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Double O,C,O-chelated diorganotin(IV) derivatives

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Abstract

Novel diorganotin(IV) compounds $(L^{1,2})_2SnCl_2$, where $L^{1,2}$ are O,C,O-chelating ligands (called the pincer ligands), 2,6-bis(alkoxymethyl)phenyl-, $2,6\text{-}(ROCH_2)_2C_6H_3^-$, ($L^1$, R = Me, L^2, R = *t*-Bu), have been synthesized and characterized by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy, MS-ESI spectrometry and elemental analysis. The structure of both compounds $(L^1)_2SnCl_2$ (**1**) and $(L^2)_2SnCl_2$ (**2**) was determined by X-ray crystallography. Determination of crystal structures reveals different shapes of coordination polyhedra. While deformed octahedron was found for **1**, tetrahedral geometry of the tin atom was determined for **2**. The NMR spectroscopy indicates a similar structural arrangement of **1** and **2** in solution. The reaction of **1** with silver salts of low nucleophilic anions X^- (X = OTf and 1-$CB_{11}H_{12}$) resulted in $(L^1)_2SnCl(OTf)$ (**3**), $(L^1)_2Sn(OTf)_2$ (**4**), and $(L^1)_2SnCl(CB_{11}H_{12})$ (**5**). The compounds **4** and **5** are of ionic nature both in solid state and in solution of CH_3CN.

Keywords: Tin; NMR; Chelating ligand; X-ray structure

1. Introduction

The phenomenon of hypervalent or hypercoordinated organotin compounds is well known and such organotin compounds are interesting because of their unexpected structural aspects, biological activity and reactivity [1–4]. Introduction of Y,C,Y-chelating ligands (Y = donor atom) to organotin fragment is a possible way to achieve this hypercoordination. The first mention about organotin compounds with Y,C,Y-chelating ligand was published by van Koten in 1978 [5], where nitrogen donor atom was used for this purpose (Chart 1**A**) and these are studied so far.

On the other hand, only few examples of oxygen donor atom-containing ligands of Y,C,Y-type are known. In 1998, Jurkschat et al. reported synthesis of organotin compounds containing an O,C,O-pincer ligand (Chart 1**B**), in which the possibility of hypercoordination of the tin atom through Sn–O interaction has been demonstrated [6]. This information led us to synthesise different O,C,O-chelating ligands (Chart 1**C**) and their tetra-, tri-, di- and monoorganotin derivatives [7]. It has been published that the presence of Y,C,Y-ligands together with an appropriate polar group in triorganotin compounds led to preparation of hypercoordinated organotin cations having two strong Sn–Y interactions [5,8]. Chemistry of organotin(IV) cations [9] is of current interest playing an important role in cytotoxic activity of organotin compounds [10] or in catalytic applications involving organic reactions such as esterification [11]. While triorganotin cations, $[R_3SnY_2]^+$ (Y = donor atom), possessing pentacoordinated tin atoms have been known since the 1960s (triorganotin cations containing Y,C,Y-ligand also represent this type of compounds) [12], diorganotin(IV) dications of $(R_2SnY_4)^{2+}$ type have been isolated in limited number only [13]. This fact prompt us to prepare diorganotin compounds with two O,C,O-chelating ligands having thus four oxygen donor atoms for stabilization of such diorganotin(IV) dications $(R_2SnY_4)^{2+}$.

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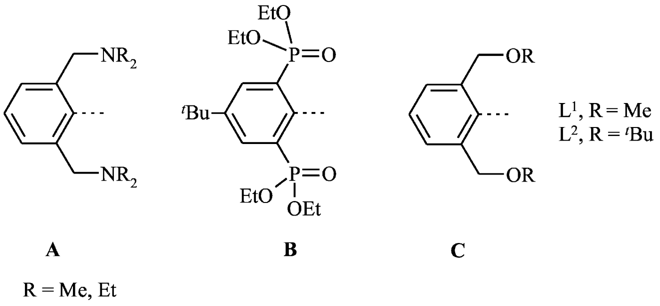

Chart 1.

This paper describes synthesis of diorganotin compounds $(L^{1-2})_2SnCl_2$ (**1 and 2**) with two O,C,O-chelating ligands 2,6-$[(CH_2OR)_2C_6H_3]^-$ (R = Me (**L**^{1}) and *t*-Bu (**L**^{2})) as well as reactivity of **1** towards silver salts of low nucleophilic anions X^- (X = OTf, $CB_{11}H_{12}$) leading to $(L^1)_2SnCl(OTf)$ (**3**), $(L^1)_2Sn(OTf)_2$ (**4**) and $(L^1)_2SnCl(CB_{11}H_{12})$ (**5**).

2. Experimental

2.1. General methods

Solvents were dried by standard methods and distilled prior to use. All moisture and air sensitive reactions were carried out in an argon atmosphere using standard Schlenk techniques. The reactions with silver salts were protected from light. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were acquired on Bruker Avance500 spectrometer in $CDCl_3$ (range 300–210 K). Appropriate chemical shifts were calibrated on: ^{1}H-residual peak of $CHCl_3$ ($\delta = 7.25$ ppm), ^{13}C-residual peak of $CHCl_3$ ($\delta = 77.23$ ppm), ^{119}Sn-external tetramethylstannane ($\delta = 0.00$ ppm). Electrospray mass spectra (ESI-MS) were recorded in positive mode on an Esquire3000 ion trap analyzer (Bruker Daltonics) in the range 100–600 *m*/*z* and in the negative mode on the Platform quadrupole analyzer in the range 100–800 *m*/*z*. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 1–10 μl/min. The IR spectra (cm^{-1}) were recorded on Perkin–Elmer 684 equipment as nujol suspensions or CH_3CN solutions. Starting compounds L^{1}Br and L^{2}Li were prepared according to the literature [7].

2.2. Crystallography studies

Colorless crystals were obtained from layering of *n*-hexane onto a dichloromethane solution of **1** and **2**. The single crystal of compounds of **1** and **2** were mounted on glass fibre with epoxy cement and measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. The crystallographic details are summarized in Table 1, The absorption correction was performed using a gaussian procedure from crystal shape [14a] or empirical absorption corrections (multiscan from symmetry-related measurements) [14b] for **1** and **2**, respectively. The structures were solved by the direct method (SIR-97) [15] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97) [16]. Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$(pivot atom), for the methyl moiety multiple of 1.5 was chosen. The final difference maps displayed no peaks of chemical significance.

Table 1
Crystal data and structure refinement for **1** and **2**

Compound	1	2
Empirical formula	$C_{20}H_{25}Cl_2O_4Sn$	$C_{32}H_{50}Cl_2O_4Sn$
Color	Colorless	Colorless
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a (Å)	14.4470(2)	16.767(2)
b (Å)	13.0060(2)	11.2190(9)
c (Å)	23.0760(3)	19.7580(19)
β (°)		110.468(5)
Z	8	4
μ (mm^{-1})	1.447	0.918
D_{calc} (Mg m^{-3})	1.593	1.313
Crystal size (mm)	0.35 × 0.075 × 0.02	0.3 × 0.3 × 0.15
Crystal shape	Bar	Prism
θ Range (°)	1–27.5	1–27.5
T_{min}, T_{max}	0.673, 0.938	0.735, 0.876
Number of reflections measured	71947	48792
Number of unique reflections, R_{int}	4969, 0.113	7962, 0.046
Number of observed reflections $[I > 2\sigma(I)]$	3462	6653
Number of parameters	248	364
S^a all data	1.071	1.060
Final R^b indices $[I > 2\sigma(I)]$	0.038	0.0295
wR_2^c indices (all data)	0.091	0.072
w_1/w_2^{d}	0.0415/3.0845	0.0310/2.2889
$\Delta\rho$ of maximum and minimum (e Å^{-3})	0.875 and −1.422	0.879 and −0.711

$R_{int} = S|F_o^2 - F_o^2(\text{mean})|/SF_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

[a–c] Definitions: $R(F) = \sum\|F_o| - \|F_c\|/\sum|F_o|$, $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2]^{1/2}$, $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{reflns} - N_{params})]^{1/2}$, Correction by SORTAV program.

[d] Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P] - 1$. $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

2.3. Synthesis of $(L^1)_2SnCl_2$ (*1*)

The 1 ml of hexane solution of BuLi (1.6 M, 1.6 mmol) was added to Et_2O (10 mL) solution of L^{1}Br (0.4 g, 1.6 mmol) at −78 °C and the solution stirred 2 h at this temperature. Then the toluene solution (20 ml) of $SnCl_4$ (0.21 g, 0.8 mmol) was added dropwise at −78 °C. The resulting suspension was stirred for 2 h at −78 °C, then for 5 days at room temperature. The solid was filtered off and the solvent was evaporated in vacuo. The residue was washed with pentane to afford **1** as a white solid. Yield: 0.40 g (95%); mp 125–128 °C. Anal. Calc.