

UNEXPECTED PRODUCTS IN REACTIONS OF DOUBLE-C,N-CHELATED DIORGANOTIN(IV) DIBROMIDE WITH CYCLOPENTADIENYL- AND FLUORENYLLITHIUM

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

From the reactions of bis{2-[(dimethylamino)methyl]phenyl}tin(IV) dibromide with two equivalents of cyclopentadienyl- or fluorenyllithium in THF, unexpected products [2-(CH₃)₂-NCH₂C₆H₄]₂Sn(μ-η¹:η¹-C₅H₄)(μ-O)Sn[2-(CH₃)₂NCH₂C₆H₄]₂ (**2**) and [2-(CH₃)₂NCH₂C₆H₄]₂-Sn(OC₁₃H₉)Br (**3**), respectively, were isolated. These compounds were characterized by elemental analysis, NMR and X-ray diffraction techniques. The tin atoms in **2** are pseudo-tetrahedrally coordinated, each of them by two carbons of ligand, oxygen and the bridging carbon originated from μ-η¹:η¹-planar cyclopentadienyl moiety. The geometry of **3** is described as a distorted tetragonal pyramid with both ligand carbon atoms, bromine and one of nitrogen atoms in the base and oxygen atom in the vertex position.

Keywords: Stannanes; Organotin(IV) compounds; C,N-ligands; Cyclopentadienyl ligands; Fluorene; Oxygen abstraction; X-ray diffraction; Crystal structure.

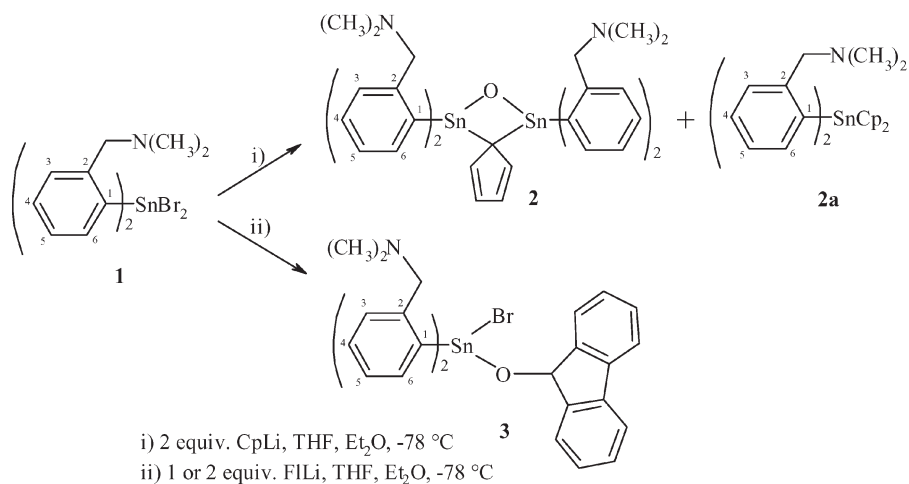
The chemistry of organotin(IV) compounds where the tin atom is σ-bonded to a cyclopentadienyl moiety is well established¹ including, for example, studies of mixed valence tin(II) and tin(IV) compounds or stability and properties of tin(III) radicals generated by irradiation of Bu_{4-n}Cp_nSn. The studies in the recent period targeted mainly to the synthesis of tin substituted ferrocenes² or ferrocenophanes³, and the use of these compounds as cyclopentadienyl group transfer agents to the transition metal centre⁴. The fluorenyltin(IV) derivatives are known, too, but much less is known about their structure and properties.

Our interest is mainly focused on the family of organotin(IV) compounds containing 2-[(dimethylamino)methyl]phenyl group (L^{CN}) or related ligands which reveal interesting structural properties^{5,6} and potential use⁷. We have reported on such class of diorganotin(IV) dihalides previously⁸⁻¹⁰. The aim of our present studies is to prepare tin(IV) bridged *ansa* metallocenes containing the mentioned C,N-chelating ligand(s). In this paper, we describe products of reactions of bis{2-[(dimethylamino)methyl]phenyl}tin(IV) dibromide¹¹⁻¹³ with two equivalents of cyclopentadienyl- or fluorenyllithium in THF.

RESULTS AND DISCUSSION

Synthetic Aspects

Two equivalents of cyclopentadienyllithium were added to one equivalent of diorganotin(IV) dibromide **1** in THF/diethyl ether mixture at $-50\text{ }^{\circ}\text{C}$ in order to prepare compound **2a** (Scheme 1). In the crude product, a small amount of unreacted $L^{CN}_2\text{SnBr}_2$ (**1**, $\delta(^{119}\text{Sn}) -262.2\text{ ppm}$), a trace of $L^{CN}_2\text{SnCpBr}$ (-154.0 ppm) and two major signals, one of desired product $L^{CN}_2\text{SnCp}_2$ (**2a**, -126.3 ppm) and **2** (-192.7 ppm), were detected and assigned by ^1H and ^{119}Sn NMR spectroscopy. The single crystals of **2** were obtained from toluene extract at $-20\text{ }^{\circ}\text{C}$. The compound **2a** of insufficient purity was obtained by reaction of two equivalents of NaCp with **1** in diethyl ether at room temperature, too.



SCHEME 1

Similar procedures and approaches to the Cp derivative were applied in the synthesis of fluorenyl (Fl) derivative of **1**¹⁴. Compound **3** was obtained as sole product of the reaction of **1** with one or two equivalents of FliLi in THF. Such reactivity of **1** with CpLi or FliLi in THF could be explained as an oxygen abstraction radical process from THF molecule in analogy to similar rhenium compounds recently published by Wilkinson¹⁵. The difference between the structure of reaction products is probably caused by sterical and/or electronic properties of CpLi and FliLi.

Structure of Compounds **2** and **3**

The molecular structures of **2** and **3** were determined by X-ray diffraction techniques (Figs 1 and 2). The selected distances and angles are collected in figure captions.

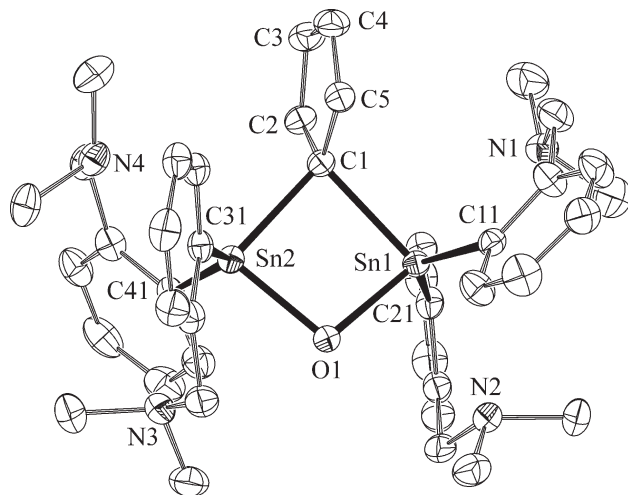


FIG. 1

The molecular structure of **2** (ORTEP, 40% probability level), hydrogen atoms are omitted for clarity. Selected interatomic distances (in Å) and angles (in °): Sn1–O1 2.012(2), Sn1–C11 2.138(3), Sn1–C21 2.146(3), Sn1–C1 2.246(3), Sn1–Sn2 3.0700(3), Sn1–N1 2.843(3), Sn1–N2 2.751(3), Sn2–O1 2.017(2), Sn2–C41 2.143(3), Sn2–C31 2.145(3), Sn2–C1 2.222(3), Sn2–N3 2.856(3), Sn2–N4 2.780(3), O1–Sn1–C11 103.82(11), O1–Sn1–C21 102.65(11), C11–Sn1–C21 138.54(13), O1–Sn1–C1 86.54(10), C11–Sn1–C1 104.89(12), C21–Sn1–C1 108.03(13), O1–Sn1–Sn2 40.42(6), O1–Sn2–C41 101.83(12), O1–Sn2–C31 103.01(11), C41–Sn2–C31 138.34(12), O1–Sn2–C1 87.08(10), C41–Sn2–C1 104.07(12), C31–Sn2–C1 110.08(12), Sn1–O1–Sn2 99.27(9), Sn2–C1–Sn1 86.79(11), N1–Sn1–N2 107.08(8), N3–Sn2–N4 102.98(9)

The tin atoms in **2** are pseudotetrahedrally (or better [4+2]) coordinated (Fig. 1), each of them by two carbons of L^{CN} groups, oxygen and the bridging carbon originated from $\mu\text{-}\eta^1\text{:}\eta^1\text{-}$ planar cyclopentadienyl moiety with localized conventional diene bonding. All nitrogen atoms interact only weakly (Sn–N ~ 2.8 Å) with the tin centre. On the other hand, the Sn1–Sn2 separation (3.0700(3) Å) is similar to the distance in gaseous hexamethyl-distannane(IV) (2.78 Å) usually taken as the distance typical of a single bond Sn–Sn or the sum of covalent radii of Sn₂. A structural study on some organotin(IV) compounds containing bridging σ -bonded Cp ring was already performed¹⁶ and, also, a compound of similar structural motif (e.g. [Re(NBu^t)₂($\eta^1\text{-C}_5\text{H}_5$)₂($\mu\text{-C}_5\text{H}_4$)($\mu\text{-O}$) is known¹⁵ but the Sn–C(Cp)–Sn and Sn–O–Sn angles are noticeably contracted from ~ 115 and $108.7(5)^\circ$, respectively, to $86.79(11)$ and $99.27(9)^\circ$ in **2**.

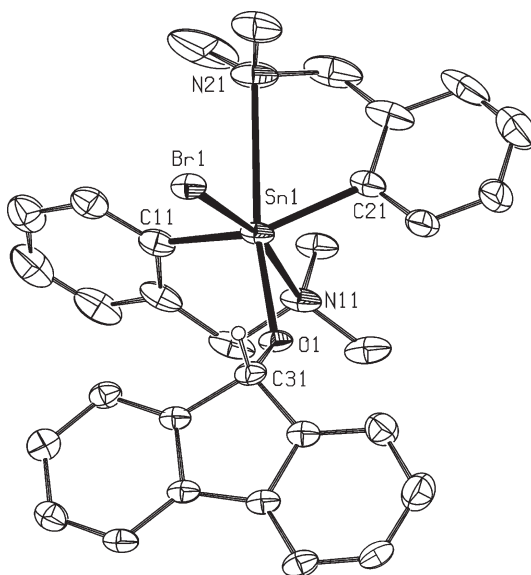


FIG. 2

The molecular structure of **3** (one of two independent molecules in asymmetric unit cell is shown, ORTEP, 40% probability level), hydrogen atoms are omitted for clarity. Selected interatomic distances (in Å) and angles (in $^\circ$): Sn1–O1 2.045(3), Sn1–C11 2.120(5), Sn1–C21 2.127(5), Sn1–N11 2.461(3), Sn1–Br1 2.6278(5), Sn1–N21 2.856(5), O1–Sn1–C11 104.99(16), O1–Sn1–C21 101.38(17), C11–Sn1–C21 146.57(18), O1–Sn1–N11 79.18(12), C11–Sn1–N11 76.05(17), C21–Sn1–N11 89.26(15), O1–Sn1–Br1 93.37(8), C11–Sn1–Br1 96.45(13), C21–Sn1–Br1 102.18(11), N11–Sn1–Br1 167.46(9), N21–Sn1–O1 169.33(14), N21–Sn1–C11 85.63(18), N21–Sn1–N11 105.04(15)

The asymmetric crystal unit cell of **3** contains two independent molecules which differ only slightly in some distances and angles. The geometry of **3** (Fig. 2) can be described in two different ways: (i) as a distorted tetragonal pyramid with carbon, bromine and nitrogen (N11) atoms laying in the base and oxygen atom in the vertex positions, and (ii) an octahedron with C11 and C21, N11 and Br1, and N21 and O1 in mutual pseudo *trans* positions, while the Sn–N11 distance is elongated to 2.856(5) Å, which is usually taken as a weak contact only.

All products were investigated by ^{119}Sn and ^1H NMR spectroscopy. The value of $\delta(^{119}\text{Sn})$ -192.7 ppm for **2** is typical for [4+2] or five-coordinated tin atoms in triorganotin(IV) compounds and thus comparable with the values for $(\text{L}^{\text{CN}}\text{Ph}_2\text{Sn})_2\text{O}$ (-173.2 ppm)¹⁷ and $\text{L}^{\text{CN}}\text{Ph}_2\text{SnX}$ (-176.9 ppm for $\text{X} = \text{Cl}$ and -181.7 ppm for $\text{X} = \text{Br}$)¹⁸. Both ^{119}Sn and ^1H NMR spectra for **2** revealed broad signals indicating a dynamic process. The ^1H NMR spectral pattern for **2a** ($\text{L}^{\text{CN}}_2\text{SnCp}_2$) reveals one set of broad signals for the ligand and a sharp signal with unresolved satellites for the Cp group at 6.11 ppm ($^1J(^{119}\text{Sn}, ^1\text{H}) = 26.3$ Hz) showing the σ -bonded Cp ring. Also the value of $\delta(^{119}\text{Sn})$ -126.3 ppm is typical of tetraorganotin compounds (-85.3 ppm for $\text{L}^{\text{CN}}_2\text{SnBu}_2$) and the spectral patterns are similar to $\text{L}^{\text{CN}}\text{SnPh}_2\text{Cp}$ ($-\delta(^{119}\text{Sn})$ -144.9 ppm and $\delta(^1\text{H}(\text{Cp}))$ -6.03 ppm ($^1J(^{119}\text{Sn}, ^1\text{H}) = 19.4$ Hz))¹⁷. For compound **3**, the ^1H and ^{119}Sn NMR spectra reveal similar patterns and shifts to those of **1** ($\delta(^{119}\text{Sn})$ -264.7 ppm for **3**, -252.8 ppm for $\text{L}^{\text{CN}}_2\text{SnCl}_2$, -271.2 ppm for $\text{L}^{\text{CN}}_2\text{SnBr}_2$ in CDCl_3 , -347.5 ppm for $\text{L}^{\text{CN}}_2\text{SnI}_2$) but the presence of the fluorenyl moiety, including the signal of proton at the middle ring at 4.72 ppm, is clearly visible. These similarities are due to the close structures in solution and even in the solid state.

EXPERIMENTAL

General Remarks

All experiments were carried out in argon atmosphere. Cyclopentadienyllithium, cyclopentadienylsodium, fluorene and butyllithium were obtained from commercial sources (Sigma–Aldrich). Toluene, benzene, *n*-hexane, *n*-pentane, diethyl ether and THF were dried over and distilled from sodium/potassium alloy, degassed and stored over potassium mirror. Compound **1** was prepared as published elsewhere⁸.

NMR Spectroscopy

The ^1H (500.13 MHz) and $^{119}\text{Sn}\{^1\text{H}\}$ (186.50 MHz) NMR spectra of the studied compounds in solution were measured on a Bruker Avance 500 spectrometer equipped with 5-mm probes with *z*-gradient at 298 K. The solutions were obtained by dissolving 20 mg of each

compound in 0.5 ml of deuterated solvents. The ^1H NMR chemical shifts (δ , ppm) are given relative to the signal of residual toluene (δ 2.09). The ^{119}Sn chemical shifts are referenced to external neat tetramethylstannane (δ 0.0). Positive chemical shifts values denote shifts to higher frequencies relative to the standards. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. The ^1H chemical shifts were assigned using standard gs (gradient selected)-H,H-COSY. Coupling constants (J) are given in Hz.

X-ray Crystallography

Single crystals of **2** and **3** were grown from ca. 5% diethyl ether solution at $-20\text{ }^\circ\text{C}$. Data for colorless crystals were collected at 150(2) K on a Nonius KappaCCD diffractometer using MoK α radiation ($\lambda = 0.71073\text{ \AA}$), a graphite monochromator, the structure was solved by direct methods (SIR92¹⁹). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97²⁰). Hydrogen atoms were mostly localized on a difference Fourier map; however, to ensure uniformity of treatment of all crystals, all hydrogens were recalculated in idealized positions (riding model) and assigned temperature factors $H_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{pivot atom})$ or of $1.5U_{\text{eq}}$ for the methyl moiety. Absorption corrections were carried on, using either multi-scans procedure (PLATON²¹ or SORTAV²²) or Gaussian integration from crystal shape (Coppens²³).

For **2**: Empirical formula $\text{C}_{41}\text{H}_{52}\text{N}_4\text{OSn}_2$; formula weight 854.25; crystal system monoclinic; space group $P21/n$; unit cell dimensions $a = 10.1930(2)\text{ \AA}$, $b = 25.2280(3)\text{ \AA}$, $c = 15.2310(3)\text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 99.5440(7)^\circ$, $\gamma = 90.00^\circ$; $V = 3862.42(12)\text{ \AA}^3$; $Z = 4$; $D_{\text{calc}} = 1.469\text{ Mg/m}^3$; absorption coefficient 1.329 mm^{-1} ; $F(000) = 1736$.

For **3**: Empirical formula $\text{C}_{31}\text{H}_{33}\text{BrN}_2\text{OSn}$; formula weight 648.19; crystal system triclinic; space group $P-1$; unit cell dimensions $a = 12.9210(5)\text{ \AA}$, $b = 13.8030(5)\text{ \AA}$, $c = 17.1170(4)\text{ \AA}$, $\alpha = 106.071(2)^\circ$, $\beta = 105.9110(19)^\circ$, $\gamma = 92.5850(18)^\circ$; $V = 2796.82(16)\text{ \AA}^3$; $Z = 1$; $D_{\text{calc}} = 1.539\text{ Mg/m}^3$; absorption coefficient 2.368 mm^{-1} ; $F(000) = 1304$.

CCDC 283558 (for **2**) and 283559 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

(μ -Cyclopentadienylidene)tetrakis{2-[(dimethylamino)methyl]phenyl}-(μ -oxo)ditin(IV) (**2**): A solution of CpLi (0.3 g, 4.16 mmol) in diethyl ether (30 ml) was added dropwise to $\text{L}^{\text{CN}}_2\text{SnBr}_2$ (1.14 g, 2.1 mmol) in THF (50 ml) at $-50\text{ }^\circ\text{C}$ in 30 min. The deep brown reaction mixture was stirred for additional 30 min, then warmed to $40\text{ }^\circ\text{C}$ and heated for additional 3 h. The resulting dark red solution was evaporated and the residue extracted with hot hexane ($2 \times 50\text{ ml}$) and filtered. The solvent from mother liquor was evaporated and the residue dissolved in diethyl ether (10 ml). Compound **2** crystallized as the sole product. White crystals, isolated yield 0.97 g (63%) based on **1**. M.p. $223\text{ }^\circ\text{C}$ (decomp.). ^1H NMR (500.13 MHz, toluene- d_8): 8.08 (bs, 4 H, H(6)); 7.41 (m, 8 H, H(4,5)); 7.25 (bs, 4 H, H(3)); 3.36 (bs, 8 H, NCH₂); 1.96 (s, 24 H, N(CH₃)₂); 6.27 (m, 2 H, Cp); 6.46 (m, 2 H, Cp). $^{119}\text{Sn}\{^1\text{H}\}$ NMR: -192.7 . For $\text{C}_{31}\text{H}_{33}\text{N}_2\text{OSn}$ (499.7) calculated: 50.69% C, 7.08% H, 7.63% N; found: 50.5% C, 7.2% H, 7.5% N.

Attempted synthesis of bis{2-[(dimethylamino)methyl]phenyl}di(η^1 -cyclopentadienyl)tin(IV) (**2a**): A solution of CpLi (0.44 g, 6.13 mmol) in diethyl ether (30 ml) was added dropwise to $\text{L}^{\text{CN}}_2\text{SnBr}_2$ (1.67 g, 3.06 mmol) in the same solvent (50 ml) at room temperature in 30 min.

The light-brown reaction mixture was stirred for additional 30 min, then the solvent was evaporated and the residue extracted with toluene (50 ml). After evaporation of toluene, a yellowish oil was obtained. All purification attempts failed. ^1H NMR (500.13 MHz, toluene- d_8): 8.00 (bs, 2 H, H(6)); 7.25–7.40 (m, 6 H, H(3,4,5)); 2.69 (bs, 4 H, NCH_2); 1.86 (s, 12 H, $\text{N}(\text{CH}_3)_2$); 6.11 ($^1J(^{119}\text{Sn}, ^1\text{H}) = 26.3$). $^{119}\text{Sn}\{^1\text{H}\}$ NMR: –126.3.

Bis-{2-[(dimethylamino)methyl]phenyl}(fluoren-9-olato)tin bromide (3): Similarly to **2**, FliI (0.84 g, 4.9 mmol) in diethyl ether (30 ml) was added dropwise to a solution of $\text{L}^{\text{CN}}_2\text{SnBr}_2$ (1.31 g, 2.4 mmol) in THF (30 ml) at -78°C within 10 min. The deep brown reaction mixture was stirred for additional 30 min, then warmed to room temperature and stirred overnight. The resulting orange solution was evaporated, the residue was extracted with toluene/diethyl ether mixture (1:1, 50 ml) and the extract was filtered. The solution was concentrated to 10 ml and hexane (5 ml) was added. Compound **3** crystallized after several days at -20°C . Yield 0.66 g (42%). M.p. 183–184 $^\circ\text{C}$. ^1H NMR (500.13 MHz, toluene- d_8 , 300 K): 8.55 (d, 2 H, H(6)), $^3J(^1\text{H}(5), ^1\text{H}(6)) = 7.79$, $^3J(^{119}\text{Sn}, ^1\text{H}) = 111.4$; 7.74 (d, 2 H, H(FI)), $^3J(^1\text{H}, ^1\text{H}) = 7.35$; 7.67 (d, 2 H, H(FI)), $^3J(^1\text{H}, ^1\text{H}) = 7.25$; 7.30–7.40 (m, 6 H, H(3,4,5)); 7.14 (m, 4 H, H(FI)); 4.72 (s, 1 H, H(FI)); 3.99 (d, 2 H, NCH_2), $^2J(^1\text{H}(\text{A}), ^1\text{H}(\text{X})) = 14.0$; 2.75 (d, 2 H, NCH_2), $^2J(^1\text{H}(\text{A}), ^1\text{H}(\text{X})) = 14.0$; 1.88 (bs, 12 H, $\text{N}(\text{CH}_3)_2$). $^{119}\text{Sn}\{^1\text{H}\}$ NMR: –264.7 ppm., For $\text{C}_{31}\text{H}_{33}\text{BrN}_2\text{OSn}$ calculated (647.6): 57.41% C, 5.09% H, 4.32% N; found: 57.3% C, 5.0% H, 4.4% N.

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