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Coordination behaviour of the 2-(*N*,*N*-dimethylaminomethyl)phenyl ligand towards the di-t-butylchlorotin(IV) moiety

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{2-(*N*,*N*-Dimethylaminomethyl)phenyl}(di-t-butyl)tin(IV)chloride, {2-[$(CH_3)_2NCH_2]C_6H_4$}Sn(t-Bu)$_2$ Cl, has been prepared and characterized using NMR and crystallography. This is the first example of a triorganotin(IV) halide containing the 2-[$(CH_3)_2NCH_2]C_6H_4$—group as a C,N-chelating ligand with a weak intramolecular Sn—N interaction because of the steric hindrance of t-butyl groups. The interatomic Sn—N distance is elongated to 2.904(14) Å and the central tin atom is distorted trigonal bipyramidal. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: triorganotin(IV) compound; NMR; crystal structure; C,N-chelating ligand

INTRODUCTION

There are many examples of triorganotin(IV) compounds containing the 2-(*N*,*N*-dimethylaminomethyl)phenyl group as a C,N-chelating ligand. All such compounds show significant intramolecular contact between the tin and nitrogen. This coordination bond has been proven by means of crystallography[1] and ^{119}Sn CP-MAS NMR[2] techniques in the solid state, and recently by multinuclear magnetic resonance spectroscopy[3,4] in solution.

Here, we report the synthesis and structure of the triorganotin(IV) chloride **1** containing one 2-(*N*,*N*-dimethylaminomethyl)phenyl as a C,N-chelating ligand and two t-Bu groups. This is the first compound of this family without donor–acceptor connection of common strength.

RESULTS AND DISCUSSION

The coordination geometry of the tin atom in this compound is distorted trigonal bipyramidal ($\sum$C—Sn—C = 358.05(14)°). The distances between tin and the bonding partners in its primary coordination sphere lie in the typical range for triorganotin(IV) compounds. The Sn—N distance of 2.904(14) Å is significantly elongated in comparison with the distances of 12 known triorganotin(IV) compounds containing the title ligand (L). These distances were found in the narrow interval 2.42–2.55 Å, e.g.: LSnMe$_2$Cl,[5] 2.53 Å; LSnPh$_2$Cl,[6] 2.52 Å; LSnPh$_2$Br,[7] 2.51 Å; LSnMe$_2$F,[8] 2.49 Å; LSnPh$_2$F,[8] 2.53 Å. The magnitudes of interatomic C—Sn—C, C—Sn—Cl, and Cl—Sn—N angles show no noticeable change from previously observed ones (see Fig. 1 caption). The title compound has the largest observed torsion angle (C1—C2—C7—N: 43.2(3)°) in triorganotin LSnR$_2$X-type compounds, indicating the deviation of the ligand CH$_2$ group from the plane defined by the C1, tin, and nitrogen atoms. The tin atom is slightly deviated from the C1–C10–C14 plane (4.8°, 0.19 Å) facing the chlorine atom. We tested **1** by the structural-correlation method original given by Bürgi[9] and elaborated for tin compounds by Britton and Dunitz[10] that maps the pathway for the S$_N$2 reaction of triorganotin halides SnC$_3$XY with nucleophiles. In the case of **1**, the relevant geometrical data, i.e. the Sn—N and Sn—Cl bond lengths and the average C—Sn—Cl bond angle versus Sn—Cl bond length, match perfectly well with the theoretical curves deduced from crystallographic evidence.[10] On the other hand, the correlation of the average C—Sn—N bond angle versus Sn—N bond length show the major deviation from theoretical data.

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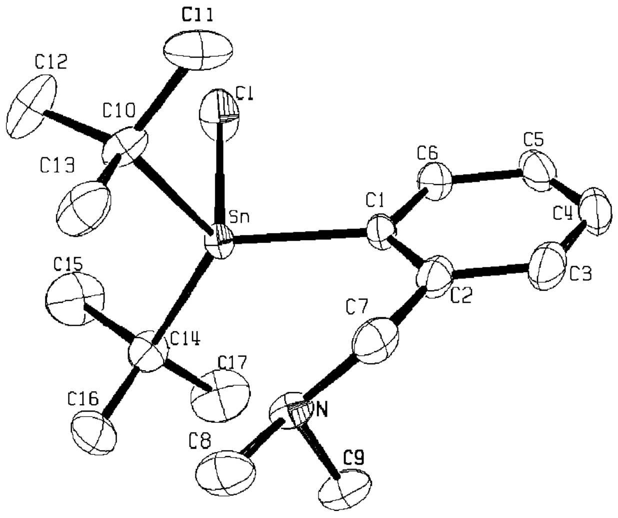

Figure 1. Molecular structure of compound **1** (ORTEP 40% probability level), hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn—Cl 2.4666(5), Sn—C1 2.1569(19), Sn—C10 2.190(2), Sn—C14 2.185(2), Sn—N 2.904(14), C1—Sn—C10 114.14(8), C10—Sn—C14 118.92(7), C1—Sn—C14 124.99(8), Cl—Sn—N 161.94(5), Cl—Sn—C1 93.59(8), Cl—Sn—C14 95.86(7), Cl—Sn—C10 94.40(7), C1—C2—C7—N 43.2(7).

Table 1. Selected NMR parameters for 1

	$\delta(^{119}Sn)$ (ppm)/ $[\delta(^1H)H6/NCH_2$ (ppm)]	
Solvent	300 K	220 K
Chloroform	18.5 [8.30/3.49]	1.4 [8.34/3.50]
Toluene	19.4 [8.59/3.13]	4.5 [8.87/2.90[a]]
Methanol	5.9[a] [8.05/3.58]	−3.7 [8.20/3.48]
Solid state	3.6	—

[a] Broad signal.

The structure of the compound studied in chloroform solution at 300 K has been established by various multinuclear magnetic resonance techniques. The resonances in the ^1H spectrum were assigned on the basis of common two-dimensional (2D) NMR techniques. The ^1H and ^{119}Sn NMR spectra in different solvents and at variable temperature (VT) were measured in order to detect previously described (e.g. ionization of compounds or weakening of the Sn—N bond) intramolecular processes.[3,4] The VT spectra were measured in the range 185–300 K. Toluene and chloroform (as non-coordinating solvents) and methanol (as a coordinating solvent) were selected for these purposes. The value of the ^{119}Sn NMR shift in chloroform solution at 300 K is 18.5 ppm. This value does not correlate with previously found chemical shifts ($LSn(n\text{-}Bu)_2Cl$, −51.7 ppm;[3] $LSn(n\text{-}Bu)_2F$, −77.1 ppm;[8] $LSn(t\text{-}Bu)_2F$, −92.1 ppm;[8] $LSnMe_2Cl$, −47.1 ppm (unpublished results); $LSnMe_2$,F −53.8 ppm;[8] L^*SnMe_2Br (L*: one benzylic hydrogen of the ligand is substituted by a methyl group), −55.7 ppm;[11] $LSn(n\text{-}Bu)_2Br$, −44.4 ppm[3]) for triorganotin halides with a strong Sn—N bond. Also, obtained the value is not in keeping with the values found for $[(t\text{-}Bu)_2PhSn]_2O$ (53.9 ppm)[12] and for $PhSnMe_2Cl$ (98.0 ppm),[13] the representatives of mixed dialkyl/aryl triorganotin compounds. The ^1H and ^{13}C NMR spectral patterns in the same conditions are similar to those published for analogs.[3,8] Both the ^1H and ^{119}Sn NMR spectra for all solvents and temperatures used reveal similar chemical shifts (see Table 1) and signal patterns as in chloroform at room temperature. The only exception found is in the case of toluene solution at low temperature: a broad signal for the NCH_2—group (upfield shifted −2.90 ppm) was observed at 220 K. This signal reveals a decoalescence at 192 K and is caused by independent hydrogen atoms (a similar type of CH_2N—geometry was found in the solid state). The $^3J(^1H(H6),^{119}Sn) \approx 52$ Hz and $^3J(^1H((CH_3)_3),^{119}Sn) \approx 84$ Hz coupling constants are very similar in all used solvents and temperatures and are typical for tetra- or triorganotin compounds with a weak intramolecular interaction.[1] This hypothesis is also supported by the value[14–16] of $^{3,6}J(^1H,(NCH_3),^{119}Sn) = 0.97$ Hz obtained from 2D $^1H,^{119}Sn$ J-HMBC spectra, measured in chloroform at 300 K, and the chemical shift of the central band (3.6 ppm) in the ^{119}Sn CP-MAS NMR spectra of single crystals of **1**. All spectral parameters are rather concentration independent.

From these findings we can conclude that the compound studied has a similar geometry in all solvents and at all temperatures, and in the solid state, i.e. strongly distorted trigonal bipyramidal with a significantly weaker intramolecular Sn—N interaction than for the rest of the known compounds of this type.

EXPERIMENTAL

2-[(*N*,*N*-Dimethylaminomethyl)phenyl]di-t-butylstannyl chloride (1)

The initial *N*,*N*-dimethylbenzylamine was *ortho*-lithiated using *n*-butyllithium in hexane solution. The organolithium salt (1.20 g, 8.4 mmol) that formed was filtered off, washed twice with pentane, suspended in benzene, added to a solution di-t-butyltin dichloride (2.50 g, 8.3 mmol) in benzene and stirred for 2 h. The reaction mixture was evaporated *in vacuo* and the crude product was washed with chloroform, filtered, the filtrate concentrated *in vacuo* and hexane added. The resulting solid was crystallized from a chloroform/hexane mixture (1 : 3). M.p. 99–101 °C, yield 2.77 g (84%).

^1H NMR ($CDCl_3$, 300 K, ppm): 7.15 (d, 1H, H3), 7.30 (m, 2H, H4 and H5), 8.30 (d, 1H, $^3J(^{117/119}Sn,^1H) = 51.7$ Hz, $^3J(^1H,^1H) = 7.2$ Hz, H6), 3.48 (s, 2H, NCH_2), 2.23 (s, 6H, $N(CH_3)_2$), 1.40 (s, 18H, $^3J(^{117/119}Sn,^1H) = 86.1$ Hz, $(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 300 K, ppm): 141.7, C1;

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143.8, $^{2}J(^{117/119}\text{Sn},^{13}\text{C}) = 42.8$ Hz, C2; 127.3, $^{3}J(^{117/119}\text{Sn},^{13}\text{C}) = 46.9$ Hz, C3; 128.8, $^{4}J(^{117/119}\text{Sn},^{13}\text{C}) = 12.2$ Hz, C4; 129.0, $^{3}J(^{117/119}\text{Sn},^{13}\text{C}) = 48.3$ Hz, C5; 139.0, $^{2}J(^{117/119}\text{Sn},^{13}\text{C}) = 26.6$ Hz, C6; 67.1, $^{n}J(^{117/119}\text{Sn},^{13}\text{C}) = 18.6$ Hz, NCH_2; 46.9, NCH_3; 39.2, $^{1}J(^{119}\text{Sn},^{13}\text{C}) = 422.4$ Hz, C10 and C14; 31.3, $^{2}J(^{117/119}\text{Sn},^{13}\text{C}) = 24.4$ Hz, C11–C13, C15–C17. ^{119}Sn NMR ($CDCl_3$, 300 K, ppm): 18.5.

Elemental analysis. Found: C, 50.7; H, 7.4; N, 3.5. Calc. for $C_{17}H_{30}ClNSn$ (402.54): C, 50.68; H, 7.45; N, 4.48%. The single crystals suitable for X-ray measurements were obtained from ~5% solution of **1** in diethyl ether at −30 °C.

NMR measurements

The solution-state ^{1}H (500.13 MHz), ^{13}C (125.76 MHz) and ^{119}Sn (186.50 MHz) NMR spectra of the compound studied were measured on a Bruker Avance500 spectrometer equipped with 5 mm broadband probe in the temperature range 185–300 K. The ^{1}H chemical shifts were calibrated relative to the signal of residual toluene ($\delta = 2.09$ ppm), $CHCl_3$ ($\delta = 7.25$ ppm) and methanol ($\delta = 3.31$ ppm), the ^{13}C on residual signal of chloroform ($\delta = 77.0$ ppm) and ^{119}Sn on external tetramethylstannane ($\delta = 0.00$ ppm). The 2D ^{1}H,^{119}Sn J-HMBC spectrum was recorded as explained elsewhere.[14–16]

The solid-state ^{119}Sn RAMP CP-MAS NMR spectra were measured at 300 K on a Bruker Avance500 spectrometer at 9 and 11 kHz. The $\delta(^{119}\text{Sn})$ were calibrated indirectly with reference to tetracyclohexyltin ($\delta = -97.35$ ppm).

Crystallography

Data for a colorless crystal were collected at 150(2) K on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The absorption correction was based on symmetry-related measurements (SORTAV).[17] The structure was solved by direct methods (SIR92[18]). All reflections were used in the refinement, which was based on F^2 (SHELXL97[19]). All hydrogen atoms were included in their idealized positions (riding model approximation) and assigned temperature factors $H_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ (pivot atom) or $1.5U_{\text{eq}}$ for the methyl moiety.

Crystallographic parameters for compound:

Formula: $C_{17}H_{30}ClNSn$; $M = 402.56$; crystal system: orthorhombic; space group: *Pbca*; $a = 15.4170(2)$ Å, $b = 14.7120(2)$ Å, $c = 16.8730(2)$ Å, $Z = 8$, $V = 3827.05(9)$ Å^3, $D_c = 1.397$ g cm^{-3}; dimensions: $0.2 \times 0.3 \times 0.3$ mm^3; $\mu = 1.468$ mm^{-1}; reflections measured: 52 681; independent reflections: 4373 ($R_{\text{int}} = 0.037$); reflections observed [$I > 2\sigma(I)$]: 3679; parameters refined: 189; S value: 1.08; $R(F$: 0.024 (obs. data); $wR(F^2)$: 0.064; $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$: 0.68, −0.74 e Å^{-3}.

A full list of crystallographic data and parameters, including fractional coordinates, is deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk]. CCDC deposition number: 225190.

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