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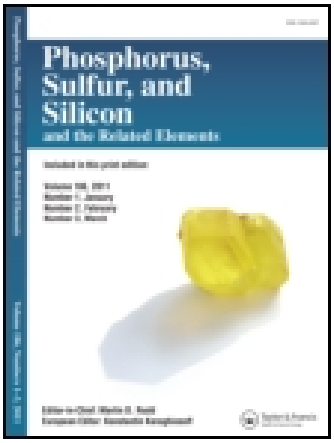

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Synthesis, Characterization, and Structure of Some Silicon Containing Diorganotin(IV) Complexes of Salicylaldehyde Thiosemicarbazones

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SYNTHESIS, CHARACTERIZATION, AND STRUCTURE OF SOME SILICON CONTAINING DIORGANOTIN(IV) COMPLEXES OF SALICYLALDEHYDE THIOSEMICARBAZONES

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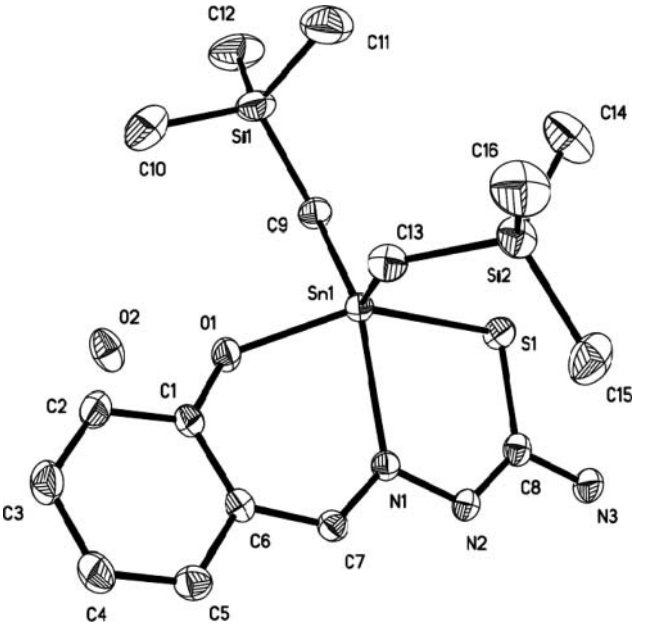
GRAPHICAL ABSTRACT



Abstract *Four diorganotin(IV) complexes, bis[(trimethylsilyl)methyl]tin salicylaldehyde thiosemicarbazonate monohydrate(**1**), bis[(trimethylsilyl)methyl]tin 3-methoxysalicylaldehyde thiosemicarbazonate (**2**), bis[(trimethylsilyl)methyl]tin 5-tert-butyl-3-methylsalicylaldehyde*

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*thiosemicarbazonate (**3**), and bis[(trimethylsilyl)methyl]tin 2-oxylnaphthaldehyde thiosemicarbazonate (**4**) have been synthesized by reactions of $(Me_3SiCH_2)_2SnCl_2$ with the corresponding semicarbazone. The four complexes were characterized by IR and NMR spectroscopy and elemental analyses. The X-ray studies of compounds **1** and **4** showed that the thiosemicarbazone ligands act as tridentate ligands chelating to the central tin atoms, and thus the tin atoms were five coordinated in trigonal bipyramidal geometry for both compounds.*

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Keywords Organotin compounds; thiosemicarbazones; silicon; crystal structure; spectral studies

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INTRODUCTION

The use of organosilanes as bioactive agents in pharmaceutical applications have been of long standing interest,[1] and the design of bioactive organosilanes was often involved in systematic replacement studies of a bioactive molecule's stable carbon atoms with silicon, based on the bioisosterism model.[2] Chen et al. reported several silanediol analogs of a carbinol-based inhibitor of the HIV protease, and studies showed that these analogs can easily cross cell membranes and deliver their antiviral effects with less toxicity.[3] Tacke also reported two sila-substitutions of M_3 subtype-preferring muscarinic antagonists. Studies showed that these sila-substitutions display a pronounced selectivity for M_3 versus M_2 muscarinic receptors.[4] Organotin(IV) complexes have been extensively studied as wood preservatives, antitumorals, antibacterials, antifungals, and biocides, even if their toxicity and their environmental effects are now limiting their uses.[5] Previous studies mostly focused on designing new types of organotin complexes by changing the ligands to minimize its drawbacks.[6] So far few studies have been conducted toward changing the carbon atoms of the tin-bound alkyl groups based on bioisosterism.

On the other hand, thiosemicarbazones and their metal complexes present a wide range of bioactivities, and their chemistry and pharmacological applications have been investigated.[7,8] We synthesized the silicon containing diorganotin(IV) compound $(Me_3SiCH_2)_2SnCl_2$ and studied its reaction with salicylaldehyde thiosemicarbazones and related ligands. The details of this study are reported herein.

RESULTS AND DISCUSSION

IR Spectroscopy

The IR bands of compounds **1**–**4** have been assigned by comparison with the IR spectra of the free thiosemicarbazones. As a result, the ν(OH) and ν(C=S) absorptions, present in the spectra of the free thiosemicarbazones at 3627∼3633 and 847∼852 cm^{-1}, disappeared in **1**–**4**. Four new intense bands at 1539∼1555 cm^{-1} found in the spectra of compounds **1**–**4** were assigned to new C=N double bonds, which were C–N single bonds in thiosemicarbazones.[9] Moreover the ν(C=S) absorption disappeared in **1**–**4**, and four new bands appeared at 761∼767 cm^{-1} assigned to ν(C–S). All of these indicate that the sulfur atoms coordinate to the central tin atoms via thiolate rather than thione.[10]

NMR Spectroscopy

The absence of the OH and NH protons in compounds **1**–**4** indicate deprotonation, which supports the evidence from IR spectroscopy that the ligands are O,N,S-coordinated

and existing in the thiol form. The chemical shift of the protons of azomethine (CH=N) groups exhibit signals at 8.49∼9.40 ppm as singlet for **1–4**. The singlets at 0.03∼0.05 ppm were assigned to $SiMe_3$ protons. The double dublets at 0.52∼0.55 ppm were assigned to $SnCH_2$ protons, and the spin–spin coupling constant $J_{Sn–H}$ is 58∼86 Hz.

^{13}C NMR signals for each carbon atom appear at their usual positions and compare well with the reported values.[11,12]

The ^{119}Sn chemical shift values in compounds **1–4** are found to be in the range of –107.6 to –111.7 ppm. The appearance of chemical shift values in this region indicates five-coordination environment around the central tin atoms in compound **1–4**.[13]

X-Ray Studies

Crystallographic data for compounds **1** and **4** are listed in Table 1. The crystal data were collected on a Bruker APEX II CCD area-detector diffractometer. The diffractometer was equipped with graphite-monocromators, using MoK_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and anisotropically refined except the hydrogen atoms. Hydrogen atoms were placed into calculated positions and refined using a riding model with fixed isotropic thermal parameters. Structures were solved and refined using SHELXS-97[14] and SHELXL-97,[15] respectively. Additional information to the structure is given in Table 1 and selected bond distances and angles can be seen in Table 2.

Table 1 Crystallographic data and refinement details for compound **1** and **4**

Data	**1**	**4**
Formula	$C_{16}H_{31}N_3O_2SSi_2Sn$	$C_{20}H_{31}N_3OSSi_2Sn$
M (g·mol^{-1})	504.37	536.41
Temperature (K)	296 (2)	293 (2)
Crystal dimensions (mm)	0.27 × 0.20 × 0.15	0.25 × 0.21 × 0.13
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	C2/c
Unit cell		
a (Å)	17.179 (2)	38.814 (18)
b (Å)	13.8752 (19)	7.206 (3)
c (Å)	10.0618 (14)	19.538 (9)
β (°)	96.891 (2)	111.096 (5)
V (Å^3)	2381.0 (6)	5098 (4)
Z	4	8
D_{calc} (g·cm^{-3})	1.407	1.398
Linear absorption coefficient (mm^{-1})	1.275	1.193
F(000)	1032	2192
Index ranges	$16 \le h \le 20$	$46 \le h \le 46$
	$-16 \le k \le 16$	$-8 \le k \le 8$
	$-11 \le l \le 9$	$-23 \le l \le 23$
Reflections collected	11,404	16,126
Independent reflections	4172	4487
Refined parameters	244	268
Absorption correction	Multiscan	Multiscan
Max./min. transmission	0.8318, 0.7247	0.8603, 0.7547
Goodness-of fit (F^2)	1.110	1.302
Final R indices ($I > 2\sigma$ (I))	0.0338	0.1015
R indices(all data)	0.0433	0.1257

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Table 2 Selected bond lengths (Å) and angles (°) for compounds **1** and **4**

Compound **1**		Compound **4**	
Sn(1)–O(1)	2.078 (3)	Sn(1)–O(1)	2.104 (8)
Sn(1)–C(13)	2.133 (4)	Sn(1)–C(13)	2.129 (13)
Sn(1)–C(9)	2.148 (4)	Sn(1)–C(17)	2.154 (14)
Sn(1)–N(1)	2.264 (3)	Sn(1)–N(1)	2.190 (9)
Sn(1)–S(1)	2.5242 (10)	Sn(1)–S(1)	2.569 (4)
S(1)—C(8)	1.749 (4)	S(1)–C(12)	1.722 (12)
O(1)–C(1)	1.348 (4)	O(1)–C(3)	1.331 (14)
N(1)–C(7)	1.301 (5)	N(1)–C(1)	1.323 (13)
N(1)–N(2)	1.388 (4)	N(1)–N(2)	1.423 (12)
N(2)–C(8)	1.303 (5)	N(2)–C(12)	1.297 (14)
N(3)–C(8)	1.337 (5)	N(3)–C(12)	1.381 (14)
O(1)–Sn(1)–C(13)	100.63 (13)	O(1)–Sn(1)–C(13)	90.0 (5)
O(1)–Sn(1)–C(9)	87.82 (13)	O(1)–Sn(1)–C(17)	98.2 (4)
C(13)–Sn(1)–C(9)	122.35 (16)	C(13)–Sn(1)–C(17)	127.1 (6)
O(1)–Sn(1)–N(1)	80.58 (11)	O(1)–Sn(1)–N(1)	81.0 (3)
C(13)–Sn(1)–N(1)	97.40 (14)	C(13)–Sn(1)–N(1)	114.0 (4)
C(9)–Sn(1)–N(1)	140.06 (13)	C(17)–Sn(1)–N(1)	118.9 (5)
O(1)–Sn(1)–S(1)	142.83 (8)	O(1)–Sn(1)–S(1)	157.6 (2)
C(13)–Sn(1)–S(1)	110.80 (12)	C(13)–Sn(1)–S(1)	98.6 (4)
C(9)–Sn(1)–S(1)	91.58 (11)	C(17)–Sn(1)–S(1)	93.1 (4)
N(1)–Sn(1)–S(1)	76.27 (8)	N(1)–Sn(1)–S(1)	76.6 (2)

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In the solid structure of compound **1** (shown in Fig. 1), the thiosemicarbazone ligand acts as tridentate ligand chelating to the central tin atom, and thus the tin atom is five coordinated in a trigonal bipyramidal geometry. In the coordination polyhedron two carbon atoms, C(9) and C(13) of the trimethylsilylmethyl groups, and the imine N(1) atom occupy the equatorial plane, whereas the S(1) and O(1) atoms occupy the axial positions. Bond lengths of C(7)–N(1) 1.276 Å, N(1)–N(2) 1.380 Å, C(8)–N(2) 1.346 Å, and C(8)–S(1) 1.689 Å were found in the uncoordinated ligand,[16] while in compound **1** the C(7)–N(1) [1.301(5) Å], C(8)–N(2) [1.303(5) Å], and C(8)–S(1) [1.749(4) Å] bond lengths are quite different from those of the ligand. The shortening of the C(8)–N(2) and lengthening of the C(9)–S(1) show that deprotonation of the imine N(2) atom results from a conversion from thione to thiolate,[17–19] which accords with the results of IR and NMR spectra. The same changes were also found in compound **4**.

In the crystal structure of compound **1**, the N–H···N hydrogen bonding interactions cause two neighboring molecules to become a dimer, and the O–H···O and O–H···S hydrogen bonds between the dimers and the water molecules lead to a one-dimensional chain structure (Figure 2). Significant contacts are represented by N(3)–H(3A)···N(2) ($-x + 1, -y + 1, -z$) 3.067 Å, 167.72 °; N(3)–H(3B)···O(2) ($x, y, z - 1$) 2.871 Å, 152.3 °; O(2)–H(2A)···O(1) 2.812 Å, 160.58 °; and O(2)–H(2B)···S(1) ($x, -y + 0.5, z + 0.5$) 3.384 Å, 171.44 °.

The X-ray structure determination of compound **4** revealed similar molecular structures as compound **1** (Figure 3), and the bond lengths and angles were also similar with those of the compound **1**.

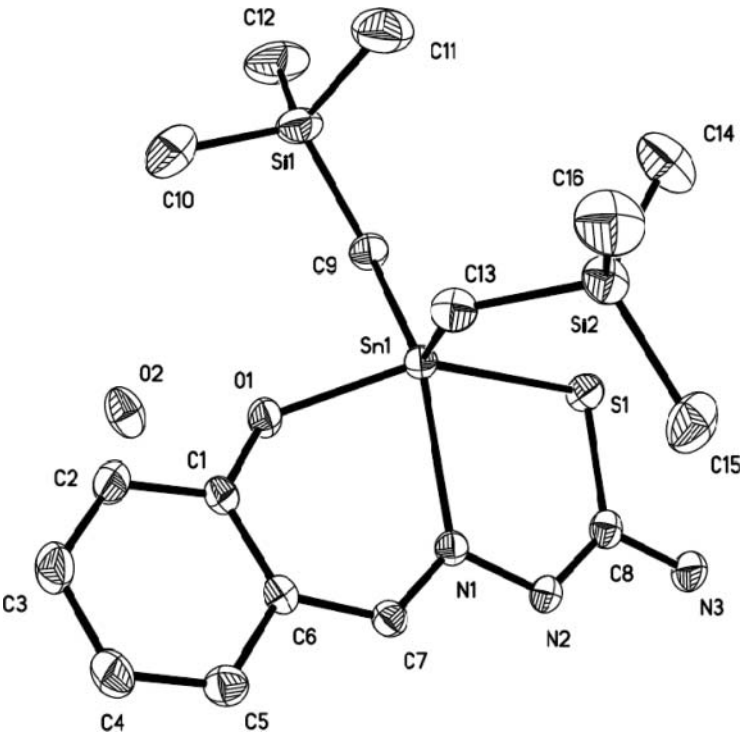

Figure 1 Crystal structure of compound **1**. Ellipsoids are drawn at the 30% probability level. H atoms, not involved in hydrogen bonding, are omitted for clarity.

EXPERIMENTAL

Materials

All air-sensitive and volatile materials were handled either in vacuo or under Argon by using standard Schlenk techniques. $(Me_3SiCH_2)_2SnPh_2$ was prepared by a published procedure.[20] Salicylaldehyde, 3-methoxysalicylaldehyde, 2-hydroxy-1-naphthaldehyde, 5-*tert*-butyl-3-methyl-salicylaldehyde, and thiosemicarbazide were used as received from

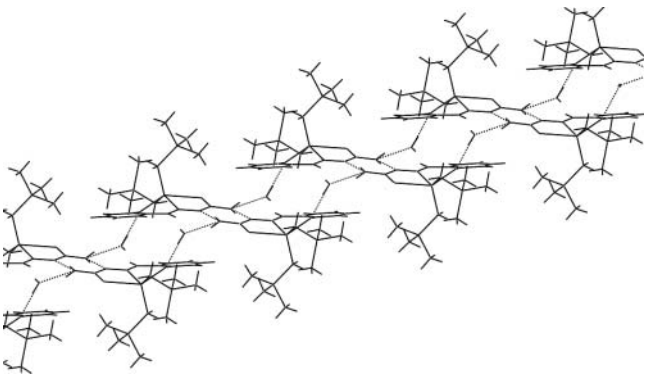

Figure 2 One-dimensional chain structure with intermolecular hydrogen bonds of compound **1**.

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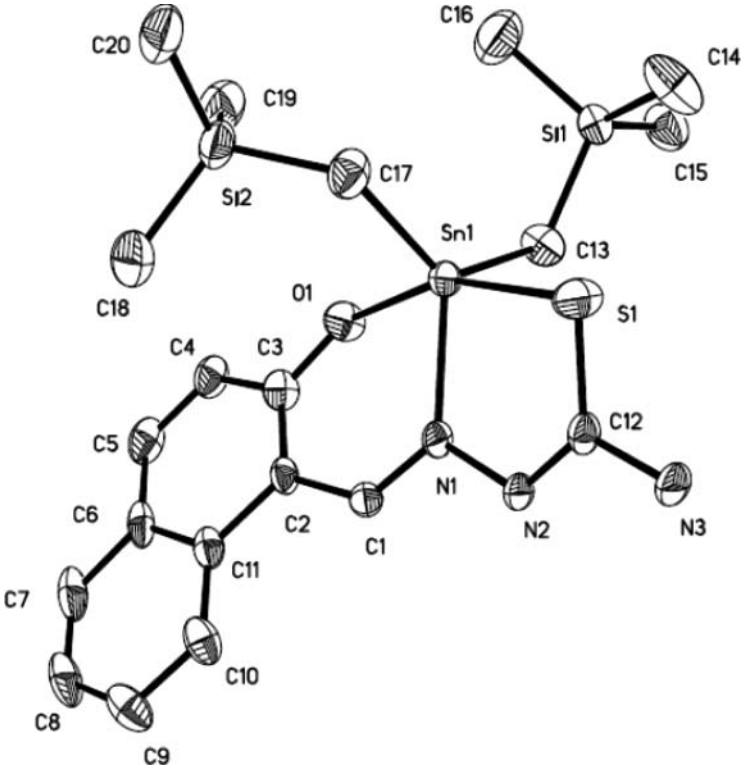

Figure 3 Crystal structure of compound **4**. Ellipsoids are drawn at the 30% probability level. H atoms, not involved in hydrogen bonding, are omitted for clarity.

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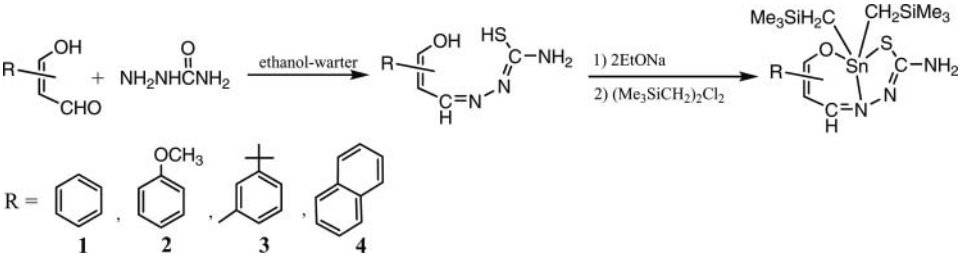
commercial sources. The solvents used in the reactions were of AR grade and dried using standard literature procedures. IR spectra were recorded on a Bruker TENSOR 27 spectrometer, NMR spectra on Bruker AMX 400 in $CDCl_3$. ^1H and ^{13}C signals were referred to TMS via the solvent signals (7.27 for ^1H in $CDCl_3$), and ^{119}Sn to external neat $Sn(CH_3)_4$.

Preparation of Ligands

The thiosemicarbazones were prepared by reacting equimolar amounts of thiosemicarbazides and respective salicylaldehyde/substituted salicylaldehydes in a 1:1 ethanol–water mixture (Equation 1). The products were recrystallized from ethanol.



$(Me_3SiCH_2)_2SnCl_2\cdot H_2O$. The syntheses of $(Me_3SiCH_2)_2SnCl_2\cdot H_2O$ via hydrolysis of $(Me_3SiCH_2)_2SnCl_2$ was reported by Beckmann.[13] In this report, $(Me_3SiCH_2)_2SnCl_2\cdot H_2O$ was prepared by reaction of $(Me_3SiCH_2)_2SnPh_2$ (0.447 g, 1 mmol) with excess conc. HCl (15 mL, 37%) in 30 mL $CHCl_3$. The reaction mixture was stirred and maintained at 70 °C for 24 h. The organic layer was separated and the aqueous layer extracted with $CHCl_3$ (3 × 30 mL). The organic extracts were combined, the solvent was removed under vacuum, and the residue was crystallized from CH_2Cl_2/hexane to give colorless crystals (0.269 g, 73.9%), m.p. 46–48 °C, ^{119}Sn NMR: δ –51.7. The data were in agreement with those reported in the literature (m.p. 48–49 °C, ^{119}Sn NMR: δ –53.9).[13]

Preparation of the Tin Complexes

The tin complexes **1–4** were prepared by reaction of the ligands with $(Me_3SiCH_2)_2SnCl_2\cdot H_2O$ (equ. 1).

Bis[(trimethylsilyl)methyl]tin salicylaldehyde thiosemicarbazonate monohydrate (1). To a solution of salicylaldehyde thiosemicarbazone (0.215 g, 1.10 mmol) in 30 mL THF (tetrahydrofuran) was added sodium ethoxide (0.119 g, 2.20 mmol) under stirring. The mixture was stirred for 2 h and then a 10 mL a THF solution of $(Me_3SiCH_2)_2SnCl_2\cdot H_2O$ (0.347 g, 1.00 mmol) was added. The yellow reaction mixture was refluxed for 24 h under inert conditions. The volatiles were removed and the residue was crystallized from acetonitrile to give yellow crystals 0.418 g, yield 83%. IR: $\nu_{C=N}$ 1614, 1549 cm^{-1}, ν_{C-S} 764 cm^{-1}. ^{1}H NMR: δ 0.05 (s, 18H, $SiMe_3$), 0.53 (dd, 4H, $^2J_{Sn-H}$ = 58 Hz, $SnCH_2$), 1.71 (s, 2H, H_2O), 4.93 (s, 2H, NH_2), 6.69 (d, 1H, aromatic-H), 6.71 (d, 1H, aromatic-H), 7.10 (dd, 1H, aromatic-H), 7.30 (t, 1H, aromatic-H), 8.51 (s, 1H, CH=N). ^{13}C NMR: δ 1.2 ($SiMe_3$), 13.2 (CH_2Sn), 116.6, 116.8, 121.5, 133.7, 134.7, 161.1 (aromatic-C), 166.0 (CH=N), 167.9 (C=N). ^{119}Sn NMR: δ –107.6. Anal. Calcd. for $C_{16}H_{31}N_3O_2SSi_2Sn$: C, 38.10; H, 6.19; N, 8.33; Found: C, 38.03; H, 6.11; N, 8.40.

Bis[(trimethylsilyl)methyl]tin 3-methoxylsalicylaldehyde thiosemicarbazonate (2). The preparation follows the procedure described for compound **1**, yield 80%. IR: $\nu_{C=N}$ 1617, 1542 cm^{-1}, ν_{C-S} 762 cm^{-1}. ^{1}H NMR: δ 0.05 (s, 18H, $SiMe_3$), 0.52 (dd, 4H, $^2J_{Sn-H}$ = 63 Hz, $SnCH_2$), 3.71 (s, 3H, OCH_3), 4.92 (s, 2H, NH_2), 6.52 (br, 1H, aromatic-H), 6.75 (d, 1H, aromatic-H), 7.23 (dd, 1H, aromatic-H), 8.50 (s, 1H, CH=N). ^{13}C NMR: δ 1.2 ($SiMe_3$), 13.1 (CH_2Sn), 57.3 (OCH_3), 111.2, 112.7, 117.7, 144.2, 151.4, 160.4, (aromatic-C), 164.3 (CH=N), 167.2 (C=N). ^{119}Sn NMR: δ –109.3. Anal. Calcd. for $C_{17}H_{31}N_3O_2SSi_2Sn$: C, 39.54; H, 6.05; N, 8.14; Found: C, 39.48; H, 6.16; N, 8.20.

Bis[(trimethylsilyl)methyl]tin 5-*tert*-butyl-3-methylsalicylaldehyde thiosemicarbazonate (3). The preparation follows the procedure described for compound **1**, yield 75%. IR: $\nu_{C=N}$ 1611, 1539 cm^{-1}, ν_{C-S} 761 cm^{-1}. ^{1}H NMR: δ 0.03 (s, 18H, $SiMe_3$), 0.52 (dd, 4H, $^2J_{Sn-H}$ = 86 Hz, $SnCH_2$), 1.42 (s, 9H, $C(CH_3)_3$), 2.24 (s, 3H, CH_3), 4.89 (s, 2H, NH_2), 6.76 (s, 1H, aromatic-H), 7.16 (s, 1H, aromatic-H), 8.49 (s, 1H, CH=N). ^{13}C NMR: δ 1.2 ($SiMe_3$), 12.9 (CH_2Sn), 20.5[$(CH_3)_3$], 29.6 (CH_3), 34.8 [C–$(CH_3)_3$], 116.6, 124.9, 128.5, 131.6, 133.5, 140.5 (aromatic-C), 163.0 (CH=N), 167.5 (C=N). ^{119}Sn NMR: δ –117.7. Anal. Calcd. for $C_{21}H_{39}N_3OSSi_2Sn$: C, 45.32; H, 7.06; N, 7.55; Found: C, 45.27; H, 6.99; N, 7.51.

Bis[(trimethylsilyl)methyl]tin 2-oxylnaphthaldehyde thiosemicarbazonate (4). The preparation follows the procedure described for compound **1**, yield 73%. IR: $\nu_{C=N}$ 1609, 1555 cm^{-1}, ν_{C-S} 767 cm^{-1}. ^{1}H NMR: δ 0.05 (s, 18H, $SiMe_3$), 0.55 (dd, 4H, $^2J_{Sn-H}$ = 60 Hz, $SnCH_2$), 4.90 (s, 2H, NH_2), 6.90 (d, 1H, aromatic-H), 7.28 (dd, 1H, aromatic-H),

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7.48 (t, 1H, aromatic-H), 7.69 (d, 1H, aromatic-H), 7.74 (d, 1H, aromatic-H), 7.93 (d, 1H, aromatic-H), 9.40 (s, 1H, CH=N). ^{13}C NMR: δ 1.2 ($SiMe_3$), 12.6 (CH_2Sn), 107.0, 112.6, 119.1, 122.9, 124.2, 127.4, 129.1, 133.6, 136.2, 156.8 (aromatic-C), 166.3 (CH=N), 168.2 (C=N). ^{119}Sn NMR: δ –111.2. Anal. Calcd. for $C_{20}H_{31}N_3OSSi_2Sn$: C, 44.78; H, 5.82; N, 7.83; Found: C, 44.85; H, 5.91; N, 7.76.

CONCLUSION

Four silicon containing diorganotin (IV) complexes of thiosemicarbazones have been synthesized by reaction of $(Me_3SiCH_2)_2SnCl_2$ with the corresponding semicarbazone. The four complexes have been characterized by IR, NMR, and elemental analysis. The X-ray studies of compounds **1** and **4** showed that the thiosemicarbazone ligands act as tridentate ligand chelating to the central tin atoms, and thus the tin atom is five coordinated in a trigonal bipyramidal geometry for both compounds.

SUPPLEMENTARY MATERIAL

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CSD numbers CCDC 884067 to complex **1**, CCDC 884066 to complex **2**. Copies of the data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +441223 336033; e-mail: deposit@ccdc.cam.ac.uk.

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