STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLV, 2, TOM II, 2010

Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

METHYLTIN(IV) TRICHLORIDE COMPLEXES OF *β*-KETIMINE, $MeSnCl_3[OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]_n$ (n = 1,2). SOLUTION BEHAVIOR AND SOLID STATE STRUCTURE

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ABSTRACT. Reaction of $MeSnCl_3$ with the *β*-ketimine $OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4$, in 1:1 and 1:2 molar ratio, gave the new methyltin(IV) trichloride adducts $MeSnCl_3[OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]_n$ [n = 1 (**1**), n = 2 (**2**)]. The compounds were characterized by multinuclear NMR studies in solution. The crystal and molecular structure of **1** and **2** was established by single-crystal X-ray diffraction. The crystals contain discrete molecules in which the *β*-ketimine ligand is coordinated to a metal center through its oxygen atom. This results in trigonal bypyramidal $CSnCl_3O$ and octahedral $CSnCl_3O_2$ cores in **1** and **2**, respectively. In the crystals intermolecular Cl···H contacts result in supramolecular architectures.

Keywords: *methyltin(IV), trichloride complexes, β-ketimine, solution NMR studies, single-crystal X-ray diffraction.*

INTRODUCTION

The *β*-diketiminato ligands [Scheme 1 (a)] were widely used to stabilize unusual species and coordination numbers in metal complexes which can show interesting catalytic effects [1]. In contrast to the *β*-diketiminato ligands [1-6], the coordination potential of the *β*-ketiminato ligands [Scheme 1 (b)] in tin(II) and tin(IV) chemistry is much less investigated. Some three, four and six-coordinate, monomeric Sn(II) and Sn(IV) derivatives containing the chelated *β*-ketiminato $[OC(Me)CHC(Me)N(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]^-$ ligand, *i.e.* SnCl(L), $Sn(L)_2$ and $SnX_2(L)_2$, were reported only recently [7]. The *β*-diketimines and *β*-ketimines can also been used as neutral ligands. We have previously reported on some di- and triorganotin(IV) chloride adducts containing $OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4$ [8,9] and the molecular structures, established by single-crystal X-ray diffraction, were also described for some few other complexes of Ti [10], Zr [12], Mo [12], W [13], Al [14] and Sb [15].

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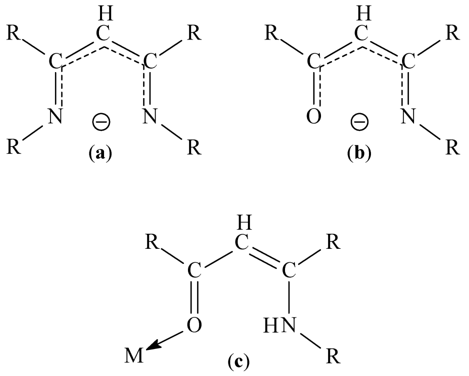
In all these complexes the *β*-ketimine ligand is coordinated to the metal centre through its oxygen atom in a monometallic monoconnective fashion [Scheme 1 (c)].

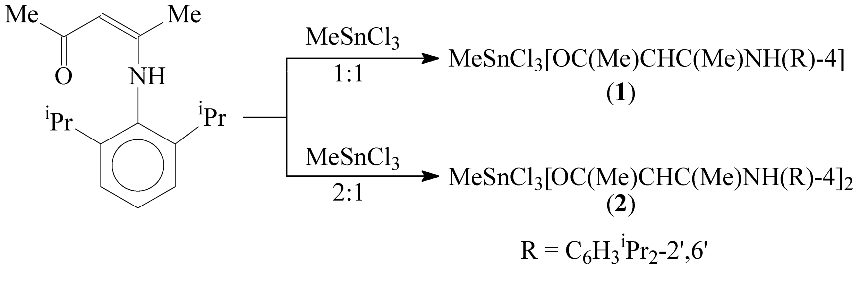


Scheme 1

We report here on the synthesis, solution behavior and solid state molecular structure of 1:1 and 1:2 adducts of methyltin(IV) trichloride, $MeSnCl_3[OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]_n$ [n = 1 (**1**), n = 2 (**2**)].

RESULTS AND DISCUSSION

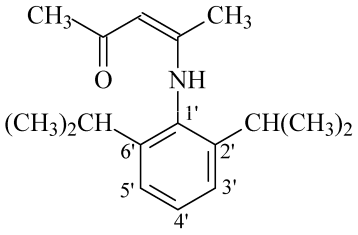
The new complexes **1** and **2** were obtained by reacting $MeSnCl_3$ with the *β*-ketimine in 1:1 and 1:2 molar ratio, respectively, in diethyl ether, at room temperature (Scheme 2).



Scheme 2

The new adducts were isolated in very good yields (ca. 90%) as white-yellow powders. They are air-stable and soluble in common organic solvents. The compounds were investigated by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{119}Sn) in solution and their molecular structures were established by single-crystal X-ray diffraction.

The NMR spectra were recorded in $CDCl_3$, at room temperature. The assignment of the ^1H and ^{13}C chemical shifts was made according to the numbering scheme shown in Scheme 3, based on 2D experiments.



Scheme 3

The NMR (^1H, ^{13}C) spectra of compounds **1** and **2** are very similar. They exhibit in the alkyl and aryl regions the expected resonances for the *β*-ketimine ligand. In addition, a singlet resonance is observed for the protons of methyl group attached to tin. In the ^1H spectra for both compounds these resonances are surrounded by ^{117}Sn / ^{119}Sn satellites due to tin-proton couplings. The integral ratio between ^1H resonances for the protons in the *β*-ketimine ligand and CH_3Sn is consistent with the formation of 1:1 and 1:2 adducts, respectively. The presence of a resonance for the hydrogen attached to nitrogen of the *β*-ketimine ligand is indicative of its coordination to the metal centre in the protonated form.

For both compounds the ^{119}Sn NMR spectra exhibit only one resonance, indicative for the presence of only one tin-containing species in solution, with very likely a similar structure as found in solid state.

Single-crystals suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into a solution of **1** or **2** in CH_2Cl_2. In both cases the crystals contain discrete monomers separated by distances between heavy atoms larger than the sum of the van der Waals radii for the corresponding atoms. The ORTEP diagrams of the molecular structures of **1** and **2**, with the atom numbering scheme, are shown in Figures 1 and 2. Selected interatomic distances and angles are listed in Tables 1 and 2.

A common structural feature for both adducts is the coordination of the *β*-ketimine ligand through its oxygen atom to tin. As in the free ligand, the acidic hydrogen of the *β*-ketimine is attached to the nitrogen atom and is involved in an intramolecular hydrogen bonding to the oxygen atom. A similar coordination pattern was observed in all the organotin(IV) complexes of the same *β*-ketimine described so far [8,9].

In the molecule of the 1:1 adduct **1** the oxygen atom is placed almost *trans* to a halogen atom [Cl(1)–Sn(1)–O(1) 169.12(12)°], thus resulting in a distorted trigonal bipyramidal $CSnCl_3O$ core.

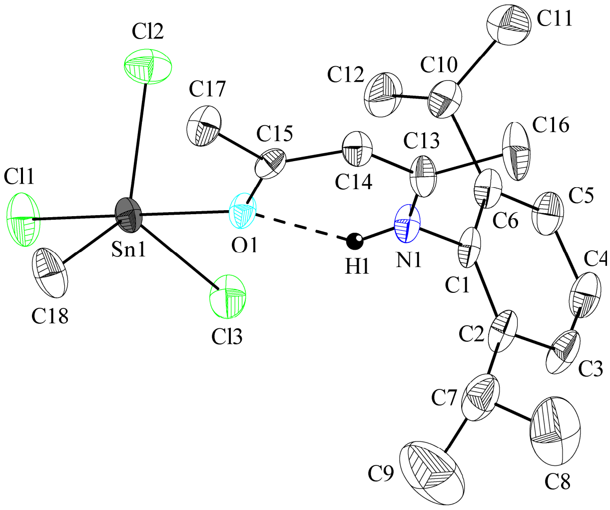


Figure 1. ORTEP representation at 20% probability and atom numbering scheme for **1**. Hydrogen atoms, except H(1) attached to nitrogen, are omitted for clarity.

Table 1. Interatomic bond distances (Å) and angles (°) for compound **1**.

Sn(1)–C(18)	2.099(7)	O(1)–C(15)	1.291(7)
Sn(1)–Cl(1)	2.408(2)	C(15)–C(17)	1.505(9)
Sn(1)–Cl(2)	2.312(2)	C(15)–C(14)	1.359(9)
Sn(1)–Cl(3)	2.335(2)	C(13)–C(16)	1.504(10)
Sn(1)–O(1)	2.191(4)	C(13)–C(14)	1.395(9)
		N(1)–C(13)	1.306(9)
Cl(1)–Sn(1)–O(1)	169.12(12)	N(1)–C(1)	1.448(8)
		N(1)–H(1)	0.856(19)
C(18)–Sn(1)–Cl(2)	123.9(3)	O(1)···H(1)	2.01(4)
C(18)–Sn(1)–Cl(3)	121.5(3)		
Cl(2)–Sn(1)–Cl(3)	113.36(10)	O(1)–C(15)–C(14)	121.5(6)
		O(1)–C(15)–C(17)	118.2(6)
Cl(1)–Sn(1)–C(18)	97.4(3)	C(14)–C(15)–C(17)	120.3(6)
Cl(1)–Sn(1)–Cl(2)	92.42(9)	C(13)–C(14)–C(15)	124.6(6)
Cl(1)–Sn(1)–Cl(3)	91.06(8)	N(1)–C(13)–C(14)	122.4(6)
		N(1)–C(13)–C(16)	118.8(7)
O(1)–Sn(1)–C(18)	92.5(3)	C(14)–C(13)–C(16)	118.9(7)
O(1)–Sn(1)–Cl(2)	85.74(14)	C(1)–N(1)–C(13)	126.5(6)
O(1)–Sn(1)–Cl(3)	79.89(12)	C(1)–N(1)–H(1)	113(4)
		C(13)–N(1)–H(1)	120(4)
Sn(1)–O(1)–C(15)	137.6(4)	C(15)–O(1)···H(1)	101(1)
		N(1)–H(1)···O(1)	129(3)

The length of the Sn(1)–O(1) bond [2.191(4) Å] suggests a stronger coordination [cf. the sums of the covalent and van der Waals radii are Σr_{cov}(Sn,O) ca. 2.06 Å and Σr_{vdW}(Sn,O) ca. 3.60 Å] [16]. As expected, the tin-oxygen distance in **1** is shorter than in the 1:1 adduct $Me_2SnCl_2[OC(Me)CHC(Me)N(C_6H_3{}^iPr_2$-2',6')-4] [Sn–O 2.375(3) Å] [8], the presence of three chlorine atoms attached to tin increasing the acidity of the metal centre. The Sn(1) atom is displaced only 0.147 Å from the CCl_2 equatorial plane on the side of the axial Cl(1) atom and the Sn(1)–Cl(1) bond is slightly elongated [2.408(2) Å] in comparison with the equatorial Sn–Cl bonds [Sn(1)–Cl(2) 2.312(2), Sn(1)–Cl(3) 2.335(2) Å] due to the *trans* effect of the oxygen.

The molecule of **2** is centrosymmetric and features a distorted octahedral $CSnCl_3O_2$ core achieved due to almost *trans* coordination of two β-ketimine ligands [O(1)–Sn(1)–O(1') 170.9(2)°], which forces a square planar geometry of the covalent $CSnCl_3$ fragment. The strength of the tin-oxygen bonds in **2** is similar to that observed for **1**. In the equatorial plane, a difference in the length of the tin-chlorine bonds should be noted, *i.e.* those placed *trans* to each other are significantly elongated [Sn(1)–Cl(1) 2.462(2) Å] compared to Sn(1)–Cl(2) [2.386(3) Å], which is *trans* to the carbon atom attached to tin.

In both compounds, regardless the coordination geometry achieved around tin, the planar $OC_3N(H)$ core of the β-ketimine ligands is twisted to allow intramolecular interaction between an equatorial chlorine and the N*H* proton [Cl(3)···H(1) 2.70 Å in **1**, and Cl(1)···H(1) 2.73 Å in **2**].

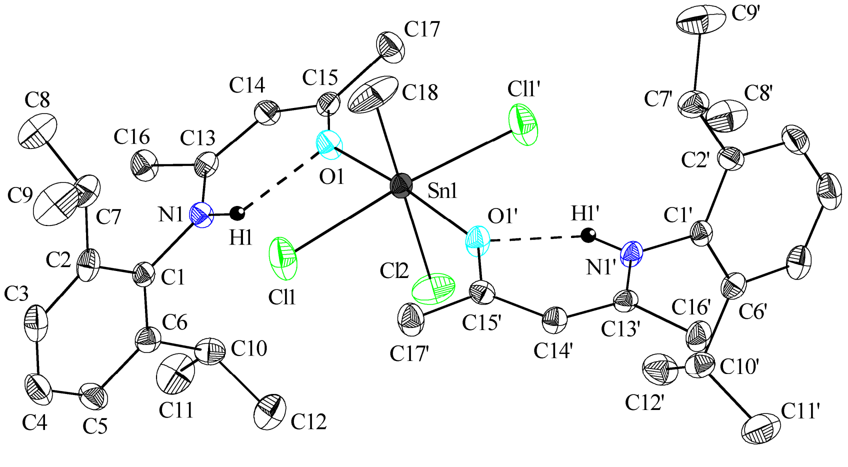


Figure 2. ORTEP representation at 20% probability and atom numbering scheme for **2**. Hydrogen atoms, except H(1) attached to nitrogen, are omitted for clarity [symmetry equivalent atoms (1 – *x*, *y*, 1.5 – *z*) are given by “prime”].

A closer check of the crystal structures of **1** and **2** revealed some supramolecular associations based on intermolecular Cl···H contacts between the molecular units [cf. Σr_{vdW}(Cl,H) ca. 3.0 Å] [16]. Thus, the molecules of **1** are associated into parallel polymeric chains through weak contacts which involve the axial chlorine atom [Cl(1)···H(17Ca)$_{\text{ketimine-methyl}}$ 2.93 Å] (Figure 3) and further weaker inter-chain contacts between the equatorial chlorine atoms from one chain and an aromatic proton from the neighbouring chain [Cl(3)···H(5')$_{\text{aryl}}$ 2.93 Å] led to a 3D architecture.

Table 2. Interatomic bond distances (Å) and angles (°) for compound **2**.

Sn(1)–C(18)	2.094(9)	O(1)–C(15)	1.287(6)
Sn(1)–Cl(1)	2.4620(19)	C(15)–C(17)	1.476(8)
Sn(1)–Cl(2)	2.386(3)	C(15)–C(14)	1.389(7)
Sn(1)–O(1)	2.158(4)	C(13)–C(16)	1.501(7)
		C(13)–C(14)	1.384(7)
Cl(1)–Sn(1)–Cl(1')	173.42(13)	N(1)–C(13)	1.321(7)
C(18)–Sn(1)–Cl(2)	180.000(1)	N(1)–C(1)	1.443(7)
O(1)–Sn(1)–O(1')	170.9(2)	N(1)–H(1)	0.848(19)
		O(1)···H(1)	2.01(4)
O(1)–Sn(1)–C(18)	94.56(11)		
O(1)–Sn(1)–Cl(1)	82.73(11)	O(1)–C(15)–C(14)	119.6(5)
O(1)–Sn(1)–Cl(2)	85.44(11)	O(1)–C(15)–C(17)	120.2(5)
O(1)–Sn(1)–Cl(1')	96.74(11)	C(14)–C(15)–C(17)	120.3(5)
		C(13)–C(14)–C(15)	126.1(5)
O(1')–Sn(1)–C(18)	94.56(11)	N(1)–C(13)–C(14)	122.5(5)
O(1')–Sn(1)–Cl(1)	96.74(11)	N(1)–C(13)–C(16)	118.3(5)
O(1')–Sn(1)–Cl(2)	85.44(11)	C(14)–C(13)–C(16)	119.1(5)
O(1')–Sn(1)–Cl(1')	82.73(11)	C(1)–N(1)–C(13)	127.5(4)
		C(1)–N(1)–H(1)	117(3)
Cl(1)–Sn(1)–C(18)	93.29(6)	C(13)–N(1)–H(1)	116(3)
Cl(1)–Sn(1)–Cl(2)	86.71(6)	C(15)–O(1)···H(1)	101(1)
Cl(1')–Sn(1)–C(18)	93.29(6)	N(1)–H(1)···O(1)	134(3)
Cl(1')–Sn(1)–Cl(2)	86.71(6)		
Sn(1)–O(1)–C(15)	144.8(4)		

By contrast, in the crystal of **2** the molecular units are doubly connected (Figure 4) through intermolecular interactions based on the *trans* chlorine atoms [Cl(1)···H(16Ab)$_{\text{ketimine-methyl}}$ 2.81 Å], while the third halogen is not involved in any Cl···H contact. No further inter-chain contacts are established in the crystal of **2**.

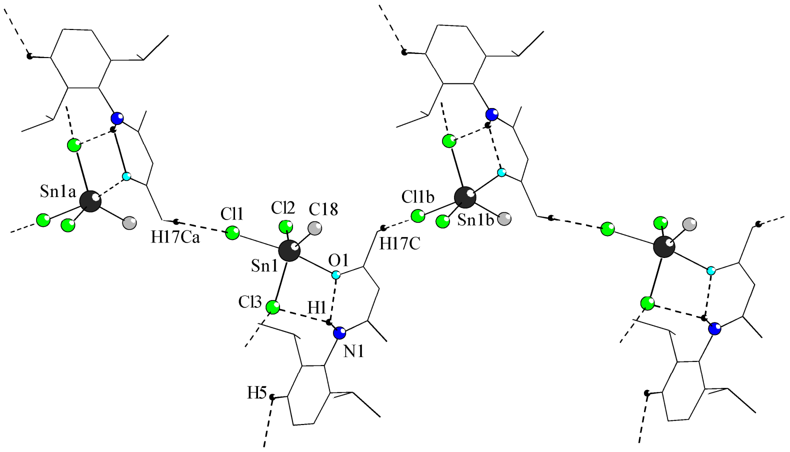


Figure 3. View of a chain polymer based on Cl···H contacts in the crystal of **1** (only H1 attached to nitrogen and hydrogens involved in intermolecular interactions are shown) [symmetry equivalent atoms: Sn1a (–*x*, 0.5+*y*, 1.5–*z*) and Sn1b (–*x*, –0.5+*y*, 1.5–*z*)].

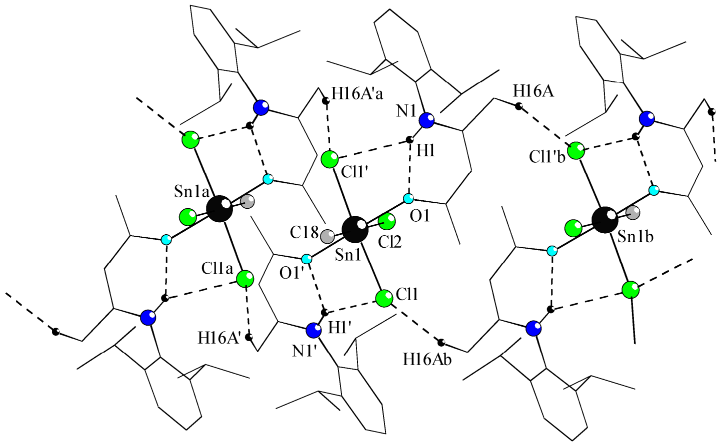


Figure 4. View of a polymeric ribbon-like association based on Cl···H contacts in the crystal of **2** (only H1 attached to nitrogen and hydrogens involved in intermolecular interactions are shown) [symmetry equivalent atoms: Sn1a (1–*x*, 1–*y*, 2–*z*); H16A'a (*x*, 1–*y*, 0.5+*z*); Sn1b (1–*x*, 1–*y*, 1–*z*) and Cl1b' (*x*, 1–*y*, –0.5+*z*)].

CONCLUSION

The first 1:1 and 1:2 adducts of an organotin(IV) trihalide with β-ketimine as neutral ligand, *i.e.* $\mathrm{MeSnCl_3[OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]_n}$ [n = 1 (**1**), n = 2 (**2**)], were isolated as stable, crystalline solids. They were characterized in solution using multinuclear and 2D NMR spectroscopy, the data being consistent with the proposed formulation. The solid-state molecular structure, as established by single-crystal X-ray diffraction, revealed the monometallic monoconnective nature of the β-ketimine, resulting in distorted trigonal bipyramidal $CSnCl_3O$ (oxygen and chlorine in axial positions) and octahedral $CSnCl_3O_2$ (*trans* O–Sn–O fragment) for **1** and **2**, respectively.

EXPERIMENTAL SECTION

Solvents were dried and distilled prior to use. $MeSnCl_3$ was commercially available. The β-ketimine, OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4, was prepared according to a published procedure [9]. ^1H, ^{13}C and ^{119}Sn NMR spectra, including 2D experiments, were recorded on Bruker Avance 300 instrument using solutions in $CDCl_3$. The chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. $CHCl_3$: ^1H 7.26, ^{13}C 77.0 ppm) for ^1H and ^{13}C NMR spectra and neat $SnMe_4$ for and ^{119}Sn NMR spectra. The NMR spectra were processed using the *MestReC* and *MestReNova* software [17].

Preparation of $MeSnCl_3[OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]$ (1)

A solution of $MeSnCl_3$ in Et_2O (1.85 g, 7.70 mmol) was added to a stirred solution of OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4 (2 g, 7.71 mmol) in 50 mL Et_2O, at room temperature, and the reaction mixture was stirred for 24 h. Then the solvent was removed in vacuum to give the title compound as a white-yellow powder. Yield: 3.5 g (91%), m.p. 124-125 ^oC. ^1H NMR (300 MHz, 20 ℃): δ 1.19d [6H_A, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ 7.2 Hz], 1.21d [6H_B, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ 7.4 Hz], 1.54s (3H, SnC*H*$_3$, $^2J_{117SnH}$ 106.0, $^2J_{119SnH}$ 110.8 Hz), 1.76s [3H, C*H*$_3$C(N)], 2.25s [3H, C*H*$_3$C(O)], 2.88hept [2H, -C*H*(CH$_3$)$_2$, $^3J_{HH}$ 6.8 Hz], 5.29s (1H, -C*H*=), 7.21d (2H, $H_{3',5'}$, $^3J_{HH}$ 7.7 Hz), 7.36t (1H, $H_{4'}$, $^3J_{HH}$ 7.7 Hz), 11.85s (1H, -N*H*-). ^{13}C NMR (75.4 MHz, 20 ℃): δ 16.47s (Sn*C*H$_3$), 20.03s [*C*H$_3$C(N)], 22.67s [-CH(*C*H$_3$)$_2$, (B)], 24.46s [-CH(*C*H$_3$)$_2$, (A)], 27.23s [*C*H$_3$C(O)], 28.62s [-*C*H(CH$_3$)$_2$], 97.76s (-*C*H=), 123.99s ($C_{3',5'}$), 129.44s ($C_{4'}$), 131.61s ($C_{1'}$), 145.15s ($C_{2',6'}$), 170.15s [CH$_3$*C*(N)], 191.61s [CH$_3$*C*(O)]. ^{119}Sn NMR (111.9 MHz): -210.4s.

Preparation of $MeSnCl_3[OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]_2$ (2)

A solution of $MeSnCl_3$ in Et_2O (0.46 g, 1.92 mmol) was added to a stirred solution of OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4 (1 g, 3.85 mmol) in 50 mL Et_2O, at room temperature. The reaction mixture was stirred for 24 h and then the solvent was removed in vacuum to give the title compound as a white-yellow powder. Yield: 1.3 g (89%), m.p. 134-135 ^oC. ^1H NMR (300 MHz, 20 ℃): δ 1.17d [12H_A, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ 6.8 Hz], 1.21d [12H_B, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ 6.9 Hz], 1.53s (3H, SnC*H*$_3$, $^2J_{117SnH}$ 107.4, $^2J_{119SnH}$ 112.1 Hz), 1.70s [6H, C*H*$_3$C(N)], 2.19s [6H, C*H*$_3$C(O)], 2.95hept [4H, -C*H*(CH$_3$)$_2$, $^3J_{HH}$ 6.8 Hz], 5.25s (2H, -C*H*=), 7.20d (4H, $H_{3',5'}$, $^3J_{HH}$ 7.6 Hz), 7.33t (2H, $H_{4'}$, $^3J_{HH}$ 7.7 Hz), 11.94s (2H, -N*H*-). ^{13}C NMR (75.4 MHz, 20 ℃): δ 17.07s (Sn*C*H$_3$), 19.65s [*C*H$_3$C(N)], 22.69s [-CH(*C*H$_3$)$_2$, (B)], 24.52s [-CH(*C*H$_3$)$_2$, (A)], 28.10s [*C*H$_3$C(O)], 28.55s [-*C*H(CH$_3$)$_2$], 96.75s (-*C*H=), 123.78s ($C_{3',5'}$), 128.89s ($C_{4'}$), 132.46s ($C_{1'}$), 145.67s ($C_{2',6'}$), 166.99s [CH$_3$*C*(N)], 193.63s [CH$_3$*C*(O)]. ^{119}Sn NMR (111.9 MHz): -238.3s.

X-ray Crystallographic Study

Data were collected with a SMART APEX diffractometer (*National Center for X-Ray Diffractometry*, “Babes-Boyai” University, Cluj-Napoca, Romania) at 297 K, using a graphite monochromator to produce a wavelength (Mo-$K\alpha$) of 0.71073 Å. The crystal structure measurement and refinement data for compounds **1** and **2** are given in Table 3. Absorption correction was applied for both compounds (semi-empirical from equivalents). The structure was solved by direct methods (full-matrix least-squares on F^2). All non hydrogen atoms were refined with anisotropic thermal parameters. For structure solving and refinement a software package SHELX-97 was used [18]. The drawings were created with the Diamond program [19].

CCDC-770827 (**1**) and -770826 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystallographic data for compounds **1** and **2**.

	1	**2**
chemical formula	$C_{18}H_{28}Cl_3NOS$	$C_{35}H_{53}Cl_3N_2O_2S$
crystal habit	colorless block	colorless block
crystal size [mm]	0.40 x 0.28 x 0.23	0.31 x 0.28 x 0.2
crystal system	orthorhombic	monoclinic
space group	*Pbca*	*C2/c*
a [Å]	13.995(3)	15.575(5)
b [Å]	14.977(3)	18.136(6)
c [Å]	22.255(4)	14.000(5)
α [deg]	90	90
β [deg]	90	100.651(6)
γ [deg]	90	90
U [Å^3]	4664.9(15)	3886(2)
Z	8	4
D_c [g cm^{-3}]	1.422	1.297
M	499.45	758.83
F(000)	2016	1576
θ range [deg]	2.19 – 25.00	2.12 – 25.00
μ(Mo Kα) [mm^{-1}]	1.444	0.894
no. of reflections collected	32026	13862
no. of independent reflections	4102 (R_{int} = 0.0648)	3436 (R_{int} = 0.0548)
R_1 [$I > 2\sigma(I)$]	0.0745	0.0651
wR_2	0.1373	0.1412
no. of parameters	228	206
no. of restraints	1	1
GOF on F^2	1.327	1.139
largest difference electron density [e Å^{-3}]	0.617, –0.940	0.755, –1.465

ACKNOWLEDGEMENTS

This work was supported by the National University Research Council of Romania (CNCSIS, Research Project Nos. A-709/2006 and TD-340/2007). We also thank the NATIONAL CENTER FOR X-RAY DIFFRACTION (”Babes-Bolyai” University, Cluj-Napoca, Romania) for the support in the solid state structure determinations.

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