2H, d, <i>J</i> = 7.7)	7.31 (1H, t, <i>J</i> = 7.8)	6.82–7.61 (27H, m)	6.82–7.61 (27H, m)						
<b>2c</b>	3.55 and 3.73 (4H, AB, <i>J</i> = 14)	6.70 (2H, d, <i>J</i> = 7.7)	6.77–7.36 (22H, m)	6.77–7.36 (22H, m)	6.77–7.36 (22H, m)	0.66 (3H, s)					
C-1		C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9		CH <sub>3</sub> Si
<b>1</b>	77.6	48.3	157.3	123.1	137.4	142.3	127.9 (d, <sup>3</sup> <i>J</i> <sub>C-F</sub> = 8.2)	114.9 (d, <sup>2</sup> <i>J</i> <sub>C-F</sub> = 22.6)	161.7 (d, <sup>1</sup> <i>J</i> <sub>CF</sub> = 245.9)		
<b>2</b>	81.9	46.4	155.2	121.7	136.1	143.9	127.9 (d, <sup>3</sup> <i>J</i> <sub>C-F</sub> = 8.2)	114.9 (d, <sup>2</sup> <i>J</i> <sub>C-F</sub> = 21.9)	161.5 (d, <sup>1</sup> <i>J</i> <sub>CF</sub> = 244.1)		5.3
<b>2b<sup>a</sup></b>	83.2	45.8	155.8	122.2	136.7	143.3		114.7 (d, <sup>2</sup> <i>J</i> <sub>C-F</sub> = 21.9)	161.6 (d, <sup>1</sup> <i>J</i> <sub>CF</sub> = 244.1)		
<b>2c<sup>a</sup></b>	82.5	46.1	155.5	122.0	136.6		128.1 (d, <sup>3</sup> <i>J</i> <sub>C-F</sub> = 8.1)	114.5 (d, <sup>2</sup> <i>J</i> <sub>C-F</sub> = 21.9)	162.5 (d, <sup>1</sup> <i>J</i> <sub>CF</sub> = 244.2)		5.1

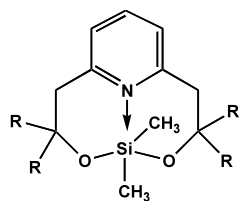
<sup>a</sup> C-7 and C-6 for **2b** and **2c** were not assigned due to the overlapping with phenyl carbons of the silicon.



Tables 2 and 3. The molecular structures are represented in Figs. 1–3; the silicon compounds show penta-coordinated geometries. The N→Si distances for **2a** and **2c** are 2.665(2) and 2.570(4) Å, respectively, which are much lower than the sum of the van der Waals radii (3.65 Å) [20]. However, the examination of the structure of **2a** revealed that the N→Si distance is slightly shorter than that observed for **3a** 2.703(2) Å and **4a** 2.727(2) Å (Chart 1). The nature of the substituents

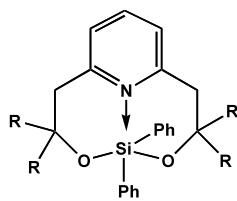
attached to the quaternary carbon could explain the differences observed in the N→Si bond lengths due to electronic effects exerted on the silicon atom. Taking into account this fact, one could expect short distances if electrowithdrawing groups are used.

The geometries for both silicon compounds show distortions toward a trigonal bipyramid, where the nitrogen occupies one apical site and the phenyl the second one. The bond angles around the silicon for **2a**

**2a**

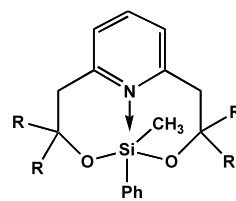
$^{29}\text{Si}$ ,  $\delta$ : -31.7  
Si-N 2.665(2) Å

$\Delta G^\ddagger$  10.7 kcal/mol

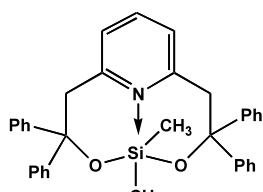
**2b**

$^{29}\text{Si}$ ,  $\delta$ : -60.9

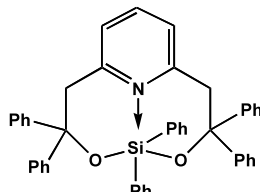
$\Delta G^\ddagger$  13.0 kcal/mol

**2c**

$^{29}\text{Si}$ ,  $\delta$ : -48.9 at 45 °C  
Si-N 2.570(4) Å

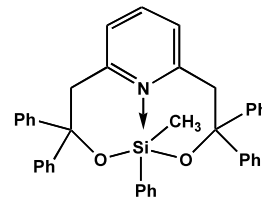
**3a**

$^{29}\text{Si}$ ,  $\delta$ : -32.4 [ref 13]  
Si-N 2.703(2) Å

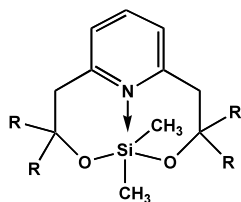
**3b**

$^{29}\text{Si}$ ,  $\delta$ : -61.9 [ref 14]  
Si-N 2.790(3) Å

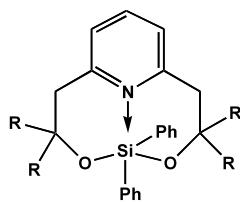
$\Delta G^\ddagger$  13.2 kcal/mol

**3c**

$^{29}\text{Si}$ ,  $\delta$ : -49.4 at 60°C [ref 15]

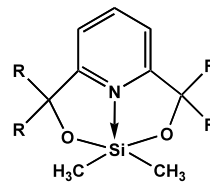
**4a** RR= adamantyl [ref 9]

$^{29}\text{Si}$ ,  $\delta$ : -41.6  
Si-N Å 2.727(2)

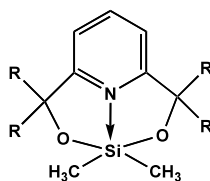
**4b** RR= adamantyl [ref 12]

$^{29}\text{Si}$ ,  $\delta$ : -72.6

$\Delta G^\ddagger$  13.5 kcal/mol

**5a** R= *p*-Br-C<sub>6</sub>H<sub>4</sub>

$^{29}\text{Si}$ ,  $\delta$ : -56.5 [ref 12]  
Si-N Å 1.950(8)

**5b** R= *p*-C(CH<sub>3</sub>)<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>

$^{29}\text{Si}$ ,  $\delta$ : -58.0 [ref 12]

Chart 1. All chemical shifts are reported at room temperature except for **2c** and **3c**.

Table 2  
Crystallographic data for compounds **1**, **2a** and **2c**

	<b>1</b>	<b>2a</b>	<b>2c</b>
Empirical formula	C <sub>33</sub> H <sub>25</sub> F <sub>4</sub> NO <sub>2</sub>	C <sub>35</sub> H <sub>29</sub> F <sub>4</sub> NO <sub>2</sub> Si	C <sub>40</sub> H <sub>31</sub> F <sub>4</sub> NO <sub>2</sub> Si
Formula weight (g mol <sup>-1</sup> )	542.54	599.68	661.75
Crystal size (mm)	0.64 × 0.60 × 0.48	0.60 × 0.48 × 0.30	0.68 × 0.48 × 0.30
Color	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	P $\bar{1}$	P2 <sub>1</sub> /C
<i>a</i> (Å)	34.830(2)	9.780(2)	9.372(1)
<i>b</i> (Å)	10.023(2)	11.038(1)	16.087(1)
<i>c</i> (Å)	16.861(1)	14.955(3)	23.186(2)
$\alpha$ (°)	90	88.97(1)	90
$\beta$ (°)	113.56	71.71(1)	98.80(1)
$\gamma$ (°)	90	81.99(1)	90
<i>V</i> (Å <sup>3</sup> )	5394.5(12)	1517.3(5)	3454.5(5)
<i>Z</i>	8	2	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.338	1.313	1.272
Number of collected reflections	4820	5675	6480
Number of independent reflections ( <i>R</i> <sub>int</sub> )	739	5337(0.0442)	6081(0.0338)
Number of observed reflections	4739	5337	6081
Number of parameters	367	388	433
<i>R</i> <sup>a</sup>	0.0742	0.0498	0.0690
<i>R</i> <sub>w</sub> <sup>b</sup>	0.1909	0.1146	0.1834
Goodness-of-fit	1.121	1.030	1.095

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

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

and **2c** are C(39)–Si(5)–N(13) 172.05 (1) and C(39)–Si(5)–N(13) 173.4(2), which approach the theoretical value of 180°; on the other hand, the equatorial bond angles (O4)–Si(5)–O(6), (O4)–Si(5)–C(38) and (O6)–Si(5)–C(38), range from 98.2(2) to 117.7(1). The two apical Si–C bonds Si(5)–C(38) 1.856(3) in compound **2a** and Si(5)–C(38) 1.867(5) in **2c** are slightly longer than the corresponding equatorial bond lengths which is usual in trigonal bipyramidal structures.

The difference observed in values of activation energy for the monomeric compounds **2a** and **2b** can be explained by the difficulty of interchanging a phenyl group from the equatorial to the axial position instead of methyl group.

### 3. Conclusions

From the N → Si distances of structures summarized in Chart 1 we conclude that an electronic effect induced by the substituents attached to the beta carbon of 2,6-pyridine ligands accounts for the lengthening or shortening of the N–Si distance. Additionally the series analyzed showed that the shield of <sup>29</sup>Si-NMR shift does not correlate with the decrease in the silicon–nitrogen distance as observed for previous silatrane type structures [21,22]. Furthermore, the increase observed in  $\Delta G^\ddagger$  for compounds with phenyl substituents on the silicon atom is in agreement with the difficulty of exchanging a phenyl group from the axial to equatorial position.

### 4. Experimental

2,6-Lutidine, *n*-BuLi, 4,4'(difluoro)benzophenone bis-dimethylamine(dimethyl)silane, dichlorodiphenylsilane, and dichloromethylphenylsilane were purchased from Aldrich. 2-{6-[2,2-Bis-(4-fluorophenyl)-2-hydroxy-ethyl-pyridin-2-yl]-1,1-bis-(4-fluorophenyl)-ethanol (**1**) was prepared according to a procedure described in the literature [23]. All reactions were carried out under nitrogen atmosphere, and the solvent were carefully dried and distilled from the appropriate drying agents prior to use. <sup>1</sup>H-, <sup>13</sup>C-, and <sup>29</sup>Si-NMR spectra were recorded on a JEOL Eclipse + 300, chemical shifts (ppm) are relative to the TMS. The <sup>29</sup>Si-NMR was obtained using the INEPT pulse sequence [24]. The mass spectra were obtained on JEOL JMS-AX505 HA. Melting points were measured on a Mettler Temp II and are uncorrected. Elemental microanalyses were performed by Galbraith Laboratories, Inc. The X-ray crystallography studies were done on a Siemens P4/PC diffractometer  $\lambda_{(Mo-K\alpha)} = 0.71073$  Å, graphite monochromator, *T* = 293 K,  $\omega$ -2 $\theta$  scan, range 1.5 <  $\theta$  < 25°. Corrections were done for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS-86); all nonhydrogen atoms were refined anisotropically, by full least-squares (SHELXL-97) [25]. Absorption correction for compounds **2a** and **2b** based on psi-scans were applied; hydrogen atoms bound to carbon atoms inserted at calculated position with isotropic temperature factor 1.2 times the *U*<sub>iso</sub> of the parent carbon atom.

#### 4.1. 2-{6-[2,2-Bis-(4-fluorophenyl)-2-hydroxy-ethyl-pyridin-2-yl]-1,1-bis-(4-fluorophenyl)-ethanol (1)

Compound 1 was prepared according to a procedure described in the literature [20]. The resulting yellow oil was chromatographed on silica gel with *n*-hexane–ethyl acetate (95:5) obtaining 1.52 g (60%), of colorless crystals; m.p. 132–135 °C; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 3.59 (4H, s, H-2), 5.21 (2H, s, OH), 6.72 (2H, d, *J* = 7.8

Table 3  
Selected bond lengths (Å) and angles (°) for 2a and 2c

	2a	2c
<i>Bond lengths</i>		
Si(5)–N(13)	2.665(2)	2.570(4)
Si(5)–C(38)	1.856(3)	1.867(5)
Si(5)–C(39)	1.862(3)	1.886(5)
Si(5)–O(4)	1.6372(2)	1.622(3)
Si(5)–O(6)	1.626(2)	1.641(3)
O(4)–C(3)	1.419(3)	1.415(5)
O(6)–C(7)	1.415(3)	1.424(4)
C(2)–C(3)	1.543(4)	1.541(6)
C(3)–C(14)	1.531(4)	1.534(6)
C(3)–C(20)	1.535(4)	1.551(6)
C(1)–N(13)	1.336(4)	1.322(6)
C(7)–C(8)	1.550(3)	1.545(6)
C(7)–C(26)	1.526(4)	1.537(6)
C(7)–C(32)	1.538(4)	1.542(6)
<i>Bond angles</i>		
O(4)–Si(5)–O(6)	113.3(1)	116.0(2)
O(4)–Si(5)–C(38)	117.7(1)	115.6(2)
O(4)–Si(5)–C(39)	101.5(1)	98.2(2)
O(4)–Si(5)–N(13)	73.4(1)	79.7(1)
O(6)–Si(5)–N(13)	78.1(1)	76.2(1)
O(6)–Si(5)–C(38)	115.7(1)	119.0(2)
O(6)–Si(5)–C(39)	98.9(1)	98.4(2)
C(38)–Si(5)–N(13)	81.4(1)	83.1(2)
C(39)–Si(5)–N(13)	172.1(1)	173.4(2)
C(3)–O(4)–Si(5)	140.7(2)	148.0(3)
C(7)–O(6)–Si(5)	149.4(2)	139.8(3)
N(13)–C(9)–C(8)	114.4(2)	114.6(4)
N(13)–C(1)–C(2)	114.2(2)	115.3(4)
C(38)–Si(5)–C(39)	106.5(2)	103.4(2)
C(9)–N(13)–Si(5)	119.6(2)	117.1(3)
C(1)–N(13)–Si(5)	116.9(2)	121.4(3)

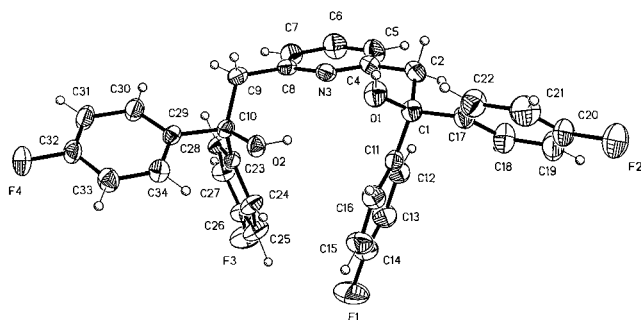


Fig. 1. Molecular structure of compound 1.

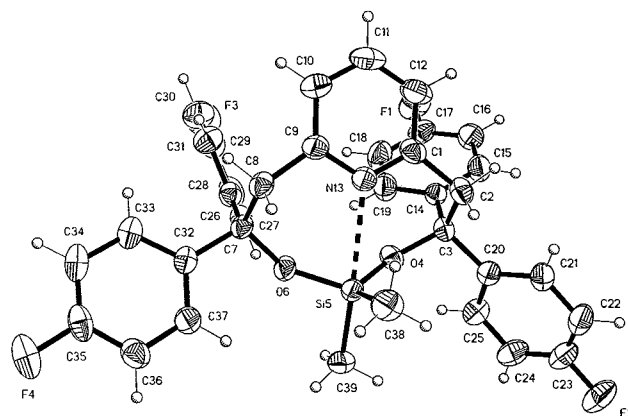


Fig. 2. Molecular structure of compound 2a.

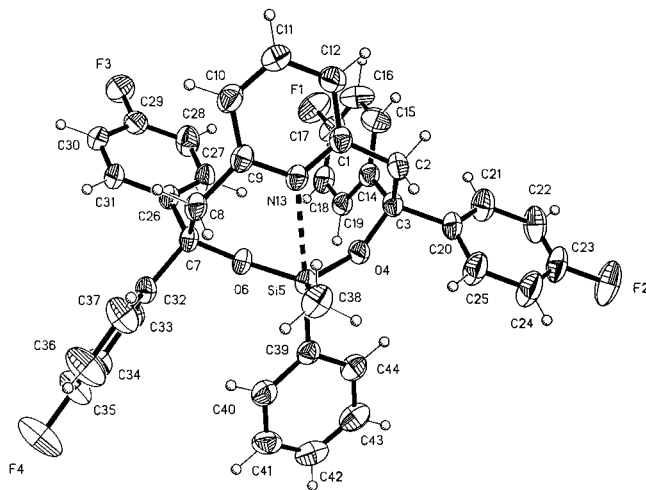


Fig. 3. Molecular structure of compound 2c.

Hz, H-4), 6.89–6.95 (4H, m, H-8), 7.23–7.29 (4H, m, H-7), 7.31 (1H, t, *J* = 7.8 Hz, H-5); <sup>13</sup>C-NMR (75.412 MHz, CDCl<sub>3</sub>) δ: 48.3 (C-2), 77.6 (C-1), 114.9 (d, *J* = 22.6 Hz, C-8), 123.1 (C-4), 127.9 (d, *J* = 8.2 Hz, C-7), 137.4 (C-5), 142.3 (C-6), 157.3 (C-3), 161.7 (d, *J* = 245.9 Hz, C-9); MS, *m/z* (%): 543 [M<sup>+</sup>, (6)], 430 (14), 406 (3), 325 (54), 307 (100), 219 (31), 212 (6), 188 (6), 123 (54), 107 (31), 95 (18), 28 (6), 4 (6); Anal. Found: C, 72.78, H, 4.70, N, 2.55. Calc. for C<sub>33</sub>H<sub>25</sub>F<sub>4</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.93; H, 4.60; N, 2.58%.

#### 4.2. 3,3,7,7-Tetrakis-(4-fluorophenyl)-5,5-dimethyl-4,6-dioxo-13-aza-5-silabicyclo[7.3.1]trideca-1(12),9(13),10-triene (2a)

To a solution of 1 g (1.84 mmol) of 2-{6-[2,2-bis-(4-fluorophenyl)-2-hydroxy-ethyl-pyridin-2-yl]-1,1-bis-(4-fluorophenyl)-ethanol (1) in 30 ml of toluene, 0.27 g (1.84 mmol) of bis(dimethylamino)dimethylsilane dropwise was added. After 24 h of refluxing, the solvent was evaporated and Et<sub>2</sub>O was added to the resulting yellow

oil, and the slow evaporation affords 0.33 g (30%) of colorless crystals; m.p. 230–236 °C; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 0.27 (6H, s, CH<sub>3</sub>), 3.62 (4H, s, H-2), 6.57 (2H, d, *J* = 7.7, H-4), 6.83–6.91 (4H, m, H-8), 7.17–7.23 (4H, m, H-7), 7.22 (1H, t, *J* = 7.7, H-5); <sup>13</sup>C-NMR (75.58 MHz, CDCl<sub>3</sub>) δ: 5.3 (CH<sub>3</sub>), 46.4 (C-2), 81.9 (C-1), 114.6 (d, *J* = 21.9 Hz, C-8), 121.7 (C-4), 127.9 (d, *J* = 8.1 Hz, C-7), 136.1 (C-5), 143.9 (C-6), 155.2 (C-3), 161.5 (d, *J* = 244.1 Hz, C-9); <sup>29</sup>Si-NMR (59.71 MHz, CDCl<sub>3</sub>) δ: –31.72; MS, *m/z* (%), 584 [M<sup>+</sup> – CH<sub>3</sub>, (28)], 508 (6), 381 (100), 366 (10), 306 (7), 286 (49), 275 (4), 247 (3.1), 212 (3), 201 (3), 163 (4), 123 (4), 97 (3), 69 (5), 57 (4), 43 (4); Anal. Found: C, 69.64, H, 5.05, N, 2.32. Calc. for C<sub>35</sub>H<sub>29</sub>F<sub>4</sub>NO<sub>2</sub>Si: C, 70.12; H, 4.84; N, 2.34%.

4.3. 3,3,7,7-Tetrakis-(4-fluorophenyl)-5,5-di-phenyl-4,6-dioxa-13-aza-5-silabicyclo[7.3.1]trideca-1(12),9(13),10-triene (**2b**)

To a solution of 0.7 g (1.29 mmol) 2-{6-[2,2-bis-(4-fluorophenyl)-2-hydroxy-ethyl-pyridin-2-yl]-1,1-bis-(4-fluorophenyl)-ethanol (**1**) in 30 ml of methylene chloride 0.26 g (2.6 mmol) of Et<sub>3</sub>N was added and then 0.33 g (1.29 mmol) dropwise of dichlorodiphenylsilane. The reaction mixture was refluxed for 24 h, the solvent was evaporated under vacuum and the resulting yellow solid was treated with water to eliminate Et<sub>3</sub>NHCl after extraction with methylene chloride (3 × 30 ml), 0.65 g (70%) of crystalline **2b** was obtained; m.p. 219–221 °C; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 3.61 (4H, s, H-2), 6.71 (2H, d, *J* = 7.7 Hz, H-4), 6.82–7.61 (27H, m, H-arom); <sup>13</sup>C-NMR (75.58 MHz, CDCl<sub>3</sub>) δ: 45.8 (C-2), 83.2 (C-1), 114.7 (d, *J* = 21.9 Hz, C-8), 122.2 (C-4), 127.2, 127.7, 127.8, 128.3, 128.4, 128.5, 130.5, 134.1, 134.4, 134.8, 136.7 (C-5), 143.3 (C-6), 155.8 (C-3), 161.6 (d, *J* = 245.2 Hz, C-9); <sup>29</sup>Si-NMR (59.71 MHz CD<sub>2</sub>Cl<sub>2</sub>,) δ: –60.90; MS, *m/z* (%); 793 (4), 715 (5), 643 [M<sup>+</sup> – Ph, (100)], 637 (15), 594 (8), 505 (24), 428 (24), 414 (9), 362 (3), 337 (11), 280 (9), 259 (23), 241 (9), 197 (6), 182 (4), 123 (5), 83 (5), 57 (7), 43 (6), 18 (4); Anal. Found: C, 73.90, H, 4.71, N, 1.82. Calc. for C<sub>45</sub>H<sub>33</sub>F<sub>4</sub>NO<sub>2</sub>Si: C, 74.69; H, 4.56; N, 1.94%.

4.4. 3,3,7,7-Tetrakis-(4-fluorophenyl)-5-methyl-5-phenyl-4,6-dioxa-13-aza-5-sila-bicyclo[7.3.1]trideca-1(12),9(13),10-triene (**2c**)

To a solution of 0.5 g (0.92 mmol) of 2-{6-[2,2-bis-(4-fluorophenyl)-2-hydroxy-ethyl-pyridin-2-yl]-1,1-bis-(4-fluorophenyl)-ethanol (**1**) in 30 ml of toluene and 0.19 g (1.84 mmol) of Et<sub>3</sub>N, 0.18 g (0.92 mmol) of dichloromethylphenylsilane was added dropwise. The reaction mixture was refluxed during 24 h, the solvent was removed under vacuum and the resulting yellow solid was treated with water for removing Et<sub>3</sub>NHCl,

after extraction with methylene chloride (3 × 30 ml) a yellow oil was obtained and then Et<sub>2</sub>O was added, and the slow evaporation yields 0.2 g (33%) of colorless crystals of **2c**; m.p. 174–176 °C; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 0.66 (3H, s, CH<sub>3</sub>), 3.55 and 3.73 (4H, AB, *J* = 14.0 Hz, H-2), 6.7 (2H, d, *J* = 7.7 Hz, H-4), 6.77–7.36 (22H, m, H-arom); <sup>13</sup>C-NMR (75.58 MHz, CDCl<sub>3</sub>) δ: 5.1 (CH<sub>3</sub>), 46.1 (C-2), 82.5 (C-1), 114.6 (d, *J* = 21.9 Hz, C-8) 122.0 (C-4), 128.2 (d, *J* = 8.1 Hz, C-7), 136.6 (C-5), 133.9, 142.7, 144.0, 155.5 (C-3), 161.7 (d, *J* = 245.2 Hz, C-9), 163.3 (d, *J* = 245.2 Hz, C-9); <sup>29</sup>Si-NMR (59.6 MHz, CDCl<sub>3</sub>) δ: –48.87 (45 °C). MS, *m/z* (%), 646 [M<sup>+</sup> – CH<sub>3</sub>, (21)], 584 (100), 508 (14), 443 (37), 428 (5), 366 (17), 348 (13.), 313 (3), 306 (4), 275 (5), 255 (6), 197 (6), 185 (2), 137 (4), 129 (7), 97 (4), 71 (8), 57 (12), 32 (8.1); Anal. Found: C, 71.92, H, 4.83, N, 2.03. Calc. for C<sub>40</sub>H<sub>31</sub>F<sub>4</sub>NO<sub>2</sub>Si: C, 72.62; H, 4.69; N, 2.12%.

## 5. Supplementary material

The crystallography data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 171497, 171499 and 171498 for compounds **1**, **2a**, and **2c**, respectively. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

## Acknowledgements

Financial support from CONACyT is grateful acknowledged. We thank M. en C. Francisco Javier Pérez Flores for recording mass spectrometry.

## References

- [1] M. Weinmann, A. Gehrig, B. Schiemenz, G. Huttner, B. Nuber, G. Rheinwald, H. Lang, J. Organomet. Chem. 563 (1998) 61.
- [2] A.R. Bassindale, M. Borbaruah, S.J. Glynn, D.J. Parker, P.G. Taylor, J. Chem. Soc. Perkin Trans. 2 (1999) 2099.
- [3] A.R. Bassindale, M. Borbaruah, S.J. Glynn, D.J. Parker, P.G. Taylor, J. Organomet. Chem. 606 (2000) 125.
- [4] M. Spiniello, J.M. White, Organometallics 19 (2000) 1350.
- [5] S. Belwal, R.V. Slingh, M.V. Voronkov, Russ. J. Gen. Chem. 69 (1999) 1793.
- [6] Y.I. Baukov, Y.E. Ovchinnikov, A.G. Shipov, E.P. Kramarova, V.V. Negrebetsky, Y.T. Struchkov, J. Organomet. Chem. 536–537 (1997) 399.
- [7] F. Jäkle, E. Vejzovic, K.N. Power-Billard, M.J. MacLachlan, A.J. Lough, I. Manners, Organometallics 19 (2000) 2826.
- [8] M. Gielen, M. Bouâlam, M. Biesemans, B. Mahieu, R. Willem, Heterocycles 34 (1992) 549.
- [9] B. Rezzonico, M. Grignon-Dubois, M. Laguerre, J.M. Léger, Organometallics 17 (1998) 2656.

- [10] H. Höpfl, N. Farfán, *Heteroatom Chem.* 9 (1998) 377.
- [11] J.M. Berg, R.H. Holm, *Inorg. Chem.* 22 (1983) 1768.
- [12] J.J.H. Edema, R. Libbers, A. Ridder, R.M. Kellog, A.L. Spek, J. *Organomet Chem.* 464 (1994) 127.
- [13] T.K. Prakasha, A. Chandrasekaran, R.O. Day, R.R. Holmes, *Inorg. Chem.* 35 (1996) 4342.
- [14] E. Gómez, V. Santes, V. de la Luz, N. Farfán, J. *Organomet. Chem.* 590 (1999) 237.
- [15] E. Gómez, V. Santes, V. de la Luz, N. Farfán, J. *Organomet. Chem.* 622 (2001) 54.
- [16] H. Kessler, *Angew. Chem. Int. Ed. Engl.* 9 (1970) 219.
- [17] A. Chandrasekaran, R.O. Day, R.R. Holmes, *Organometallics* 15 (1996) 3182.
- [18] A. Chandrasekaran, R.O. Day, R.R. Holmes, *Organometallics* 15 (1996) 3189.
- [19] S.D. Pastor, J.D. Spivack, *J. Org. Chem.* 49 (1984) 1297.
- [20] A. Bondy, *J. Phys. Chem.* 68 (1964) 441.
- [21] N.V. Timosheva, A. Chandrasekaran, R.O. Day, R.R. Holmes, *Organometallics* 19 (2000) 5614.
- [22] N.V. Timosheva, A. Chandrasekaran, R.O. Day, R.R. Holmes, *Organometallics* 20 (2001) 2331.
- [23] J.M. Berg, R.H. Holm, *J. Am. Chem. Soc.* 107 (1985) 917.
- [24] T.A. Blinka, B.J. Helmer, R. West, *Adv. Organomet. Chem.* 23 (1984) 193.
- [25] G.M. Sheldrick, *SHELXL-97*, Program for Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.