

Synthesis and structural characterization of new functionalized bis (fluorenyl)stannane derivatives



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ABSTRACT

New stable functionalized bis(fluorenyl)stannane derivatives with the general formula $(9\text{-SiMe}_3\text{-CR}_2)(9\text{-R}'\text{-CR}_2)\text{SnX}_2$ ($\text{CR}_2 = 9\text{-fluorenyl}$, $\text{R}' = \text{H, SiMe}_3$, $\text{X} = \text{Br, Cl, OCOCH}_3$) were obtained starting from the corresponding tetraorgano-tin compounds of $\text{Ph}_2(9\text{-SiMe}_3\text{-CR}_2)(9\text{-R}'\text{-CR}_2)\text{Sn}$ type. All new compounds were completely characterized in solution by multinuclear NMR spectroscopy and mass spectrometry. The structure in solid state for derivatives **2** ($\text{R}' = \text{H, X} = \text{Ph}$), **3** ($\text{R}' = \text{SiMe}_3$, $\text{X} = \text{Ph}$), **4** ($\text{R}' = \text{H, X} = \text{Br}$) and **6** ($\text{R}' = \text{H, X} = \text{Cl}$), has been elucidated by single crystal X-ray diffraction. The influence of the functional groups X and of the intramolecular $\text{C}\cdots\pi$ interactions on the adopted molecular geometry has been analyzed.

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1. Introduction

Organotin derivatives have received a great interest, especially during the last period, due to their applications in catalysis and in the synthesis of new materials with controlled properties [1–13]. It is well known that the Sn–C bond is more labile than the one formed by the lighter analogues in group 14 [14]. In order to increase the stability of this bond, organotin derivatives containing two fluorenyl units are very promising, due to both electronic and steric effects [2,15–19] induced by this organic group. To enhance the steric hindrance induced by the fluorenyl group, the H atom in position 9 can be easily substituted with larger group such as $-\text{SiMe}_3$ [19,20]. Several organotin derivatives containing two fluorenyl groups substituted or not at the position 9, have been reported. Depending on the R' and R'' groups attached to this position, the compounds with the general formula $\text{Me}_2\text{E}(\text{CR}_2\text{-R}')(\text{CR}_2\text{-R}'')$ ($\text{E} = \text{Si, Ge, Sn}$, $\text{CR}_2 = 9\text{-fluorenyl}$, $\text{R}', \text{R}'' = \text{H, Me, SiMe}_3$) can adopt preferentially *in-out* or *out-out* conformations in solid state (Scheme 1), which differ by the relative orientation of the R' and R'' towards the opposite fluorenyl groups [15,16,19,20].

The adopted geometry can be correlated with the steric hindrance induced by the R' and R'' groups and the presence of $\text{C-H}\cdots\pi$ or $\pi\cdots\pi$ intra- and intermolecular interactions, respectively. While the influence of differently substituted fluorenyl groups in adopting one of the two conformations has been studied, the role of the other two groups connected to the heavy group 14

element (Si, Ge, Sn) was not yet investigated. Moreover, apart from the methylated bis(fluorenyl) compounds $\text{Me}_2\text{E}(\text{CR}_2\text{-R}')(\text{CR}_2\text{-R}'')$ ($\text{E} = \text{Si, Ge, Sn}$), only one functionalized bis(fluorenyl)derivative $(9\text{-Me-CR}_2)_2\text{SiCl}_2$ has been reported previously [21].

This paper presents the synthesis and structural characterization of new stable derivatives with the general formula $(9\text{-SiMe}_3\text{-CR}_2)(9\text{-R}'\text{-CR}_2)\text{SnX}_2$ ($\text{CR}_2 = 9\text{-fluorenyl}$, $\text{R}' = \text{H, SiMe}_3$, $\text{X} = \text{Ph, Br, Cl, OCOCH}_3$) that can function as molecular building blocks for new organometallic materials with controlled properties.

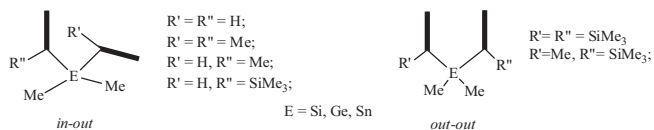
2. Experimental

2.1. General remarks

All the reactions were carried out under argon atmosphere, using Schlenk techniques. Dry diethyl ether and toluene were obtained from an MBraun Automatic Solvent Purifying System. All others solvents and reagents were used as commercially available (99.8% purity in case of methanol and 99–99.7% purity for the solvents used for purifications). NMR spectra were recorded in CDCl_3 on Bruker Avance 400 (at operation frequencies of 400.13 MHz for ^1H , 100.61 MHz for ^{13}C and 149.21 MHz for ^{119}Sn), and Avance 600 (at operation frequencies of 600.13 MHz for ^1H and 150.9 MHz for ^{13}C). Chemical shifts are given relative to the solvent residual peak for ^1H and ^{13}C and relative to neat SnMe_4 for ^{119}Sn NMR. Mass spectroscopy experiments were performed on a LTQ Orbitrap XL-Thermo-Scientific mass spectrometer. Elemental analyses were recorded on a Thermo Flash EA 1112 Analyzer.

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Scheme 1.

2.2. X-ray crystallography

The details of the crystal structure determination and refinement for compounds **2**, **3**, **4** and **6** are given in Table 1. Data were collected on a Bruker SMART APEX diffractometer by using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The crystals were attached with paratone/N oil to cryoloops and the data were collected at room temperature (294 K). The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement, the software package SHELX-97 was used [22]. The drawings were created with the Diamond program [23]. The crystallographic data for the structural determinations have been deposited with the Cambridge Crystallographic Data Centre with the following numbers: CCDC 1436911 (**2**) CCDC 1436910 (**3**) CCDC 1436908 (**4**) CCDC 1436909 (**6**).

2.3. Experimental procedures

2.3.1. General procedure for the synthesis of lithiated derivatives

A solution of reagent in diethyl ether was treated at -50 °C with *n*-butyllithium (3% excess of a 1.6 or 2.5 M solution in hexane). The reaction was completed within 30 min by allowing it to warm to

0 °C and was cooled at low temperature before the second reagent was added dropwise.

A general notation of the hydrogen and carbon atoms of the fluorenyl groups used in the assignment of the NMR signals is presented in Scheme 2:

2.3.2. Synthesis of (9-SiMe₃-fluorene-9-yl)diphenyl-chloro-stannane **1**

(9-(trimethylsilyl)-fluorene-9-yl)lithium was obtained from 3 g (12.6 mmol) of 9-SiMe₃-fluorene [24] and *n*-butyllithium (5.1 ml of 2.5 M solution in hexane, 12.75 mmol) as described in the general procedure. To this mixture, at -60 °C, dichlorodiphenylstannane (4.33 g, 12.6 mmol) dissolved in diethylether was added dropwise. The resulting solution was allowed to slowly turn to room temperature. After filtration of lithium salts and concentration of the filtrate under reduced pressure, compound **1** crystallized at low temperature. Compound **1** was obtained as air sensitive yellow crystals (84%, 6.3 g).

¹¹⁹Sn NMR [149.21 MHz] $\delta = -9.82$ ppm.

¹H NMR [600.13 MHz] $\delta = -0.03$, 9H, s, SiMe₃; 7.10, 4H, d (³J_{HH} = 6.9 Hz, ³J_{SnH} = 67.4 Hz), H-orto-Ph; 7.24, 4H, t (³J_{HH} = 7.4 Hz), H-meta-Ph; 7.31, 2H, t, (³J_{HH} = 7.4 Hz), H-para-Ph, 7.35–7.41, 4H, m, H-2,3,6 and 7; 7.77, 2H, d, (³J_{HH} = 7.4 Hz), H-1,8; 7.94, 2H, d, (³J_{HH} = 7.6 Hz), H-4,5.

¹³C NMR [150.90 MHz] $\delta = -1.2$ (²J_{Csn} = 12.0 Hz), 42.9, 120.3, 120.4, 124.5, 125.3, 126.4, 128.8, 130.1, 136.0, 145.2.

Anal. Calc. for C₂₈H₂₇ClSiSn: C, 61.62; H, 4.99. Found: C, 61.94; H, 4.87%.

2.3.3. Synthesis of (9H-fluorene-9-yl)(9-SiMe₃-fluorene-9-yl)diphenylstannane **2**

Route 1: A solution of 9H-fluorene-9-yl-lithium, prepared from 1.25 g (7.53 mmol) of fluorene and *n*-BuLi (4.8 ml of 1.6 M solution

Table 1
Crystallographic data for compounds **2**, **3**, **4** and **6**.

	2	3	4	6
Empirical formula	C ₄₁ H ₃₆ SiSn	C ₄₄ H ₄₄ Si ₂ Sn	C ₂₉ H ₂₆ Br ₂ SiSn	C ₂₉ H ₂₆ Cl ₂ SiSn
Formula weight	675.48	747.66	681.10 g/mol	592.18 g/mol
T (K)	293(2)	294(2)	294(2)	294(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	P $\bar{1}$	Cc	P $\bar{1}$	P $\bar{1}$
a (Å)	10.6837(19)	19.339(12)	9.9501(12)	9.779(4)
b (Å)	12.108(2)	19.113(12)	9.9638(12)	9.800(4)
c (Å)	13.768(2)	10.694(7)	14.3005(17)	14.152(6)
α (°)	97.017(3)	90	88.357(2)	88.080(7)
β (°)	94.779(3)	102.461(12)	89.131(2)	87.963(7)
γ (°)	108.700(3)	90	75.572(2)	77.456(5)
V (Å ³)	1660.0(5)	3859(4)	1372.4(3)	1322.6(10)
Z	2	4	2	2
D _{cal} (g/cm ³)	1.351	1.287	1.648	1.487
Absorption coefficient (mm ⁻¹)	0.833	0.753	3.901	1.229
F(000)	692	1544	668	596
Crystal size (mm)	0.37 × 0.31 × 0.20	0.31 × 0.27 × 0.22	0.19 × 0.12 × 0.10	0.31 × 0.26 × 0.22
Theta range for data collection (°)	1.503–24.999	1.503–24.999	1.425–25.003	1.440–24.998
Index ranges	–12 ≤ h ≤ 12 –14 ≤ k ≤ 14 –16 ≤ l ≤ 16	–22 ≤ h ≤ 22 –22 ≤ k ≤ 22 –12 ≤ l ≤ 12	–11 ≤ h ≤ 11, –11 ≤ k ≤ 11, –17 ≤ l ≤ 17	–11 ≤ h ≤ 11, –11 ≤ k ≤ 11, –16 ≤ l ≤ 16
Reflections collected/unique	15641/5790 [R _(int) = 0.0467]	17546/6721 [R _(int) = 0.0947]	113003/4789 [R _(int) = 0.0380]	12393/4617 [R _(int) = 0.0542]
Completeness to theta maximum (%)	99.1	99.7	99.2	98.9
Absorption correction		multi-scan		
Refinement method		Full-matrix least-squares on F ²		
Data/restraints/parameters	5790/0/392	6721/2/426	4789/0/302	4617/0/302
Goodness-of-fit on F ² -S	1.001	0.942	1.049	1.092
Final R indices	R ₁ = 0.0365	R ₁ = 0.0609	R ₁ = 0.0376	R ₁ = 0.0482
[I > 2σ(I)]	wR ₂ = 0.0775	wR ₂ = 0.1277	wR ₂ = 0.0848	wR ₂ = 0.1167
R indices (all data)	R ₁ = 0.0467	R ₁ = 0.0823	R ₁ = 0.0495	R ₁ = 0.0632
	wR ₂ = 0.0819	wR ₂ = 0.1375	wR ₂ = 0.0973	wR ₂ = 0.1278
Largest difference peak and hole (e Å ⁻³)	0.491 and –0.477	1.270 and –1.206	0.632 and –0.601	0.783 and –0.768

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