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Dimethyltin(IV) 2,6-disubstituted pyridine complexes

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Abstract

The synthesis and characterization of hypervalent pentacoordinated dimethyltin complexes obtained from the reaction of 2,6-disubstituted pyridine ligands with dichlorodimethyltin are reported. The complexes were characterized by mass spectrometry, ^{1}H-, ^{13}C- and ^{119}Sn-NMR and Mössbauer spectroscopy, additionally the structures for two compounds were established by X-ray diffraction analysis. The structural parameters indicated pentacoordinated structures, which present Sn–N interaction and trigonal bipyramidal tin environment.

Keywords: Tin(IV); Pentacoordinated; Pyridine; ^{119}Sn-NMR; X-ray diffraction; Mössbauer spectroscopy

1. Introduction

Organotin compounds are of great interest and they have been subject of diverse studies owing to their anticancer activity [1–4] as well as their applications as biocides [5,6]. Among these fascinating compounds especial interest has been dedicated to the study of organostannyl carboxylates due to they adopt several structural variations leading to different structure activity relationships [7,8]. Tin complexes with phosphonate ligands are also important because they can provide information about metabolism in living organisms [9]. Otherwise, from the structural point of view several hypervalent organotin complexes have been reported which include derivatives containing nitrogen and calcogen atoms [10], Schiff bases [11,12] and pyridine ligands [13,14]. It is known that pyridine ligands are excellent complexing agents and various examples are described. The reaction of 2-pyridylthiolate with diorganotin oxide gives monomeric molecules [15], whereas the same reaction using 2-methylthio-3-pyridinecarboxylate as ligand leads to dimeric or monomeric complexes [16]. The 2,6-pyridinedicarboxylic acid reacts with diorganotin oxide or diorganotin diacetate affording structures with pentagonal bipyramidal environment [17–22] and similar results are obtained by using the pyridine-2-phosphonate-6-carboxylate as ligand [23]. Additionally, it is also reported that the reaction of 2,6-dimethanol pyridine with diorganotin oxide yields monomeric species [24,25]. Our interest on organosilicon compounds led us to study the reactivity of different ligands containing pyridine moieties with organosilicon precursors. Interestingly, we found that the formation of monomeric or dimeric species is influenced by the nature of substituents at the pyridine ligand [26–28]. In continuing with our studies, we report herein the synthesis and characterization by multinuclear NMR, Mössbauer spectroscopy and X-ray examination of monomeric tin complexes.

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2. Results and discussion

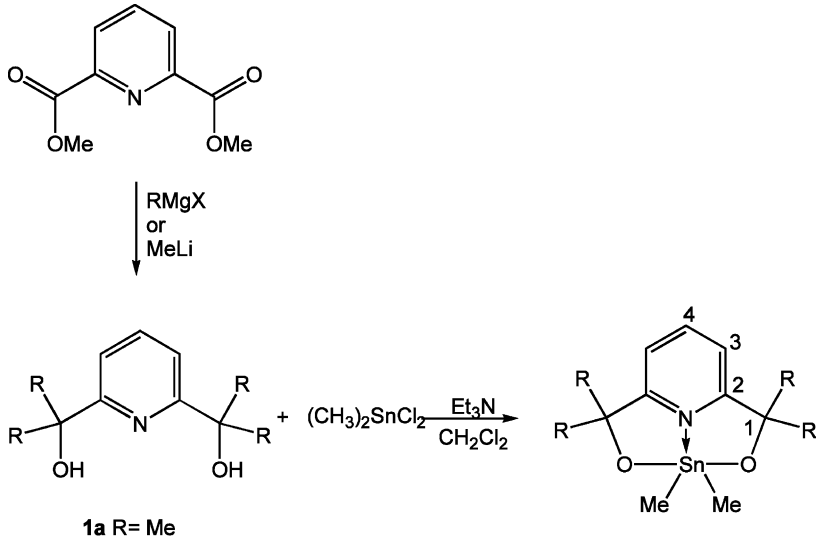
Compounds **1a**–**1c** were prepared by reaction of dimethyl 2,6-pyridinedicarboxylate with the corresponding reagent MeLi or Grignard, which were reacted with dimethyltin dichloride and triethylamine, affording the organostannyl derivatives **2a**–**2c** as shown in Scheme 1.

Mass spectrometry determination was done by using FAB^+ method which showed the molecular ions $m/z =$ 344, 592 and 816 corresponding to **2a**–**2c**, respectively. In addition, fragment ions C_5H_3N-2,6-$(CR_2O)(CRO)Sn(Me)_2^+$, C_5H_3N-2,6-$(CR_2O)_2SnMe^+$, C_5H_3N-2,6-$(CO)_2Sn^+$ were also detected. The fragmentation pattern is similar to that earlier reported [24,25].

Proton NMR spectra of **2a**–**2c** showed singlets at δ 0.52, 0.35 and 0.36 corresponding to the protons of methyl groups attached to the tin atom. Signals for the pyridine ring are slightly shifted to high frequencies compared to the ligands **1a**–**1c**. Additionally, ^{119}Sn and ^{117}Sn satellites due to coupling ^{1}H–^{119}Sn and ^{1}H–^{117}Sn were also observed. It is well known that the magnitude of $|^2J(^{119}Sn-^1H)|$ spin–spin coupling constant is function of the coordination number in dimethyl tin(IV) compounds. Values for this type of structures are in the range of 64–79 for pentacoordinated complexes as reported elsewhere [29,30]. We found values of $^2J(^{119}Sn-^1H) = 74.9$, 75.0 and 74.9 Hz for **2a**–**2c**, respectively, which are in agreement with this observation. ^{13}C-NMR signals for the pyridine ring carbons are shifted to low frequencies ($\Delta\delta = \sim 3$) with respect to ligands (see Table 1); this fact is attributed to the presence of the coordinative N→Sn bond. It is worth mentioning that silicon structures with N→Si bond exhibit the same behavior [27]. Determination of the C–Sn–C angles was based on measurement of the ^{119}Sn satellites coupling constants for CH_3–Sn ($\delta = 1.0$, $J(^{13}C-^{119}Sn) = 627.7$ Hz, for **2a**), ($\delta = 0.17$, $J(^{13}C-^{119}Sn) = 623.0$ Hz, for **2b**), ($\delta = 0.28$, $J(^{13}C-^{119}Sn) = 624.2$ Hz, for **2c**), which were used to calculate angles of 126.4, 125.6 and 125.8° for **2a**–**2c**, respectively [29]. Furthermore, ^{119}Sn-NMR spectra of **2a**–**2c** showed singlets at −95.0, −93.5 and −93.8 ppm, which agreed with those reported for pentacoordinated structures with an intramolecular N→Sn coordination. These data in combination with the spin–spin coupling constants allowed us to establish that all of these compounds exhibit pentacoordinated geometry in solution.

The X-ray diffraction structures of **2b** and **2c** were established at r.t., crystallographic data, and selected bond lengths and angles are summarised in Tables 2 and 3. The **2c** complex crystallised from ethyl acetate in the space group $P\bar{1}$, the crystal lattice also contains solvent molecules, whereas the **2b** complex crystallised in the non-centrosymmetric space group $P2_1$ despite the fact that the molecule is achiral; however, this can be attributed to deviation of the ideal symmetry *2/m*.

The coordination around the tin atom for complexes **2b** and **2c** is illustrated in Figs. 1 and 2; both compounds display similar structure where the tin atom is five-coordinated. The geometry can be considered as a distorted trigonal bipyramidal, with carbon and nitrogen atoms occupying the equatorial positions whereas the oxygen atoms the apical positions. Bond angles for the moiety C(9)–Sn–C(8) shows values of 121.8(2)/123.7(2) for **2a**/**2b** which accounts for the proposed geometry. However, it is worth noting that the bond angle O–Sn–O 138.2(1)/140.6(1)° of **2a**/**2b** is strongly



Scheme 1.

Table 1
^{1}H-, ^{13}C- and ^{119}Sn-NMR data for **1a**, **1b**, **2a**–**2c**

	CH_3	H-3	H-4	CH_3–Sn	H-arom	^{119}Sn
1a	1.56 (9H, s)	7.30 (2H, d, $J = 7.8$)	7.72 (2H, d, $J = 7.8$)			
1b		7.06 (2H, d, $J = 7.7$)	7.59 (2H, d, $J = 7.8$)		7.23–7.30 (20H, m)	
2a	1.50 (12H, s, CH_3)	7.43 (2H, d, $J = 7.7$)	7.95 (2H, t, $J = 7.7$)	0.52 (6H, s, $^{2}J(^{117}\mathrm{Sn}-^{1}\mathrm{H}) = 71.0$, $^{2}J(^{119}\mathrm{Sn}-^{1}\mathrm{H}) = 74.9$ Hz)		−95.0
2b		7.41 (2H, d, $J = 7.7$)	7.85 (1H, t, $J = 7.8$)	0.35 (6H, s, $^{2}J(^{117}\mathrm{Sn}-^{1}\mathrm{H}) = 71.7$, $^{2}J(^{119}\mathrm{Sn}-^{1}\mathrm{H}) = 75.0$ Hz)	7.25–7.31 (20H, m)	−93.5
2c		7.45 (2H, d, $J = 7.7$)	7.85 (1H, t, $J = 7.8$)	0.36 (6H, s, $^{2}J(^{117}\mathrm{Sn}-^{1}\mathrm{H}) = 72.0$, $^{2}J(^{119}\mathrm{Sn}-^{1}\mathrm{H}) = 74.9$ Hz)	7.16 and 7.26 (16H, AA′BB′, $J =$ 8.3 Hz)	−93.8

	C-1	C-2	C-3	C-4	CH_3	C-5	C-6	C-7	C-8	C-*i*	C-*o*	C-*m*	C-*p*	C-9	CH_3Sn
1a	72.3	164.5	116.8	138.1	30.6										
1b	81.4	162.5	121.6	137.1						145.9	128.0	128.2	127.5		
2a	70.9 ($J_{\mathrm{C-Sn}} =$ 34.6)	166.2 ($J_{\mathrm{C-Sn}} = 57.7$)	118.5 ($J_{\mathrm{C-Sn}} = 19.6$)	141.2	32.9										1.0 ($J_{\mathrm{C-Sn}} = 600$, 627.7)
2b	81.5 ($J_{\mathrm{C-Sn}} =$ 33.5)	163.2 ($J_{\mathrm{C-Sn}} = 48.5$)	123.0 ($J_{\mathrm{C-Sn}} = 18.5$)	139.8						148.4	128.0	127.8	127.2		0.17 ($J_{\mathrm{C-Sn}} =$ 596.5, 623.0)
2c [a]	81.0 ($J_{\mathrm{C-Sn}} =$ 33.5)	163.3 ($J_{\mathrm{C-Sn}} = 49.6$)	122.7 ($J_{\mathrm{C-Sn}} = 20.8$)	139.6	31.4	145.4	127.5	124.8	149.8					34.5	0.28 ($J_{\mathrm{C-Sn}} =$ 596.5, 624.2)

[a] The chemical shifts for C-5–C-8 correspond to C-30–C-33 according to the X-ray structure numbering.

Table 2
Crystallographic data for compounds **2b** and **2c**

	2b	**2c**
Formula	$C_{33}H_{29}NO_2Sn$	$C_{49}H_{61}NO_2Sn\cdot 0.5EtAc$
Formula weight (g mol^{-1})	590.26	858.73
Crystal size (mm^3)	0.262 × 0.214 × 0.133	0.211 × 0.116 × 0.056
Color	Colorless	Colorless
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P\bar{1}$
Unit cell dimensions		
a (Å)	8.613(1)	10.208(1)
b (Å)	13.740 (1)	15.438(1)
c (Å)	11.849(1)	15.466(3)
α (°)	90	83.041(2)
β (°)	90.732(1)	74.211(2)
γ (°)	90	85.538(2)
V (Å^3)	1402.1(1)	2325.5(3)
Z	2	2
D_{calc} (g cm^{-3})	1.398	1.226
No. of collected reflections	11566	26758
No. of independent reflections (R_{int})	4935(0.0358)	8200(0.0876)
No. of observed reflections	4935	8200
No. of parameters	336	494
R [a]	0.034	0.062
R_w [b]	0.051	0.082
GOF	1.09	1.11

[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 3
Selected bond lengths (Å) and bond angles (°) for **2b** and **2c**

	2b	**2c**
Bond lengths		
Sn(1)–O(1)	2.056(3)	2.036(3)
Sn(1)–O(2)	2.073(3)	2.028(3)
Sn(1)–C(9)	2.092(4)	2.104(5)
Sn(1)–C(8)	2.103(4)	2.095(5)
Sn(1)–N(1)	2.209(3)	2.204(4)
O(1)–C(1)	1.382(4)	1.405(5)
O(2)–C(7)	1.390(3)	1.412(5)
N(1)–C(2)	1.325(5)	1.339(6)
N(1)–C(6)	1.333(5)	1.343(5)
C(1)–C(2)	1.537(6)	1.563(6)
C(6)–C(7)	1.552(5)	1.530(7)
Bond angles		
O(1)–Sn–O(2)	138.5(1)	140.6(1)
O(1)–Sn–C(9)	95.3(2)	94.1(2)
O(2)–Sn–C(9)	92.1(2)	93.6(2)
O(1)–Sn–C(8)	104.0(2)	103.3(2)
O(2)–Sn–C(8)	106.4(2)	104.2(2)
C(9)–Sn–C(8)	121.8(2)	123.7(2)
O(1)–Sn–N(1)	73.2(1)	73.7(1)
O(2)–Sn–N(1)	73.2(1)	73.6(1)
C(9)–Sn–N(1)	135.5(2)	134.7(2)
C(8)–Sn–N(1)	102.6(2)	101.6(2)
C(1)–O(1)–Sn	120.1(2)	121.6(3)
C(7)–O(2)–Sn	121.1(2)	123.7(3)
C(2)–N(1)–C(6)	123.3(4)	124.3(5)
C(2)–N(1)–Sn	118.0(3)	117.3(4)
C(6)–N(1)–Sn	118.5(3)	118.4(4)

distorted from the ideal angle for a bipyramidal trigonal geometry, which can be the result of the ring constraint. It is important to mention that the values for C–Sn–C bond angles found in solid state are in agreement with calculations performed from the NMR data in solution.

The Sn–N bond distance for **2b** is 2.209(3) and 2.204(4) Å for **2c**, which are slightly shorter than those found for related compounds possessing penta and seven coordinated tin atom [12,17,19,20]. Furthermore, the Sn–O bond distances are in accordance with previous reports concerning pentacoordinated tin species [8].

In order to gain structural information in the solid state, we carried out a Mössbauer spectroscopic study. All spectra were obtained at 10 K and they are depicted in Fig. 3; parameters involved are summarised in Table 4. The Mössbauer spectra of **2a**–**2c** compounds show a doublet with values of IS ranging from 0.894 to 0.977 mm s^{-1} whereas QS show values from 1.844 to 2.026 mm s^{-1}, which are typical for Sn(IV) pentacoordinated compounds [25]. The differences observed in IS and QS for compounds **2a**–**2c** are negligible, it therefore means that all of these complexes posses the same geometry around the tin atom, which correspond to pentacoordinated structures displaced towards trigonal bipyramidal as supported by the X-ray diffraction for **2b** and **2c** compounds. It should be noted, that values of QS and IS for **2a**–**2c** are in agreement with those reported for similar pentacoordinated organotin structures [31].

In conclusion, pyridine diol ligands in reaction with dimethyltin dichloride afford selectively monomeric five-coordinated tin complexes. In all cases, the geometry is strongly distorted towards bipyramidal trigonal as shown by the X-ray examination and the Mössbauer spectroscopic study. In addition, it is established that the solid-state structures of dimethyltin compounds are retained in solution as deduced from the NMR spectroscopic study.

3. Experimental

2,6-Pyridinedicarboxylate, MeLi and bromobenzene were purchased from Aldrich. All reactions were carried out under nitrogen atmosphere; the solvents were carefully dried and distilled from the appropriate drying agents prior to use. ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectra were recorded on a JEOL Eclipse +300, chemical shifts (ppm) are relative to the TMS and $(CH_3)_4Sn$. Mass spectra were obtained on JEOL JMS-AX505 HA; Melting points were measured on a Melt-b Temp II and are uncorrected. The X-ray crystallography studies were done on a Siemens P4/PC diffractometer λ(Mo–

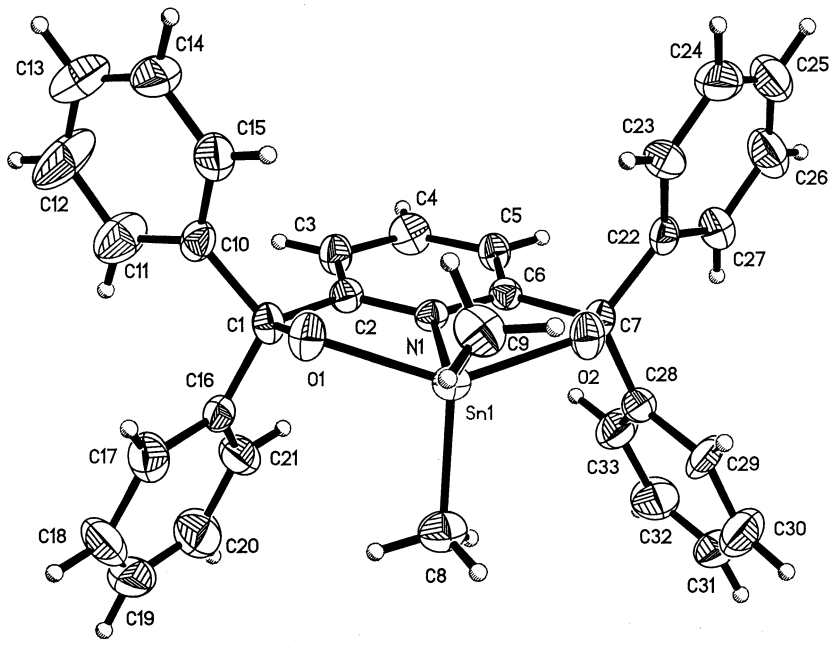


Fig. 1. Molecular structure for compound **2b**.

K_α) = 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) [32]. Absorption correction for compounds **2b** and **2c** 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_{iso} of the parent carbon atom. Mössbauer spectra were collected at 10 K, the spectrometer was operated in the constant acceleration mode in transmission experiments, with a 15 mCi (555 MBq) single-line gamma-ray source of $Ba^{119m}SnO_3$. The temperature of the source was 295 K during the measurements. Detection of the 23.8 keV γ-rays was achieved with a Kr proportional counter and

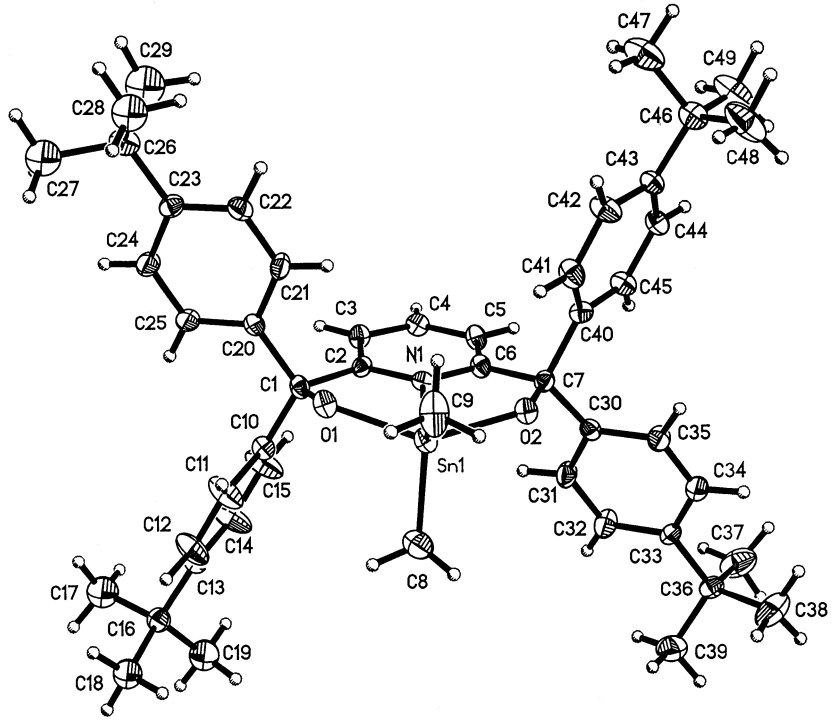


Fig. 2. Molecular structure for compound **2c**.

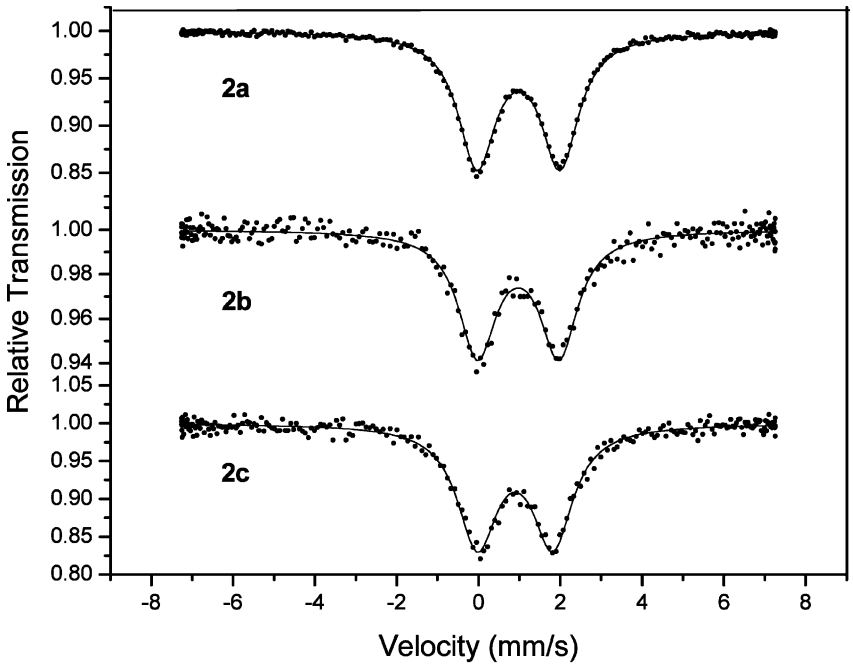


Fig. 3. Mössbauer spectra of **2a**, **2b** and **2c**.

a 0.05 mm thick Pd foil was placed between the source, and detector to filter 25.0 and 25.2 keV X-rays from the source. The source was moved by a loud-speaker drive with a sinusoidal velocity relative to the stationary absorber. Its velocity was regulated and followed the sine wave to within 0.1%. The chemical isomer shift (IS) data are quoted relative to $Ba^{119m}SnO_3$. The absorption spectra were computer fitted by using the NORMOS program.

3.1. 2,6-*Bis*-(1-hydroxy-1-methyl-ethyl) pyridine (*1a*)

MeLi (52 ml, 0.55 M) was added to a solution of dimethyl 2,6-pyridinedicarboxylate (1.1 g, 5.75 mmol) in THF, the reaction mixture was stirred 24 h at room temperature (r.t.), then it was treated with water, and after extraction with methylene chloride (3×30 ml) a dark oil was obtained, which was chromatographed on silica gel with *n*-hexane–ethyl acetate obtaining 1.52 g (60%) of colorless crystals of **1a** [33]; m.p. 94–95 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.56 (9H, s, CH_3), 7.30 (2H, d, $J = 7.8$ Hz, H-3), 7.72 (1H, t, $J = 7.8$ Hz, H-4); ^{13}C-NMR (75.412 MHz, $CDCl_3$) δ: 30.6 (CH_3), 72.3 (C-1), 116.8 (C-3), 138.1 (C-4), 164.5 (C-2); MS, *m*/*z* (%): 195 [M^+,(2)], 180 (42), 162 (100), 138 (17), 118 (24), 104 (14), 78 (10), 59(15), 43 (22), 31 (12).

Table 4
^{119}Sn Mössbauer parameters of **2a**–**2c**

Sample	IS [a] (mm s^{-1})	QS (mm s^{-1})	Γ_1; Γ_2 [b] (mm s^{-1})
2a	0.894 ± 0.008	1.844 ± 0.014	1.187 ± 0.023
2b	0.977 ± 0.002	2.026 ± 0.003	1.112 ± 0.005
2c	0.968 ± 0.011	1.989 ± 0.006	1.110 ± 0.033

[a] Isomer shift relative to $Ba^{119m}SnO_3$.

[b] Full width at half height of the resonant peaks at higher and lower velocity than the spectrum centroid, respectively; spectra with $\Gamma_1 = \Gamma_2$ were fitted as symmetrical doublets with the NORMOS program.

3.2. 2,6-Bis-(1-hydroxy-1,1-diphenyl-methyl) pyridine (*1b*)

The compound **1b** was prepared according to a procedure described in the literature [27]:From 4.3 ml (10.25 mmol) bromobenzene, 1.20 g (40.98 mmol) magnesium and 1.20 g (10.25 mmol) of dimethyl 2,6-pyridinedicarboxylate, the resulting yellow oil crystallized from acetone obtaining 2.87 g (63%) of colorless crystals; m.p. 124–128 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.06 (2H, d, $J = 7.7$ Hz, H-3), 7.23–7.30 (20H, m, arom), 7.59 (1H, t, $J = 7.8$ Hz, H-4); ^{13}C-NMR (75.412 MHz, $CDCl_3$) δ: 81.4 (C-1), 121.6 (C-3), 127.5 (C-*p*), 128.0 (C-*o*), 128.2 (C-*m*), 137.1 (C-4), 145.9 (C-*i*), 162.5 (C-2); MS, *m*/*z* (%): 444 [$M^+ + 1$, (14.6)], 443 [M^+, (42.3)], 425 (18.5), 407 (6.0), 348 (20.9), 243 (15.7), 167 (5.0), 105(12.9), 71 (8.3), 50 (53.7), 43 (100), 15 (7.6).

3.3. 2,2,4,4,6,6-Hexamethyl-3,5-dioxa-11-aza-4-stanna-bicyclo[5.3.1]undeca-1-(10),7(11),8-triene (**2a**)

Dimethyltin dichloride (0.24 g, 1.1 mmol) was added to a solution of 2,6-pyridinebis(dimethylmethanol) (**1a**) (0.216 g, 1.1 mmol) in methylene chloride and of Et_3N (0.22 g, 2.2 mmol). After 6 h of refluxing, 10 ml of water was added to remove Et_3NHCl, the solvent was evaporated resulting a yellow solid, 0.205 g (54%); m.p. 163–164 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.52 (6H, s, $^2J(^{119}Sn-^1H) = 74.2$ Hz, $^2J(^{117}Sn-^1H) = 71.0$ Hz, CH_3–Sn), 1.50 (12H, s, CH_3), 7.43 (2H,d, $J = 7.7$, H-3), 7.95 (1H, t, H-4), ^{13}C-NMR (75.58 MHz, $CDCl_3$) δ: 1.0 (CH_3-Sn, $J(^{117}Sn-^{13}C) = 599.9$, $J(^{119}Sn-^{13}C) = 627.7$ Hz), 32.9 (CH_3), 70.9 (C-1, $J(^{119/117}Sn-^{13}C) = 34.6$ Hz), 118.5 (C-3, $J(^{119/117}Sn-^{13}C) = 19.6$ Hz), 141.2 (C-4), 166.2 (C-2, $J(^{119/117}Sn-^{13}C) = 57.7$Hz); ^{119}Sn-NMR (112.06 MHz, $CDCl_3$) δ: −95.0; MS (FAB) *m/z* (%); 344 [$(M+H)^+$, (100)], 342 [$(M^+-1$ (37)], 341 [$(M^+-2$ (77)], 340 [$(M^+-3$ (31)], 339 [$(M^+-4$ (45)], 328 [$(M^+-CH_3$ (31)], 312 (11), 296 (11), 281 (5), 254(3), 102 (54), 55 (22), 43 (20), 29 (5).

3.4. 4,4-Dimethyl-2,2,6,6-tetraphenyl-3,5-dioxa-11-aza-4-stanna-bicyclo[5.3.1]undeca-1(10),7(11),8-triene (**2b**)

Compound **2b** was prepared following the procedure described for **2a** from 0.5 g (1.128 mmol) 2,6-pyridinebis(diphenylmethanol) (**1b**), 0.228 g (2.258 mmol) of Et_3N, 0.247 g (1.128 mmol) of dimethyltin dichloride, After 4 h of refluxing, 10 ml of water was added to remove Et_3NHCl, the solvent was evaporated resulting 0.424 g (63%) of colorless crystals; m.p. 213 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.35 (6H, s, $^2J(^{119}Sn-^1H) = 75.0$ Hz, $^2J(^{117}Sn-^1H) = 71.7$ Hz, CH_3–Sn), 7.25–7.31 (20H, m, H-arom), 7.41(2H, d, H-3); 7.85(1H, t, H-4); ^{13}C-NMR (75.58 MHz, $CDCl_3$) δ: 0.17(CH_3–Sn, $J(^{117}Sn-^{13}C) = 596.5$, $J(^{119}Sn-^{13}C) = 623.0$ Hz), 81.5 (C-1, $J(^{119/117}Sn-^{13}C) = 33.5$ Hz), 123.0 (C-3, $J(^{119/117}Sn-^{13}C) = 18.5$ Hz), 127.2 (C-*p*), 127.8 (C-*m*), 128.0 (C-*o*), 139.8 (C-4), 148.4 (C-*i*), 163.2 (C-2, $J(^{119/117}Sn-^{13}C) = 48.5$ Hz); ^{119}Sn-NMR (112.06 MHz, $CDCl_3$) δ: −93.5; MS (FAB), *m/z* (%); 592 [$(M+H)^+$, (100)], 590 [$(M^+-1$ (50)], 589 [$(M^+-2$ (79)], 588[$(M^+-3$ (42)], 587[$(M^+-4$ (42)], 576 [$(M^+-CH_3$ (15)], 484 (4), 408 (44), 379 (5), 348 (10), 307 (14), 343(10), 105 (20), 77 (14).

3.5. 2,2,6,6-Tetrakis-(4-tert-butyl-phenyl)-4,4-dimethyl-3,5-dioxa-11-aza-4-stanna-bicyclo[5.3.1]undeca-1(10),7(11),8-triene (**2c**)

Compound **2c** was prepared following the procedure described for **2a** from 0.25 g (0.375 mmol) 2,6-Pyridinebis(di-4-*tert*-butylphenylmethanol) (**1b**), 0.075 g (0.75 mmol) of Et_3N, 0.082 g (0.375 mmol) of dimethyltin dichloride, After 4 h of refluxing, 10 ml of water was added to remove Et_3NHCl, the solvent was evaporated resulting a pink solid, after crystallized from Ethyl Acetate 0.292 g (95%) of colorless crystals of **2c** were obtained; m.p. 231–232 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.36 (6H, s, $^2J(^{119}Sn-^1H) = 72.0$ Hz, $^2J(^{117}Sn-^1H) = 74.9$Hz, CH_3–Sn), 1.27 (9H, s, $(CH_3)_3$), 7.16 and 7.26 (16H, AA′BB′, $J = 8.3$ Hz, H-6,H-7), 7.45 (2H,d, $J = 7.7$ Hz, H-3), 7.85 (1H, t, $J = 7.6$ Hz, H-4); ^{13}C-NMR (75.58 MHz, $CDCl_3$) δ: 0.28 (CH_3–Sn, $J(^{119}Sn-^{13}C) = 596.5$, $J(^{119}Sn-^{13}C) = 624.2$ Hz), 31.4 (($CH_3)_3$–C), 34.5 (C–$(CH_3)_3$)), 81.0 (C-1, $J(^{119/117}Sn-^{13}C) = 33.5$ Hz), 122.7 (C-3, $J(^{119/117}Sn-^{13}C) = 20.8$ Hz), 124.8 (C-7), 127.5 (C-6), 145.4 (C-5), 139.6 (C-4), 149.8 (C-8), 163.3 (C-2, $J(^{119/117}Sn-^{13}C) = 49.6$ Hz); ^{119}Sn-NMR (112.06 MHz, $CDCl_3$) δ: −93.8; MS (FAB) *m/z* (%); 816 [$(M+H)^+$, (100)], 815 [M^+ (92)], 814 [$(M^+-1$ (100)], 813[$(M^+-2$ (68)], 812[$(M^+-3$ (65)], 800 [$(M^+-CH_3$ (30)], 784 (7), 767 (5), 682 (79), 632 (25), 576(9), 560 (6), 491 (12), 460 (10), 404 (10), 358 (7), 284 (6), 253 (11), 167 (14), 161 (43), 118 (6), 91 (9), 57 (33), 41(9), 29 (5).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 198709 and 188708 for compounds **2b** and **2c**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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