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*Dedicated to the memory of*
*Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

# ORGANOTIN(IV) COMPLEXES OF *β*-KETIMINES. CRYSTAL AND MOLECULAR STRUCTURE OF OC(Me)CHC(Me)NHR-4 [R = $C_6H_3{}^iPr_2$-2',6'; $C_6H_4$Me-4'], $Bu_2SnCl_2(L)$ AND $[\{Me_2SnCl\}_2(L)]_2$ [L = OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4]

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New adducts of organotin(IV) chlorides with a *β*-ketimine, *i..e.* $R_nSnCl_{4-n}$[OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4] [n = 3, R = Me (**3**), Ph (**4**); n = 2, R = Bu (**5**), Ph (**6**)] and $Me_2SnCl_2$[OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4]$_2$ (**7**), were prepared and characterized by multinuclear NMR solution studies. In attempt to grow single crystals of **5** resulted in isolation of the unexpected mixed chloro-oxide complex $[(Bu_2SnCl)_2O\{OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2$-2',6')-4$\}]_2$ (**8**), due to partial hydrolysis. The mixed chloro-oxide analogous species **9**, containing dimethyltin(IV) groups, was prepared using a rational procedure and was characterized by multinuclear NMR solution studies. The crystal and molecular structure of the *β*-ketimines OC(Me)CHC(Me)NH(R)-4 [R = $C_6H_3{}^iPr_2$-2',6' (**1**), $C_6H_4$Me-4' (**2**)], as well as of the organotin(IV) adducts **5** and **9**, were established by single-crystal X-ray diffraction. The crystals of the free *β*-ketimines **1** and **2** contain discrete molecules. For both adducts **5** and **9** the *β*-ketimine ligand is coordinated to a metal center through its oxygen atom. The mononuclear unit of **5** contains a five-coordinated tin atom, while in the tetranuclear unit of **9** both five- and six-coordinated metal centers are present. In the crystals intermolecular Cl···H contacts result in polymeric, ribbon-like association of the mononuclear units for **5** and polymeric chain association of doubly connected tetranuclear units for **9**.

## INTRODUCTION

The *β*-diketiminato [Scheme 1 (a)][1] and *β*-ketiminato [Scheme 1 (b)][2,3] ligands were often used as (*N*,*N'*)- and (*N*,*O*)-chelating systems, respectively, in coordination chemistry. Various *β*-diketiminato ligands were used in tin(II) and tin(IV) coordination chemistry[1] in order to stabilize *(i)* unusual three-coordinated divalent species as the halides SnX[{N(R)C(Me)}$_2$CH] (X = halogen, R = Ph,[4] $C_6H_2Me_3$-2',4',6',[5] $C_6H_3{}^iPr_2$-2',6',[6,7]), the hydride SnH[{N($C_6H_3{}^iPr_2$-2',6')C(Me)}$_2$CH],[8] the azide $SnN_3$[{N($C_6H_2Me_3$-2',4',6')C(Me)}$_2$CH],[5] alkoxides Sn(OR)[{N($C_6H_3{}^iPr_2$-2',6')C(Me)}$_2$CH] [R = $^i$Pr,[9] $CH_2(C_5H_4)Fe(C_6H_5)$,[10]], amides Sn($NR_2$)[{N($C_6H_3{}^iPr_2$-2',6')C(Me)}$_2$CH] (R = Me,[11] $SiMe_3$,[7]), the methyltin(II) derivative MeSn[{N($C_6H_3{}^iPr_2$-2',6')C(Me)}$_2$CH],[7] or Sn[{N($C_6H_3{}^iPr_2$-2',6')C(Me)}$_2$CH]$_2$;[6] *(ii)* transition metal complexes as [HC{(Me)C(Ph)N}$_2$](Cl)SnFe(CO)$_4$;[12] *(iii)* tin(IV) halide species, $SnX_3$[{N($C_6H_3{}^iPr_2$-2',6')C(Me)}$_2$CH] (X = Br, I);[13] or *(iv)* terminal chalcogen-containing tin(IV) species, [HC{(Me)CN(R)}$_2$](X)Sn=E (X = Cl, $NR_2$; E = S, Se).[1,4] Recently were reported some three, four and six-coordinate, monomeric Sn(II) and Sn(IV) derivatives containing chelated *β*-ketiminato ligands, *i.e.* SnCl(L), Sn(L)$_2$ and $SnX_2(L)_2$, L = [OC(Me)CHC(Me)N($C_6H_3{}^iPr_2$-2',6')-4]$^-$.[14]

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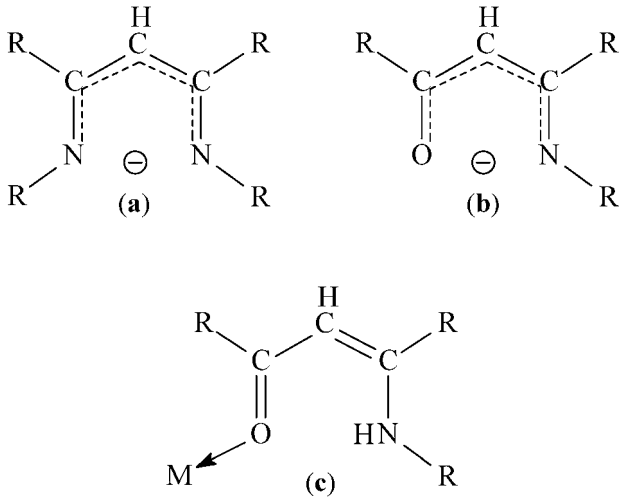



Scheme 1

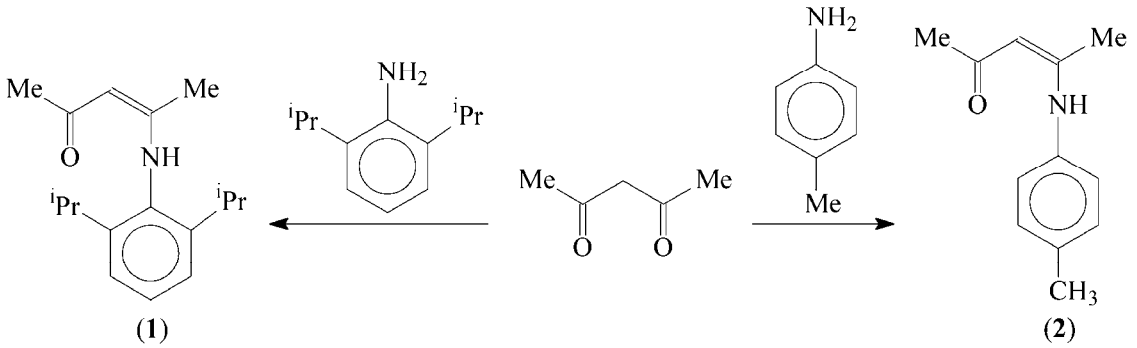
By contrast, the use of the *β*-ketimines as neutral ligands was only scarcely reported. The solid state molecular structures were reported so far for the following complexes: $MoO_2Cl_2[OC(Me)CHC(Me)NHPh]_2$,[15] $WOCl_4[OC(CF_3)CHC(Me)NH(C_6H_4Br\text{-}4')\text{-}4]$,[16] $TiCl_4[OC(Me)CHC(Me)NH(C_6H_2Me_3\text{-}2',4',6')\text{-}4]_2$,[17] $Zr(C_5Me_5)Cl_2[OC(Me)CHC(Me)N(C_6H_4CF_3\text{-}4')\text{-}4][OC(Me)CHC(Me)NH(C_6H_4CF_3\text{-}4')\text{-}4]$,[18] $[AlCl_2\{OC(Me)CHC(Me)NH(C_6H_4F\text{-}4')\text{-}4\}_4][AlCl_4]$,[19] and $SbCl_3[OC(Me)C(Me)C(Me)NH\text{-}(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]$.[20] Recently we have published the preparation, NMR characterization in solution and the molecular structure of the first organotin(IV) chloride adduct, $Me_2SnCl_2[OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]$.[21] In all these complexes the *β*-ketimine ligand is coordinated to the metal centre through its oxygen atom in a monodentate pattern [Scheme 1 (c)].

Organotin(IV) complexes have been used as biocides and their potential therapeutic properties, *e.g.* as anti-inflammatory, anti-tuberculosis or antitumor drugs, have been largely investigated.[22-29] The use of organotin compounds in organic synthesis or catalysis is also well known.[30-33]

We report here on the synthesis and characterization of new adducts of organotin(IV) chlorides with a *β*-ketimine, *i..e.* $R_nSnCl_{4-n}[OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]$ [n = 3, R = Me (**3**), Ph (**4**); n = 2, R = Bu (**5**), Ph (**6**)] and $Me_2SnCl_2[OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]_2$ (**7**), as well as the mixed chloro-oxide complexes $[(R_2SnCl)_2O\{OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4\}]_2$ [R = Bu (**8**), Me (**9**)] resulted due to partial hydrolysis.

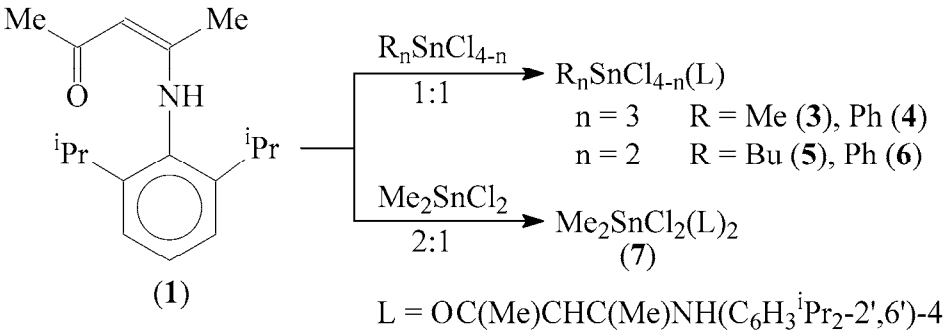
## RESULTS

Two *β*-ketimines, *i.e.* OC(Me)CHC(Me)NH(R)-4 [R = $C_6H_3{}^iPr_2$-2',6' (**1**), $C_6H_4$Me-4' (**2**)], were obtained by condensation of 2,4-pentanedione and the corresponding aromatic amines, in toluene, in the presence of $TsOH{\cdot}H_2O$ as catalyst, using slightly modified published procedures (Scheme 2).[34]




Scheme 2

The reaction of stoichiometric amounts of organotin(IV) chlorides and **1**, in diethyl ether, at room temperature, afforded the isolation of the new 1:1 adducts $R_nSnCl_{4-n}$[OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4] [n = 3, R = Me (**3**), Ph (**4**); n = 2, R = Bu (**5**), Ph (**6**)], while the use of a 1:2 molar ratio between $Me_2SnCl_2$ and **1** gave the 1:2 adduct $Me_2SnCl_2$[OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4]$_2$ (**7**) (Scheme 3).

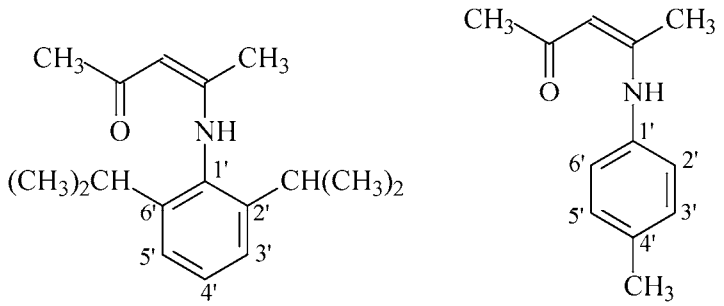



Scheme 3

Details of the preparations are given in the Experimental section. The adducts were isolated as white-yellow solids, which exhibit a good solubility in common organic solvents.

Accidental partial hydrolysis of **5** during attempts to grow single crystals affords isolation of the mixed chloro-oxide complex [{$Bu_2SnCl$}$_2$O{4-(2',6'-$^iPr_2C_6H_3$)NHC(Me)CHC(Me)O}]$_2$ (**8**) [$^{119}$Sn NMR ($CDCl_3$, 111.9 MHz, r.t.): δ –139.4 (s, $^2J_{SnSn}$ =73.2 Hz), –92.1 (s, $^2J_{SnSn}$ =72.7 Hz)]. A rational preparation of the dimethyltin(IV) analogue **9** was achieved by treating a mixture of $Me_2SnCl_2$ and the *β*-ketimine **1** (1:1 molar ratio), in toluene, with KOH, followed by elimination of water from the reaction mixture using a Dean-Stark apparatus.

The *β*-ketimines **1** and **2** as well as the new organotin adducts **3**-**9** were characterized using multinuclear ($^1$H, $^{13}$C, $^{119}$Sn) NMR spectroscopy. The solution NMR spectra of the isolated products, recorded in $CDCl_3$, are consistent with the formation of the title compounds. The $^1$H and $^{13}$C NMR signals were assigned on the basis of 2D experiments and by comparison with the spectra of the uncomplexed organotin(IV) chlorides, according to the numbering scheme shown in Scheme 4.




Scheme 4

The $^1$H and $^{13}$C NMR spectra for the *β*-ketimines **1** and **2** showed the expected resonances in the alkyl as well as in the aryl regions. For the organotin(IV) chloride adducts **3**-**7** and **9**, in addition to the resonances for the *β*-ketimine ligand **1** coordinated to tin, resonances for the organic groups attached to the tin atom, with the expected splitting due to tin-proton and tin-carbon couplings, respectively, were also observed. The presence of a resonance for the hydrogen attached to nitrogen in the *β*-ketimine **1** of the organotin adducts is indicative for the presence of the organic ligand in the protonated form.

The $^{119}$Sn NMR spectra exhibit one resonance for the adducts **3**-**7**, consistent with the presence of one tin-containing species in solution, and two

resonances for compounds **8** and **9**, consistent with two non equivalent tin atoms in a molecular unit, respectively.

Single crystals of the *β*-ketimines **1** and **2**, as well as for the adducts **5** and **9**, were grown from a $CH_2Cl_2$/n-hexane mixture using the slow diffusion technique and their molecular structures were established by X-ray diffraction studies. The crystals of all four compounds contain discrete monomers, with no unusual intermolecular distances shorter than the sum of the van der Waals radii between heavy atoms. Selected bond distances and angles are listed in Tables 1-3. Figures 1-4 show the ORTEP-like view of the molecular structure of **1**, **2**, **5** and **9**, respectively, with the atom numbering scheme.

*Table 1*

Selected interatomic distances (Å) and angles (deg) in OC(Me)CHC(Me)NHR-4 [R = $C_6H_3{}^iPr_2$-2',6' (**1**); $C_6H_4$Me-4' (**2**)]

| **1** | | **2** | |
|---|---|---|---|
| O(1)–C(16) | 1.251(5) | O(1)–C(11) | 1.243(4) |
| C(16)–C(17) | 1.508(6) | C(11)–C(12) | 1.501(4) |
| C(16)–C(15) | 1.418(6) | C(11)–C(10) | 1.405(5) |
| C(13)–C(14) | 1.506(6) | C(8)–C(9) | 1.493(4) |
| C(13)–C(15) | 1.360(5) | C(8)–C(10) | 1.356(4) |
| N(1)–C(13) | 1.341(5) | N(1)–C(8) | 1.346(4) |
| N(1)–C(1) | 1.442(5) | N(1)–C(1) | 1.405(4) |
| N(1)–H(1) | 0.86(2) | N(1)–H(1) | 0.86(3) |
| O(1)···H(1) | 1.91(3) | O(1)···H(1) | 1.89(3) |
| | | | |
| O(1)–C(16)–C(15) | 122.8(4) | O(1)–C(11)–C(10) | 123.0(3) |
| O(1)–C(16)–C(17) | 118.7(4) | O(1)–C(11)–C(12) | 118.1(3) |
| C(15)–C(16)–C(17) | 118.4(4) | C(10)–C(11)–C(12) | 118.9(3) |
| C(13)–C(15)–C(16) | 124.0(4) | C(8)–C(10)–C(11) | 125.6(3) |
| N(1)–C(13)–C(15) | 121.2(4) | N(1)–C(8)–C(10) | 119.7(3) |
| N(1)–C(13)–C(14) | 116.9(3) | N(1)–C(8)–C(9) | 119.8(3) |
| C(15)–C(13)–C(14) | 121.9(4) | C(10)–C(8)–C(9) | 120.5(3) |
| C(1)–N(1)–C(13) | 128.9(3) | C(1)–N(1)–C(8) | 131.7(3) |
| C(1)–N(1)–H(1) | 118(3) | C(1)–N(1)–H(1) | 118(2) |
| C(13)–N(1)–H(1) | 112(3) | C(8)–N(1)–H(1) | 109(2) |
| C(16)–O(1)···H(1) | 98(1) | C(11)–O(1)···H(1) | 97(1) |
| N(1)–H(1)···O(1) | 141(3) | N(1)–H(1)···O(1) | 146(3) |

*Table 2*

Selected interatomic distances (Å) and angles (deg) in $Bu_2SnCl_2$[OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4] (**5**)

| | | | |
|---|---|---|---|
| Sn(1)–C(18) | 2.132(5) | Cl(1)–Sn(1)–O(1) | 177.59(8) |
| Sn(1)–C(22) | 2.131(6) | | |
| Sn(1)–Cl(1) | 2.4812(16) | Cl(1)–Sn(1)–C(18) | 95.86(15) |
| Sn(1)–Cl(2) | 2.3828(16) | Cl(1)–Sn(1)–C(22) | 95.8(2) |
| Sn(1)–O(1) | 2.381(3) | Cl(1)–Sn(1)–Cl(2) | 95.40(7) |
| | | | |
| | | O(1)–Sn(1)–C(18) | 86.20(16) |
| | | O(1)–Sn(1)–C(22) | 83.1(2) |
| | | O(1)–Sn(1)–Cl(2) | 82.85(9) |
| | | | |
| | | C(18)–Sn(1)–C(22) | 146.0(2) |
| | | C(18)–Sn(1)–Cl(2) | 104.50(15) |
| | | C(22)–Sn(1)–Cl(2) | 106.01(19) |
| | | | |
| | | Sn(1)–O(1)–C(16) | 139.5(3) |
| | | | |
| O(1)–C(16) | 1.272(5) | O(1)–C(16)–C(15) | 121.7(4) |
| C(16)–C(17) | 1.492(6) | O(1)–C(16)–C(17) | 118.1(4) |
| C(16)–C(15) | 1.395(6) | C(15)–C(16)–C(17) | 120.2(4) |

*Table 2 (continued)*

| | | | |
|---|---|---|---|
| C(13)–C(14) | 1.503(6) | C(13)–C(15)–C(16) | 123.2(4) |
| C(13)–C(15) | 1.384(6) | N(1)–C(13)–C(15) | 121.9(4) |
| N(1)–C(13) | 1.322(6) | N(1)–C(13)–C(14) | 118.8(4) |
| N(1)–C(1) | 1.441(5) | C(15)–C(13)–C(14) | 119.2(4) |
| N(1)–H(1) | 0.75(5) | C(1)–N(1)–C(13) | 127.3(4) |
| O(1)···H(1) | 2.01(5) | C(1)–N(1)–H(1) | 113(4) |
| | | C(13)–N(1)–H(1) | 119(4) |
| | | C(16)–O(1)···H(1) | 100(1) |
| | | N(1)–H(1)···O(1) | 135(5) |

*Table 3*

Selected interatomic distances (Å) and angles (deg) in[$(Me_2SnCl)_2O${OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4}$]_2$ (**9**).[a]

| | | | |
|---|---|---|---|
| Sn(1)–C(18) | 2.080(8) | Sn(2)–C(20) | 2.092(8) |
| Sn(1)–C(19) | 2.095(7) | Sn(2)–C(21) | 2.111(7) |
| Sn(1)–Cl(1) | 2.440(3) | Sn(2)–Cl(2) | 2.696(3) |
| Sn(1)–O(2) | 2.067(4) | Sn(2)–O(2) | 2.024(4) |
| Sn(1)–Cl(2) | 2.851(3) | | |
| Sn(1)–O(1) | 2.500(5) | Sn(2)–O(2') | 2.097(4) |
| O(1)-Sn(1)-O(2) | 173.46(17) | Cl(2)–Sn(2)–O(2') | 155.81(13) |
| Cl(1)-Sn(1)-Cl(2) | 165.19(8) | | |
| C(18)-Sn(1)-C(19) | 154.3(4) | | |
| O(1)–Sn(1)–C(18) | 81.6(3) | Cl(2)–Sn(2)–C(20) | 89.6(3) |
| O(1)–Sn(1)–C(19) | 81.3(3) | Cl(2)–Sn(2)–C(21) | 89.6(2) |
| O(1)–Sn(1)–Cl(1) | 83.88(14) | Cl(2)–Sn(2)–O(2) | 79.83(13) |
| O(1)–Sn(1)–Cl(2) | 110.93(14) | | |
| O(2)–Sn(1)–C(18) | 101.0(3) | O(2')–Sn(2)–C(20) | 100.4(3) |
| O(2)–Sn(1)–C(19) | 98.2(3) | O(2')–Sn(1)–C(21) | 98.3(3) |
| O(2)–Sn(1)–Cl(1) | 89.76(13) | O(2')–Sn(1)–O(2) | 76.01(18) |
| O(2)–Sn(1)–Cl(2) | 75.44(12) | | |
| C(18)-Sn(1)-Cl(1) | 98.5(3) | C(20)-Sn(2)-C(21) | 135.0(4) |
| C(19)-Sn(1)-Cl(1) | 98.5(3) | C(20)-Sn(2)-O(2) | 112.4(3) |
| C(18)-Sn(1)-Cl(2) | 84.0(3) | C(21)-Sn(2)-O(2) | 111.7(3) |
| C(19)-Sn(1)-Cl(2) | 84.5(3) | | |
| Sn(1)-O(2)-Sn(2) | 123.5(2) | Sn(1)-O(2)-Sn(2') | 132.2(2) |
| Sn(1)-Cl(2)-Sn(2) | 81.01(6) | Sn(2)-O(2)-Sn(2') | 103.99(18) |
| Sn(1)–O(1)–C(16) | 144.0(5) | | |
| O(1)–C(16) | 1.266(8) | O(1)–C(16)–C(15) | 121.8(7) |
| C(16)–C(17) | 1.512(10) | O(1)–C(16)–C(17) | 118.1(7) |
| C(16)–C(15) | 1.379(10) | C(15)–C(16)–C(17) | 120.1(7) |
| C(13)–C(14) | 1.500(9) | C(13)–C(15)–C(16) | 124.5(7) |
| C(13)–C(15) | 1.392(9) | N(1)–C(13)–C(15) | 121.4(6) |
| N(1)–C(13) | 1.316(8) | N(1)–C(13)–C(14) | 118.3(7) |
| N(1)–C(1) | 1.441(8) | C(15)–C(13)–C(14) | 120.3(7) |
| N(1)–H(1) | 0.84(5) | C(1)–N(1)–C(13) | 125.5(6) |
| O(1)···H(1) | 2.00(5) | C(1)–N(1)–H(1) | 113(4) |
| | | C(13)–N(1)–H(1) | 118(4) |
| | | C(16)–O(1)···H(1) | 100(2) |
| | | N(1)–H(1)···O(1) | 130(4) |

[a] Symmetry equivalent positions (*2–x, 1–y, 1–z*) are denoted by "prime".

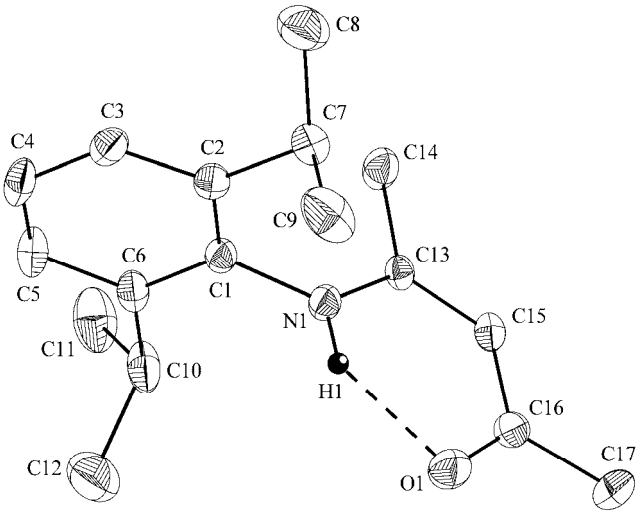



Fig. 1 – ORTEP plot of OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4 (**1**). The atoms are drawn with 20% probability ellipsoids. Hydrogen atoms, except H(1) attached to nitrogen, are omitted for clarity.

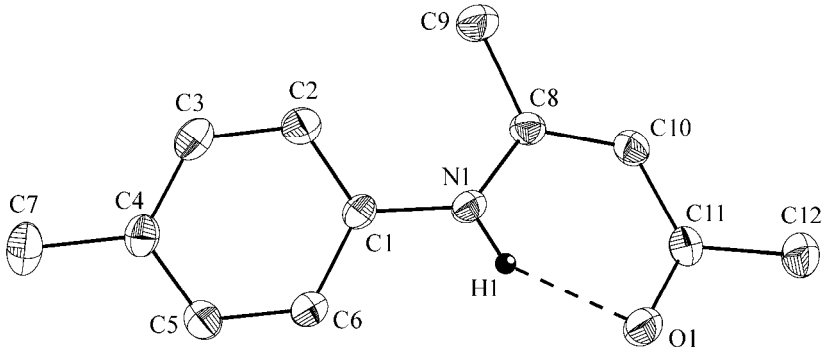



Fig. 2 – ORTEP plot of OC(Me)CHC(Me)NH($C_6H_4$Me-4)-4 (**2**).
The atoms are drawn with 20% probability ellipsoids. Hydrogen atoms, except H(1) attached to nitrogen, are omitted for clarity.

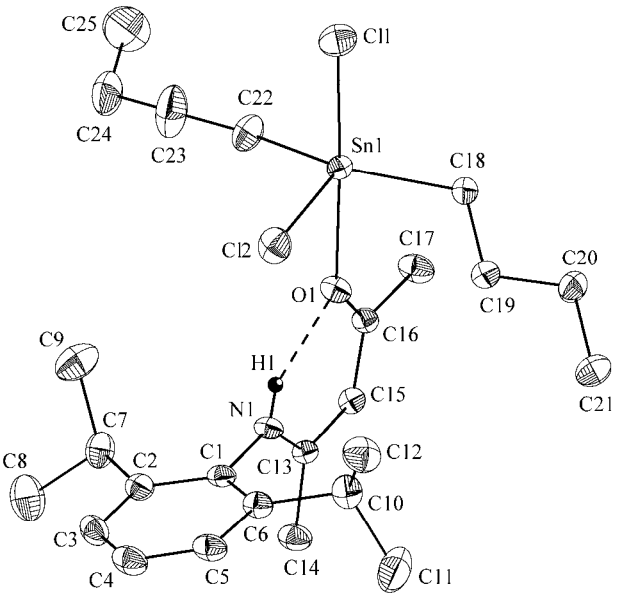



Fig. 3 – ORTEP plot of $Bu_2SnCl_2$[OC(Me)CHC(Me)NH($C_6H_3{}^iPr_2$-2',6')-4] (**5**).
The atoms are drawn with 20% probability ellipsoids. Hydrogen atoms, except H(1) attached to nitrogen, are omitted for clarity.

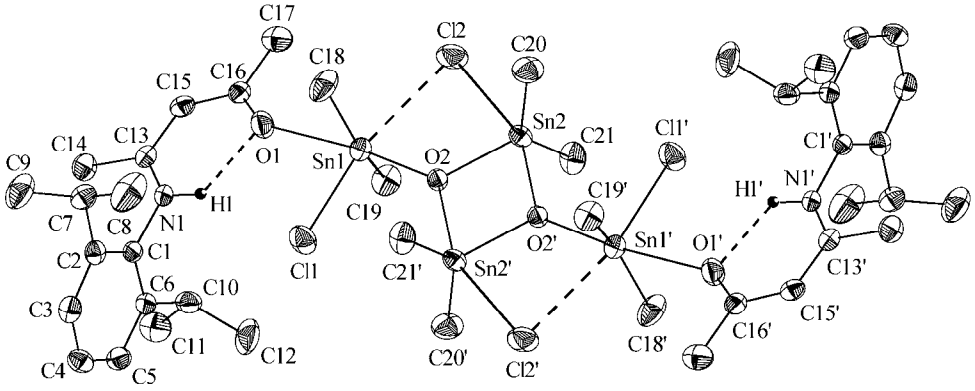



Fig. 4 – ORTEP plot of $[(Me_2SnCl)_2O\{ OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4\}]_2$ (**9**). The atoms are drawn with 20% probability ellipsoids. Hydrogen atoms, except H(1) attached to nitrogen, are omitted for clarity [symmetry equivalent atoms ($2 - x$, $1 - y$, $1 - z$) are given by ''prime''].

## DISCUSSION

### Solution behavior

The solution NMR spectra of the *β*-ketimines **1** and **2** suggest the presence of the acidic proton on nitrogen, the proposed structure in solution being similar with that observed in solid tate (see subsequent discussion).

For the organotin(IV) chloride adducts **3**-**7** the $^1H$ and $^{13}C$ NMR spectra contain, in addition to the signals for the *β*-ketimine ligand **1** (very similar chemical shifts as those observed for the free organic ligand), the characteristic resonances corresponding to equivalent organic groups bonded to tin. The $^{119}Sn$ resonances for the adducts **3**-**7** appear as sharp singlet signals. The magnitude of the $^{119}Sn$ chemical shifts for the triorganotin(IV) chloride adducts **3** ($\delta$ 140.1 ppm) and **4** ($\delta$ –51.1 ppm) are very similar to those reported for the free, four-coordinate $R_3SnCl$ ($\delta$ 164 ppm for R = Me, and –45 ppm for R = Ph)[35] in non-interacting solvents, thus suggesting weak coordination or even dissociation of the *β*-ketimine ligand in solution. This behavior is also supported by the calculated C–Sn–C angle in **3** based on the coupling constants $^2J_{119SnH}$ = 59.7 Hz or $^1J_{119SnC}$ = 398.2 Hz, using the correlations $\theta = 0.0161|^2J|^2 - 1.32|^2J| + 133.4$,[36] and $|^1J| = 11.4\theta - 875$ ($\theta$ = C–Sn–C angle);[37] the value obtained, *i.e.* 112º, being very close to that for a tetrahedral environment around tin.

Increasing the number of chlorine atoms attached to tin will result in increased Lewis acidity of the metal center. Consequently the *β*-ketimine ligand will coordinate stronger to the metal center and the $^{119}Sn$ chemical shift will move to an upfield value with the increase in coordination of the tin. Indeed, $^{119}Sn$ resonances at $\delta$ 81.0 ppm and –298.2 ppm were observed for the 1:1 adducts **5** and **6** (c.f. $\delta$ 123 ppm for $Bu_2SnCl_2$ and $\delta$ –32 ppm for $Ph_2SnCl_2$, in non-interacting solvents),[35] which suggest an increase of the coordination number to five, with the oxygen atom of the *β*-ketimine *trans* to a chlorine atom . The calculated C–Sn–C angle in **5**, *i.e.* 121º (based on the coupling constant $^1J_{119SnC}$ = 462.7 Hz and the correlation $|^1J| = 9.99\theta - 746$),[38] supports this behavior. The same considerations apply for the 1:2 adduct **7**, *i.e.* an upfield shift of the $^{119}Sn$ resonance ($\delta$ 23.0 ppm) for a six-coordinate tin atom in solution (c.f. 137 ppm for $Me_2SnCl_2$, in non-interacting solvents).[35] In this case, however, the calculated value of the C–Sn–C angle (127º on the basis of $^2J_{119SnH}$ = 76.7 Hz,[36] and 128º on the basis of $^1J_{119SnC}$ = 583.4 Hz[37]) suggests the coordination of the *β*-ketimine ligands is not enough strong to force a linear $Me_2Sn$ unit.

In the case of the mixed chloro-oxide adduct **9** the $^{119}Sn$ NMR spectrum shows two resonances ($\delta$ –65.8 and –117.3 ppm) only slightly upfield shifted with respect to the free $[(Me_2SnCl)_2O]_2$ dimer ($\delta$ –60.8 and –115.7 ppm),[39] thus suggesting weak coordination of the *β*-ketimine ligands in solution. In addition to the expected resonances corresponding to equivalent *β*-ketimine units, three resonances were observed in the $^1H$ NMR spectrum (1:2:1 integral ratio) as well as in the $^{13}C$ NMR spectrum, always surrounded by satellites due to tin-proton and tin-carbon couplings. This suggests that, in contrast to the solid state structure (see subsequent discussion), some asymmetry is

induced in solution with respect to the methyl groups attached to tin in spite of the weakness of the interaction between the metal atoms and the *β*-ketimine ligands.

### Solid state structure

The molecules of both *β*-ketimines **1** (Fig. 1) and **2** (Fig. 2) exhibit a basically planar O=C(Me)–CH=(Me)C–N(H)C skeleton, with typical double and single bonds. The acidic hydrogen is attached to the nitrogen atom and is involved in an intramolecular hydrogen bonding to the oxygen atom (Table 1). The main difference between the two molecules resides in the relative orientation of the aromatic ring with respect to the rest of the molecule (dihedral angle OCCCNH/aromatic ring: 88.5º for **1** and 30.8º for **2**). The almost orthogonal orientation observed for **1** is obviously due to the steric impediments brought by the bulky isopropyl groups in positions 2' and 6' of the aromatic ring.

In the molecule of the adduct **5** the *β*-ketimine ligand **1** is coordinated through its oxygen atom to tin (Fig. 3), resulting in a distorted trigonal bipyramidal $C_2SnCl_2O$ core with oxygen *trans* to a halogen atom [Cl(1)–Sn(1)–O(1) 177.59(8)º]. The length of the Sn(1)–O(1) bond [2.381(3) Å] suggests a strong coordination [cf. the sums of the covalent and van der Waals radii are $\Sigma r_{cov}$(Sn,O) ca. 2.06 Å and $\Sigma r_{vdW}$(Sn,O) ca. 3.60 Å].[40] As expected, the tin-oxygen distance in the adduct **5** is much longer than those observed in $SnCl_2[OC(Me)CHC(Me)N(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]_2$ [Sn–O 2.074(2) Å], which contains the deprotonated *β*-ketiminato ligand.[14] The Sn(1) atom is displaced from the $C_2Cl$ equatorial plane on the side of the axial Cl(1) atom with 0.218 Å and the difference in the chlorine atoms is reflected in the lengths of their bonds to tin: the shorter bond [Sn(1)–Cl(2) 2.3828(16) Å] is placed in the equatorial position, while the longer one [Sn(1)–Cl(1) 2.4812(16) Å] occupies the axial position. The equatorial C–Sn–C is considerable larger [C(18)–Sn(1)–C(22) 146.0(2)º] than the calculated value (121º) from the solution NMR data.

Compound **9** features a centrosymmetric structure (Fig. 4) in which a tetranuclear $[(Me_2SnCl)_2O]_2$ fragment, very similar to the free one,[39] is coordinated by two *β*-ketimine ligands in the same way as described above for the adduct **5**. The tin atoms from the central, planar $Sn_2O_2$ ring remained five-coordinated in **9**, in a distorted trigonal bipyramidal environment, with chlorine and oxygen atoms in axial positions [Cl(2)–Sn(2)–O(2') 155.81(13)º], as observed in the free $[(Me_2SnCl)_2O]_2$ dimer,[39] while the coordination number of the other two tin atoms is increased to six by *O*-donating *β*-ketimines and intramolecular coordinated chlorine atoms [Sn(1)–Cl(2) 2.851(3) Å]. The resulted distorted octahedral $C_2SnCl_2O_2$ cores exhibit an all-*trans* configuration [O(1)-Sn(1)-O(2) 173.46(17)º, Cl(1)-Sn(1)-Cl(2)º, C(18)-Sn(1)-C(19) 154.3(4)º]. As expected, the terminal Sn(1)–Cl(1) bond [2.440(3) Å] is shorter than the bridging Sn–Cl bonds [Sn(2)–Cl(2) 2.696(3), Sn(1)–Cl(2) 2.851(3) Å]. The $Sn–O_{ketimine}$ bond in **9** is considerably longer than the other tin-oxygen bonds in the adduct [range 2.024(4)-2.097(4) Å] (Table 3). It should also be noted that the *β*-ketimine is less strong coordinated to the metal in **9** than in **5**, as reflected by the Sn–O bond lengths [2.500(5) Å *vs* 2.381(3) Å]. However, no significant differences in the molecular parameters of the coordinated *β*-ketimine ligand in **5** or **9** and the free molecule of **1** were noted.

A closer check of the crystal structures revealed that for the *β*-ketimines **1** and **2** there are no intermolecular O···H or N···H contacts shorter than the sum of van der Waals radii for the corresponding atoms [cf. $\Sigma r_{cov}$(O,H) ca. 2.60 Å and $\Sigma r_{vdW}$(N,H) ca. 2.74 Å].[40] By contrast, supramolecular polymers are built in the crystals of the adducts **5** and **9** through weak intermolecular Cl···H contacts between the molecular units [cf. $\Sigma r_{vdW}$(Cl,H) ca. 3.OÅ].[40] Thus, in the crystal of the **5** (Fig. 5) dimers are formed through intermolecular $Cl(1)\cdots H(22A')_{\alpha\text{-methylene}}$ [2.83 Å] interactions and these dimers are doubly connected through weak inter-dimer $Cl(1)\cdots H(17Bb)_{ketimine\text{-}methyl}$ [2.87 Å] contacts into polymeric chains, the Cl(2) atoms being not involved in any intermolecular interaction. For the mixed chloro-oxide adduct **9** the crystal contains polymeric chains (Fig. 6) built from tetranuclear units doubly connected through $Cl(1)\cdots H(3'a)_{aryl}$ [2.92 Å] contacts. For both compounds no further inter-chain contacts are established.

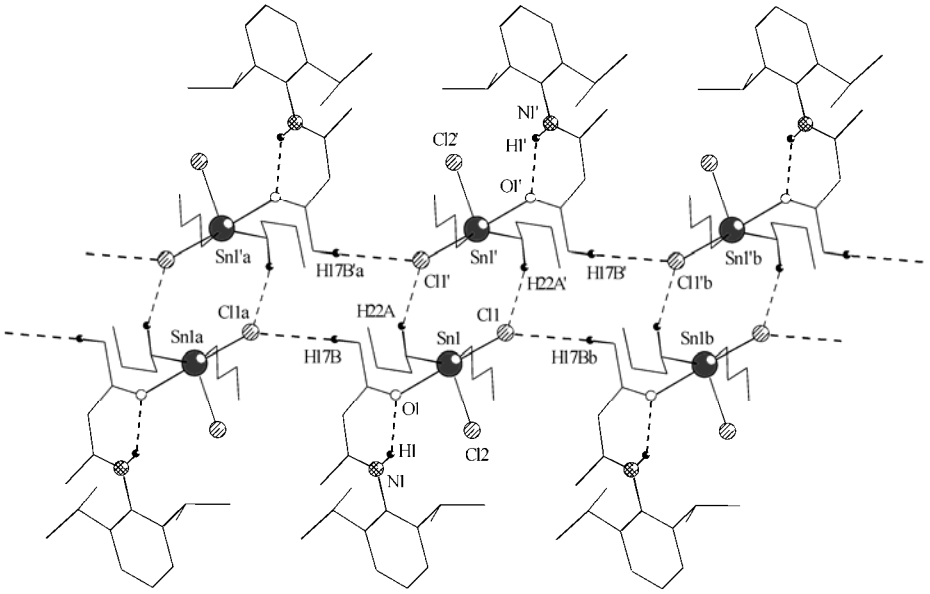



Fig. 5 – View of the polymeric ribbon-like association in the crystal of **5** based on intermolecular Cl···H contacts (only hydrogens involved in such contacts are shown) [symmetry equivalent atoms (1 – *x*, 2 – *y*, 1 – *z*), (*x*, –1 + *y*, *z*), (1 – *x*, 1 – *y*, 1 – *z*), (*x*, 1 + *y*, *z*) and (1 – *x*, 3 – *y*, 1 – *z*) are given by ''prime'', "a", "prime a", "b" and "prime b"].

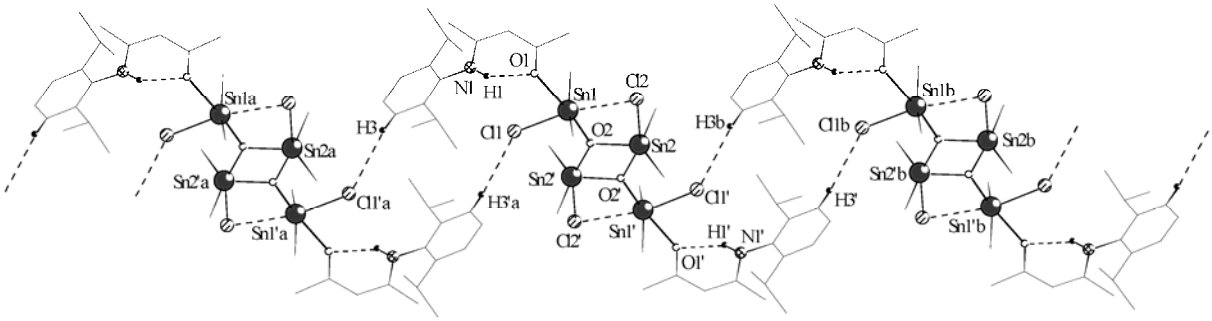



Fig. 6 – View of the polymeric chain in the crystal of **9** based on intermolecular Cl···H contacts (only hydrogens involved in such contacts are shown) [symmetry equivalent atoms (2 – *x*, 1 – *y*, 1 – *z*), (–1 + *x*, *y*, –1 + *z*), (1 – *x*, 1 – *y*,–*z*), (1 + *x*, *y*, 1 + *z*) and (3 – *x*, 1 – *y*, 2 – *z*) are given by ''prime'', "a", "prime a", "b" and "prime b"].

## EXPERIMENTAL

Solvents were dried and distilled prior to use. $^{1}$H, $^{13}$C and $^{119}$Sn NMR spectra, including 2D experiments, were recorded on Bruker Avance 300 and Bruker Avance III 500 instruments using solutions in $CDCl_3$. The chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. $CHCl_3$: $^{1}$H 7.26, $^{13}$C 77.0 ppm) for $^{1}$H and $^{13}$C NMR spectra and neat $SnMe_4$ for and $^{119}$Sn NMR spectra. Mass spectra were recorded with FINNIGAN MAT 8200.

*Synthesis of (Z)-4-(2',6'-diisopropylphenylamino)pent-3-en-2-one*, *OC(Me)CHC(Me)NH(C$_6$H$_3$$^{i}$Pr$_2$-2',6')-4* (**1**)

The compound was obtained using a slightly modified published procedure.[34] A solution of 2,4-pentanedione (40 g, d = 0.975 g/cm$^3$, 41.24 mL, 0.4 mol) in toluene was added to 2,6-diisopropylaniline (47 g, d = 0.94 g/cm$^3$, 50 mL, 0.265 mol), using $TsOH{\cdot}H_2O$ as catalyst (0.46 g, 2.5 mmol). The reaction mixture was heated at 110 °C during 8 h, using a Dean Stark apparatus to remove the water from the system. After removal of the solvent and washing of the residue with n-hexane the title compound was obtained as a pale yellow powder. Storage of the slightly yellow solution in a freezer at –32 °C gave yellow crystals. Yield: 44 g (64%). M.p. = 49-51 °C (46 °C).[34] $^{1}$H NMR (300 MHz): 1.14d [6H$_A$, -CH(C*H*$_3$)$_2$, $^{3}J_{HH}$ = 6.8 Hz], 1.21d [6H$_B$, -CH(C*H*$_3$)$_2$, $^{3}J_{HH}$ = 6.9 Hz], 1.63s [3H, C*H*$_3$C(N)], 2.12s [3H, C*H*$_3$C(O)], 3.03 hept [2H, -C*H*(CH$_3$)$_2$, $^{3}J_{HH}$ = 6.9 Hz], 5.21s (1H, -C*H*=), 7.17d (2H, *H*$_{3',5'}$, $^{3}J_{HH}$ = 7.4 Hz), 7.29t (1H, *H*$_{4'}$, $^{3}J_{HH}$ = 7.7 Hz), 12.06s (1H, -N*H*-). $^{13}$C NMR (75.5 MHz): 19.11s [*C*H$_3$C(N)], 22.64s [-CH(*C*H$_3$)$_2$, (B)], 24.56s [-CH(*C*H$_3$)$_2$, (A)], 28.45s [-*C*H(CH$_3$)$_2$], 29.03s [*C*H$_3$C(O)], 95.56s (-*C*H=), 123.51s (*C*$_{3',5'}$), 128.21s (*C*$_{4'}$), 133.48s (*C*$_{1'}$), 146.26s (*C*$_{2',6'}$), 163.23s [CH$_3$*C*(N)], 195.87s [CH$_3$*C*(O)]. MS (EI, 70 eV, 200 ºC): *m/z* (relative intensity, %) 259 (30) [M]$^+$, 244 (25) [M - CH$_3$]$^+$, 202 (100) [M - CH$_3$(CO)CH - H]$^+$, 43 (18) [CH$_3$CO]$^+$.

*Synthesis of (Z)-4-(4'-methylphenylamino)pent-3-en-2-one*, *OC(Me)CHC(Me)NH(C$_6$H$_4$Me-4')-4* (**2**)

The compound was obtained using a similar procedure as described for compound **1**. A solution of 2,4-pentanedione (100 g, d = 0.975 g/cm$^3$, 102.6 mL, 1 mol) in toluene was added to 4-methylaniline (107 g, d = 0.973 g/cm$^3$, 110 mL, 1 mol), using $TsOH{\cdot}H_2O$ as catalyst (0.46 g, 2.5 mmol). The reaction mixture was heated at 110 °C during 8 h, using a Dean Stark apparatus to remove the water from the system. The residue remained after the removal of the solvent was washed with n-hexane. The title compound was obtained as a

pale yellow solid. Storage of the slightly yellow solution in a freezer at –32 °C gave yellow crystals. Yield: 156 g (82%). M.p. = 66-69 °C (58-60 °C).[41] $^1$H NMR (300 MHz): 1.95s [3H, C$H_3$C(N)], 2.08s [3H, C$H_3$C(O)], 2.33s (3H, $C_6H_4$-C$H_3$), 5.16s (1H, -C*H*=), 6.99d (2H, $H_{2',6'}$, $^3J_{HH}$ = 8.2 Hz), 7.13d (2H, $H_{3',5'}$, $^3J_{HH}$ = 8.1 Hz), 12.40s (1H, -N*H*-). $^{13}$C NMR (75.5 MHz): 19.72s [*C*H$_3$C(N)], 20.86s [*C*H$_3$C(O)], 29.08s ($C_6H_4$-*C*H$_3$), 97.13s (-*C*H=), 124.79s ($C_6H_4$, $C_{2',6'}$), 129.59s ($C_6H_4$, $C_{3',5'}$), 135.41s ($C_{4'}$), 135.98s ($C_{1'}$), 160.60s [CH$_3$*C*(N)], 195.83s [CH$_3$*C*(O)]. MS (EI, 70 eV, 200 ºC): *m/z* (relative intensity, %) 189 (68) [M]$^+$, 174 (100) [M - CH$_3$]$^+$, 146 (23) [M - CH$_3$CO]$^+$, 43 (5) [CH$_3$CO]$^+$.

*General procedure for the preparation of $R_nSnCl_{4-n}$[OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4]$_x$ (Table 4)*

A solution of organotin(IV) chloride was added to a stirred solution of **1** 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. Details of the preparations, yields and melting points are given in Table 4. Microanalyses (C, H, N) and NMR spectra are consistent with the given composition of the isolated products.

*Table 4*

Preparation data and m.p. for $R_nSnCl_{4-n}$[OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4]$_x$derivatives

| Starting materials | | | Product | Yield | m.p. |
|---|---|---|---|---|---|
| $R_nSnCl_{4-n}$ (g / mmol) | L[a] (g / mmol) | x | | g (%) | (°C) |
| $Me_3SnCl$ (0.76 / 3.81) | 1.0 / 3.85 | 1 | $Me_3SnCl$(L) (**3**) | 1.00 (57) | 90-91 |
| $Ph_3SnCl$ (1.48 / 3.84) | 1.0 / 3.85 | 1 | $Ph_3SnCl$(L) (**4**) | 1.00 (40) | 95-96 |
| $Bu_2SnCl_2$ (1.17 / 3.85) | 1.0 / 3.85 | 1 | $Bu_2SnCl_2$(L) (**5**) | 1.22 (56) | 78-79 |
| $Ph_2SnCl_2$ (1.32 / 3.84) | 1.0 / 3.85 | 1 | $Ph_2SnCl_2$(L) (**6**) | 1.30 (56) | 154-155 |
| $Me_2SnCl_2$ (0.42 / 1.91) | 1.0 / 3.85 | 2 | $Me_2SnCl_2(L)_2$ (**7**) | 0.80 (57) | 132-133 |

[a] L = OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4.

*Trimethylchlorotin(IV)[(Z)-4-(2',6'-diisopropylphenylamino)pent-3-en-2-one], $Me_3SnCl$[OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4]* (**3**). $^1$H NMR (300 MHz): 0.66s (9H, Sn*C*H$_3$, $^2J_{117SnH}$ = 57.2, $^2J_{119SnH}$ = 59.7 Hz), 1.14d [6H$_A$, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz], 1.20d [6H$_B$, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 1.63s [3H, C*H*$_3$C(N)], 2.10s [3H, C*H*$_3$C(O)], 2.99hept [2H, -C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 5.20s (1H, -C*H*=), 7.17d (2H, $H_{3',5'}$, $^3J_{HH}$ = 7.6 Hz), 7.30t (1H, $H_{4'}$, $^3J_{HH}$ = 7.6 Hz), 11.98s (1H, -N*H*-). $^{13}$C NMR (75.5 MHz): –0.18s (Sn*C*H$_3$, $^1J_{117SnC}$ = 380.5, $^1J_{119SnC}$ = 398.2 Hz), 19.15s [*C*H$_3$C(N)], 22.61s [-CH(*C*H$_3$)$_2$, (B)], 24.53s [-CH(*C*H$_3$)$_2$, (A)], 28.42s [-*C*H(CH$_3$)$_2$], 28.79s [*C*H$_3$C(O)], 95.73 (s, -*C*H=), 123.56s ($C_{3',5'}$), 128.37s ($C_{4'}$), 133.10s ($C_{1'}$), 146.06s ($C_{2',6'}$), 163.01s [CH$_3$*C*(N)], 195.56s [CH$_3$*C*(O)]. $^{119}$Sn NMR (111.9 MHz): 140.1s.

*Triphenylchlorotin(IV)[(Z)-4-(2',6'-diisopropylphenylamino)pent-3-en-2-one], $Ph_3SnCl$[OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4]* (**4**). $^1$H NMR (300 MHz): 1.15d [6H$_A$, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz], 1.22d [6H$_B$, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 1.64s [3H, C*H*$_3$C(N)], 2.11s [3H, C*H*$_3$C(O)], 3.03hept [2H, -C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz], 5.21s (1H, -C*H*=), 7.18d (2H, $H_{3',5'}$, $^3J_{HH}$ = 7.5 Hz), 7.30t (1H, $H_{4'}$, $^3J_{HH}$ = 7.7 Hz), 7.47m (9H, Sn$C_6H_5$-*meta*+*para*), 7.68m (6H, Sn$C_6H_5$-*ortho*, $^3J_{SnH}$ = 61.5 Hz), 12.05s (1H, -N*H*-). $^{13}$C NMR (125.8 MHz): 19.16s [*C*H$_3$C(N)], 22.67s [-CH(*C*H$_3$)$_2$, (B)], 24.54s [-CH(*C*H$_3$)$_2$, (A)], 28.45s [-*C*H(CH$_3$)$_2$], 29.01s [*C*H$_3$C(O)], 95.62s (-*C*H=), 123.52s ($C_{3',5'}$), 128.24s ($C_{4'}$), 129.10s (Sn$C_6H_5$-*meta*, $^3J_{117SnC}$ = 62.0 Hz, $^3J_{119SnC}$ = 64.9 Hz), 130.40s (Sn$C_6H_5$-*para*, $^4J_{SnC}$ = 13.6 Hz), 133.43s ($C_{1'}$), 136.10s (Sn$C_6H_5$-*ortho*, $^2J_{117SnC}$ = 47.7 Hz, $^2J_{119SnC}$ = 49.9 Hz), 137.47s (Sn$C_6H_5$-*ipso*), 146.22s ($C_{2',6'}$), 163.39s [CH$_3$*C*(N)], 195.90s [CH$_3$*C*(O)]. $^{119}$Sn NMR (111.9 MHz): –51.1s.

*Dibutyldichlorotin(IV)[(Z)-4-(2',6'-diisopropylphenylamino)pent-3-en-2-one], $Bu_2SnCl_2$[OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4]* (**5**). $^1$H NMR (300 MHz): 0.94t [6H$_\delta$, Sn(CH$_2$)$_3$C*H*$_3$, $^3J_{HH}$ = 7.3 Hz], 1.15d [6H$_A$, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz], 1.21d [6H$_B$, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 1.41m [4H$_\gamma$, Sn(CH$_2$)$_2$CH$_3$], 1.65s [3H, C*H*$_3$C(N)], 1.80m [8H$_{\alpha,\beta}$, Sn(CH$_2$)$_2$CH$_3$], 2.12s [3H, C*H*$_3$C(O)], 3.00hept [2H, -C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 5.22s (1H, -C*H*=), 7.17d (2H, $H_{3',5'}$, $^3J_{HH}$ = 7.4 Hz), 7.30t (1H, $H_{4'}$, $^3J_{HH}$ = 7.7 Hz), 11.97s (1H, -N*H*-). $^{13}$C NMR (75.5 MHz): 13.49s [$C_\delta$, Sn(CH$_2$)$_3$*C*H$_3$], 19.30s [*C*H$_3$C(N)], 22.68s [-CH(*C*H$_3$)$_2$, (B)], 24.52s [-CH(*C*H$_3$)$_2$, (A)], 26.25s [$C_\gamma$, Sn(*C*H$_2$)$_3$CH$_3$, $^3J_{117SnC}$ = 86.8, $^3J_{119SnC}$ = 90.6 Hz], 26.94s [$C_\beta$, Sn(*C*H$_2$)$_3$CH$_3$, $^2J_{SnC}$ = 34.7 Hz], 27.73s [$C_\alpha$, Sn(*C*H$_2$)$_3$CH$_3$, $^1J_{117SnC}$ = 442.0, $^1J_{119SnC}$ = 462.7 Hz], 28.46s [-*C*H(CH$_3$)$_2$], 28.82s [*C*H$_3$C(O)], 95.77s (-*C*H=), 123.58s ($C_{3',5'}$), 128.41s ($C_{4'}$), 133.10s ($C_{1'}$), 146.08s ($C_{2',6'}$), 164.32s [CH$_3$*C*(N)], 195.12s [CH$_3$*C*(O)]. $^{119}$Sn NMR (111.9 MHz): 81.0s.

*Diphenyldichlorotin(IV)[(Z)-4-(2',6'-diisopropylphenylamino)pent-3-en-2-one], $Ph_2SnCl_2$[OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4]* (**6**). $^1$H NMR (300 MHz): 1.15d [6H$_A$, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz], 1.22d [6H$_B$, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 1.66s [3H, C*H*$_3$C(N)], 2.01s [3H, C*H*$_3$C(O)], 3.00hept [2H, -C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 5.20s (1H, -C*H*=), 7.18d (2H, $H_{3',5'}$, $^3J_{HH}$ = 7.6 Hz), 7.34t (1H, $H_{4'}$, $^3J_{HH}$ = 7.6 Hz), 7.50m (6H, Sn$C_6H_5$-*meta*+*para*), 7.74m (4H, Sn$C_6H_5$-*ortho*, $^3J_{SnH}$ = 80.8 Hz), 12.02s (1H, -N*H*-). $^{13}$C NMR (75.5 MHz): 19.31s [*C*H$_3$C(N)], 22. 70s [-CH(*C*H$_3$)$_2$, (B)], 24.51s [-CH(*C*H$_3$)$_2$, (A)], 28.51s [-*C*H(CH$_3$)$_2$], 28.68s [*C*H$_3$C(O)], 95.95s (-*C*H=), 123.60s ($C_{3',5'}$), 128.43s ($C_{4'}$), 129.51s (Sn$C_6H_5$-*meta*, $^3J_{117SnC}$ = 84.2 Hz, $^3J_{119SnC}$ = 88.5 Hz), 131.42s (Sn$C_6H_5$-*para*), 133.19s ($C_{1'}$), 135.04s (Sn$C_6H_5$-*ortho*, $^2J_{117SnC}$ = 62.4 Hz, $^2J_{119SnC}$ = 64.7 Hz), 138.50s (Sn$C_6H_5$-*ipso*), 146.06s ($C_{2',6'}$), 164.39s [CH$_3$*C*(N)], 195.56s [CH$_3$*C*(O)]. $^{119}$Sn NMR (111.9 MHz): –298.2s.

*Dimethyldichlorotin(IV)bis[(Z)-4-(2',6'-diisopropylphenylamino)pent-3-en-2-one], $Me_2SnCl_2$[OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4]$_2$* (**7**). $^1$H NMR (300 MHz): 1.15d [12H$_A$, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz], 1.20s (6H, Sn*C*H$_3$, $^2J_{117SnH}$ = 73.5, $^2J_{119SnH}$ = 76.7 Hz), 1.21d [12H$_B$, -CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 5.9 Hz], 1.67s [6H, C*H*$_3$C(N)], 2.11s [6H, C*H*$_3$C(O)], 2.95hept [4H, -C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz], 5.22s (2H, -C*H*=), 7.18d (4H, $H_{3',5'}$, $^3J_{HH}$ = 7.5 Hz), 7.32t (2H, $H_{4'}$, $^3J_{HH}$ = 7.7 Hz), 11.88s (2H, -N*H*-). $^{13}$C NMR (75.5 MHz): 9.71s (Sn*C*H$_3$, $^1J_{117SnC}$ = 557.7, $^1J_{119SnC}$ = 583.4 Hz), 19.42s [*C*H$_3$C(N)], 22.63s [-CH(*C*H$_3$)$_2$, (B)], 24.51s [-CH(*C*H$_3$)$_2$, (A)], 28.36s [*C*H$_3$C(O)], 28.50s [-*C*H(CH$_3$)$_2$],

96.19s (-*C*H=), 123.69s ($C_{3',5'}$), 128.70s ($C_{4'}$), 132.64s ($C_{1'}$), 145.81s ($C_{2',6'}$), 165.78s [$CH_3C$(N)], 194.37s [$CH_3C$(O)]. $^{119}$Sn NMR (111.9 MHz): 23.0s.

*Synthesis of bis($\mu_3$-oxo)-bis($\mu_2$-chloro)-dichlorooctamethyltetratin(IV)bis[(Z)-4-(2',6'-diisopropylphenylamino)pent-3-en-2-one], [$(Me_2SnCl)_2O${OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4}]$_2$* (**9**)

0.43 g KOH was added to a stirred solution of **1** (1.0 g, 3.85 mmol) and $Me_2SnCl_2$ (1.69 g, 7.69 mmol) in 50 mL toluene, resulting in a clear red-brown solution. The reaction mixture was refluxed for 5 h, using a Dean-Stark technique to remove the water from the system. After the complete elimination of the water from the system, the reaction mixture was cooled to room temperature and the resulting white precipitate was filtered off. The solvent was removed from the clear toluene solution under vacuum. The oily residue treated with hexane to give the title compound as a white solid, which was filtered and dried under vacuum. Yield: 1.5 g (61%). M.p. = 118-120 °C. $^1$H NMR (300 MHz): 1.15d [12$H_A$, -CH(C$H_3$)$_2$, $^3J_{HH}$ = 6.8 Hz], 1.17s (6$H_A$, SnC$H_3$, $^2J_{117SnH}$ = 77.1, $^2J_{119SnH}$ = 80.2 Hz), 1.19s (12$H_B$, SnC$H_3$, $^2J_{117SnH}$ = 74.0, $^2J_{119SnH}$ = 77.1 Hz), 1.21d [12$H_B$, -CH(C$H_3$)$_2$, $^3J_{HH}$ = 6.6 Hz], 1.23s (6$H_C$, SnC$H_3$, $^2J_{117SnH}$ = 81.0, $^2J_{119SnH}$ = 84.3 Hz), 1.66s [6H, C$H_3$C(N)], 2.11s [6H, C$H_3$C(O)], 2.94hept [4H, -C$H$(CH$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 5.21s (2H, -C$H$=), 7.18d (4H, $H_{3',5'}$, $^3J_{HH}$ = 7.7 Hz), 7.32t (2H, $H_{4'}$, $^3J_{HH}$ = 7.4 Hz), 11.87s (2H, -N$H$-). $^{13}$C NMR (75.5 MHz): 10.00s [Sn*C*H$_3$ (B), $^1J_{117SnC}$ = 567.6, $^1J_{119SnC}$ = 594.2 Hz], 12.58s [Sn*C*H$_3$ (A), $^1J_{117SnC}$ = 605.8, $^1J_{119SnC}$ = 633.7 Hz], 13.60s [Sn*C*H$_3$ (C), $^1J_{117SnC}$ = 644.7, $^1J_{119SnC}$ = 675.0 Hz], 19.42s [*C*H$_3$C(N)], 22.61s [-CH(*C*H$_3$)$_2$, (B)], 24.49s [-CH(*C*H$_3$)$_2$, (A)], 28.23s [*C*H$_3$C(O)], 28.48s [-*C*H(CH$_3$)$_2$], 96.16s (-*C*H=), 123.68s ($C_{3',5'}$), 128.72s ($C_{4'}$), 132.54s ($C_{1'}$), 145.72s ($C_{2',6'}$), 166.02s [$CH_3C$(N)], 194.08s [$CH_3C$(O)]. $^{119}$Sn NMR (111.9 MHz): –117.3s ($^2J_{SnSn}$ = 58.9 Hz), –65.8s,br.

*Crystal structure determination*

Block crystals of OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4 (**1**), OC(Me)CHC(Me)NH($C_6H_4$Me-4)-4 (**2**), $Bu_2SnCl_2$[OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4] (**5**) and [$(Me_2SnCl)_2O${OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4}]$_2$ (**9**) were mounted on a cryoloop. Data collection and processing was carried on a Bruker SMART APEX system (Babes-Bolyai University, Cluj-Napoca) using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Cell refinement gave cell constants corresponding to orthorhombic cell for **1**, monoclinic cell for **2** and triclinic cells for **5** and **9** (space group *Pccn* for **1**, $P2_1/c$ for **2** and *P*-1 for **5** and **9**), whose dimensions are given in Table 5 along with other experimental parameters.

*Table 5*

Crystallographic data for OC(Me)CHC(Me)NHR-4 [R = $C_6H_3^iPr_2$-2',6' (**1**); $C_6H_4$Me-4' (**2**)], $Bu_2SnCl_2$[OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4] (**5**) and [$(Me_2SnCl)_2O${OC(Me)CHC(Me)NH($C_6H_3^iPr_2$-2',6')-4}]$_2$ (**9**)

| Compound | **1** | **2** | **5** | **9** |
|---|---|---|---|---|
| Molecular formula | $C_{17}H_{25}NO$ | $C_{12}H_{15}NO$ | $C_{25}H_{43}Cl_2NOSn$ | $C_{42}H_{74}Cl_4N_2O_4Sn_4$ |
| *M* | 259.38 | 189.25 | 563.19 | 1287.67 |
| Crystal system | Orthorhombic | Monoclinic | Triclinic | Triclinic |
| Space group | *Pccn* | $P2_1/c$ | *P*–1 | *P*–1 |
| Temperature (K) | 297(2) | 297(2) | 297(2) | 297(2) |
| *a*/Å | 16.618(8) | 10.276(2) | 8.7920(18) | 10.567(7) |
| *b*/Å | 12.656(6) | 11.199(2) | 9.6170(19) | 11.899(8) |
| *c*/ Å | 15.680(8) | 9.810(2) | 18.312(4) | 12.272(8) |
| *α*/° | 90 | 90 | 81.83(3) | 110.543(13) |
| *β*/° | 90 | 107.985(3) | 78.22(3) | 97.280(12) |
| *γ*/° | 90 | 90 | 71.77(3) | 92.295(13) |
| *V*/Å$^3$ | 3298(3) | 1073.7(4) | 1434.5(5) | 1427.2(17) |
| *Z* | 8 | 4 | 2 | 1 |
| $D_{calc}$/gcm$^{-3}$ | 1.045 | 1.171 | 1.304 | 1.498 |
| *F*(000) | 1136 | 408 | 584 | 640 |
| μ(Mo-Kα)/mm$^{-1}$ | 0.064 | 0.074 | 1.092 | 1.951 |
| Crystal size (mm$^3$) | 0.30 x 0.26 x 0.23 | 0.32 x 0.22 x 0.11 | 0.28 x 0.26 x 0.21 | 0.28 x 0.28 x 0.17 |
| *θ* range for data collection (°) | 2.02 to 25.00 | 2.08 to 25.67 | 2.24 to 26.55 | 1.95 to 25.00 |
| Reflections collected | 22142 | 8026 | 15160 | 13863 |
| Independent reflections | 2903 [$R_{int}$ = 0.0683] | 2035 [$R_{int}$ = 0.0535] | 5847 [$R_{int}$ = 0.0498] | 5027 [$R_{int}$ = 0.0416] |
| Absorption correction | Multi-Scan[44] | Multi-Scan[44] | Multi-Scan[44] | Multi-Scan[44] |
| Maximum and minimum transmissions | 0.9855 and 0.9811 | 0.9919 and 0.9766 | 0.8031 and 0.7497 | 0.718 and 0.585 |
| Data / restraints / parameters | 2903 / 1 / 182 | 2035 / 0 / 134 | 5847 / 0 / 283 | 5027 / 1 / 268 |
| Goodness-of-fit on $F^2$ | 1.308 | 1.196 | 1.152 | 1.168 |
| Final *R* indices [$I>2\sigma(I)$][a] | $R_1$ = 0.1305 $wR_2$ = 0.2599 | $R_1$ = 0.0899 $wR_2$ = 0.1792 | $R_1$ = 0.0591 $wR_2$ = 0.1343 | $R_1$ = 0.0594 $wR_2$ = 0.1221 |
| *R* indices (all data)[a] | $R_1$ = 0.1489 $wR_2$ = 0.2695 | $R_1$ = 0.1287 $wR_2$ = 0.1960 | $R_1$ = 0.0690 $wR_2$ = 0.1393 | $R_1$ = 0.0788 $wR_2$ = 0.1297 |
| Largest difference peak and hole (e Å$^{-3}$) | 0.201 and –0.328 | 0.217 and –0.134 | 1.593 and –1.157 | 0.975 and –0.555 |

[a] Definition of the *R* values: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{[w\Sigma(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

The structures were refined with anisotropic thermal parameters. The hydrogen atom attached to the nitrogen atom was located from the difference map. The other 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.[42] The drawings were created with the Diamond program.[43]

**Supplementary material**

Crystallographic data for the structural analysis of **1**, **2**, **5** and **9** have been deposited with the Cambridge Crystallographic Data Centre [CCDC no. 768835 (**1**), 768836 (**2**), 768837 (**5**) and 768838 (**9**)]. Copies of the 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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