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Structure and properties of double-*C*,*N*-chelated tri- and diorganotin(IV) halides

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Tri- and di-organotin(IV) compounds containing one or two 2-(dimethylaminomethyl)phenyl- (L^{CN}) groups as chelating ligands were prepared by reactions of lithium compound $L^{CN}Li$ with an appropriate amount of (organo)tin halide. The geometry of tin in 1 ($(L^{CN})_2SnPhCl$) is on the boundary between octahedral and trigonal bipyramidal. The diorganotin compounds 2–4 ($(L^{CN})_2SnX_2$, where X = Cl, Br, I) have a distorted octahedral geometry in the solid state and show dynamic processes in solution with a lowering of activation energy of the dynamic process going from diiodide to dichloride derivative. Compound 5 ($L^{CN}SnPhCl_2$) has a trigonal bipyramidal structure with non-equivalent chlorine atoms. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: organotin(IV) compounds; *C*,*N*-ligand; structure

INTRODUCTION

The family of organotin(IV) compounds containing the 2-(dimethylaminomethyl)phenyl- group or related ligands reveal interesting structural properties[1,2] and potential uses.[3] Although the first papers from the area of hypercoordinated organotin compounds can be found in the, the number of compounds containing two or more chelating ligands, especially the 2-(dimethylaminomethyl)phenyl- group (L^{CN}), is rather limited. These reports dealt mainly with the VT ^1H NMR structural study of $(L^{CN})_2SnMe_2$,[4] $(L^{CN})_2SnMeBr$[5] and $(L^{CN})_2SnBr_2$.[6] Later reports give a more detailed study of NMR parameters of the nuclei directly involved in the C_3NSn chelate ring of $(L^{CN})_2SnBu_2$, $(L^{CN})_2SnBuCl$ and $(L^{CN})_2SnBr_2$.[7,8] On the basis of these reports one can predict the coordination geometry of the tin atom as trigonal bipyramidal with only one amine donor group bonded to the tin centre (rapid exchange) (Fig. 1A) in the case of tetra- and tri-organotin compounds, and octahedral geometry with both donor groups bound mutually in cis positions and organyl groups bound in trans positions for the diorganotin compound $(L^{CN})_2SnBr_2$ (Fig. 1B).

On the other hand, there are only three papers concerned with the solid-state structure determination of the class of organotin(II or IV) compounds containing two or more L^{CN} ligands. The first reported compound[9] is $(L^{CN})_2Sn^{II}$, the second and third are its adducts with $W(CO)_5$[10] and $Co(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2H_2)$[9] fragments respectively. The coordination geometry about tin atoms in these compounds is distorted ψ-trigonal bipyramidal with two carbon atoms and the lone electron pair in equatorial positions and nitrogen atoms in axial positions. The last example of a crystallographically determined structure containing four L^{CN} ligands is the tetraorganotin compound $(L^{CN})_4Sn$,[11] where the tin central atom is four-coordinated (distorted tetrahedron); no attack of donor groups has been observed. To the best of our knowledge, there is no crystal structure determination of a diorganotin compound containing an L^{CN} moiety.

For our study, we have selected one triorganotin compound ($(L^{CN})_2SnPhCl$ (**1**)) and four diorganotin compounds ($(L^{CN})_2SnCl_2$ (**2**), $(L^{CN})_2SnBr_2$ (**3**),[6,7] $(L^{CN})_2SnI_2$ (**4**), and

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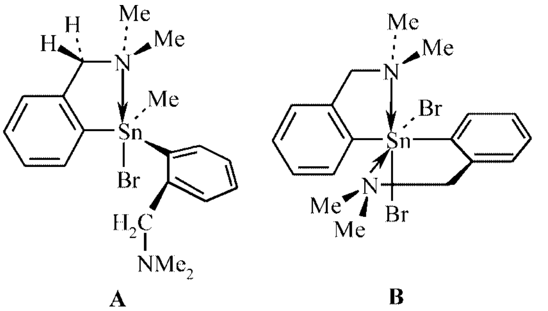


Figure 1. Proposed structure of tri- and di-organotin compounds containing two *C*,*N*-chelating ligands.

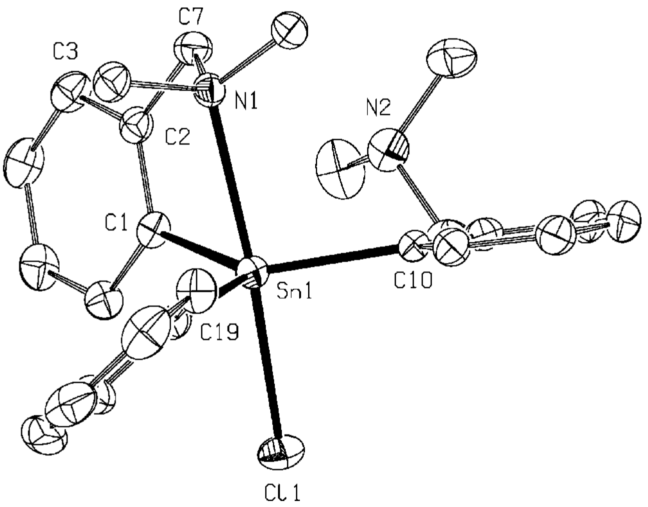


Figure 2. The molecular structure of **1** (one of the two conformers in the asymmetric unit cell is shown, ORTEP, 50% probability level); hydrogen atoms are omitted for clarity.

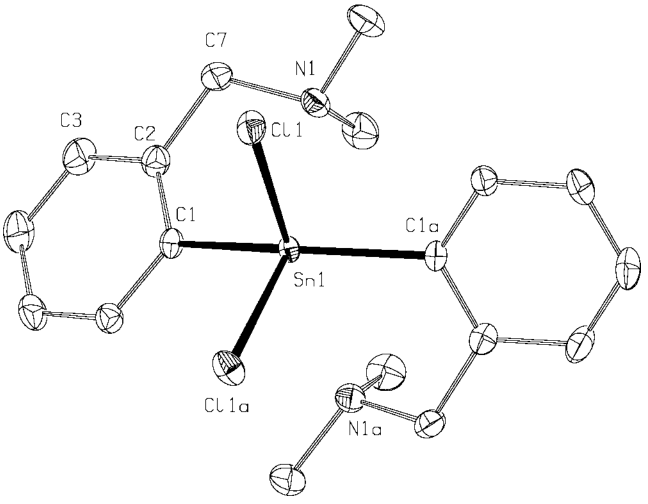


Figure 3. The molecular structure of **2** (ORTEP, 50% probability level); hydrogen atoms are omitted for clarity.

$\mathrm{L^{CN}SnPhCl_2}$ (**5**)).[6] Compound **5** has been made to confront the structure and behaviour of diorganotin compounds bearing one and two possible chelating ligands. The structure of these compounds was studied by diffraction methods (**1**, **2**, **4**, **5**) and NMR techniques.

RESULTS AND DISCUSSION

Synthesis of 1–5

Two similar synthetic procedures leading to **5** (from $\mathrm{L^{CN}{}_4Cu_4}$ and $\mathrm{PhSnCl_3}$)[6] and **3** (from $\mathrm{L^{CN}{}_4Cu_4}$[6] or $\mathrm{L^{CN}Li}$[7] and 0.5 equivalents of $\mathrm{SnBr_4}$) have been already reported. All compounds studied (**1**–**5**) were obtained by conversion of the lithium salt $\mathrm{L^{CN}Li}$ with an appropriate amount of (organo)tin(IV) halide in satisfactory yield and purity. In the case of **1**, only a poor yield was obtained after 15 min of stirring the reaction mixture ($\mathrm{L^{CN}Li}$ and $\mathrm{PhSnCl_3}$ 2 : 1) at room temperature. The products of this reaction were identified from the crude material with the help of $^{119}\mathrm{Sn}$ NMR spectroscopy in $\mathrm{CDCl_3}$ ($\mathrm{L^{CN}{}_2SnCl_2}$ ($\delta = -254.6$ ppm, 52%); $\mathrm{L^{CN}{}_2SnPhCl}$ ($\delta = -186.0$ ppm, 18%); $\mathrm{L^{CN}SnPh_2Cl}$[12] ($\delta = -176.7$ ppm, 22%); $\mathrm{L^{CN}SnCl_3}$ ($\delta = -271.2$ ppm, 8%)[13]). Surprisingly, no trace of **5** was detected. When the reaction time was prolonged to 5 days and the temperature elevated to 60 °C in an optimized attempt, **1** was observed in sufficient yield (72%) after crystallization from a dichlormethane–pentane mixture. Similarly, in the reaction leading to **5**, compound **2** was detected as a by-product in about 10% yield. It is obvious that a couple of phenyl group migrations[14] ($\mathrm{L^{CN}}$ ligand without N–Sn connection should be taken here as a substituted phenyl) occurred during these procedures. Compound **2**, presumably with a six-coordinated tin atom, seems to be the most stable species.

Structure of 1–5

The molecular structures of **1**, **2**, **4**, and **5** were determined via X-ray diffraction techniques (Figs 2–5). Selected distances and angles are collected in Table 1.

The asymmetric crystal unit cell of **1** contains two independent molecules (conformers), which differ slightly in some distances and angles (see Table 1 and Fig. 2). The geometry of **1** can be described in two different ways: (i) as a distorted trigonal bipyramid typical for triorganotin compounds containing a *C*,*N*-chelating ligand[1] with carbon atoms in equatorial positions and both atoms of chlorine and nitrogen from the coordinated arm in axial positions, while the non-coordinated nitrogen atom is out of the tin coordination sphere; (ii) octahedral, with C1 and C10, N1 and Cl1, and N2 and C19 in mutual pseudo trans positions. The Sn–N1 distances in **1** (2.4752(17) and 2.5345(18) Å), as well as the remaining geometry parameters, are comparable to those found for analogous bis[8-(dimethylamino)-1-naphthyl]methyltin iodide,[15] the geometry of which has been described as octahedral.

Table 1. Selected structural parameters (distances (Å), angles (°)) of **1**, **2**, **4** and **5**

	1 X1 = Cl1 X2 = C19	**1′** X1 = Cl1 X2 = C19	**2** X1 = Cl1 X2 = Cl2	**4** X1 = I1 X2 = I2	**5** X1 = Cl1 X2 = Cl2
Sn1–X1	2.5196(5)	2.5035(6)	2.4390(3)	2.8647(3)	2.4481(11)
Sn1–X2	2.151(2)	2.152(2)	2.4390(3)	2.8468(3)	2.3547(11)
Sn1–C10	2.152(2)	2.155(2)	2.1265(13)[a]	2.127(3)	2.1076(12)
Sn1–C1	2.133(2)	2.136(2)	2.1265(13)	2.131(3)	2.143(7)
Sn1–N1	2.4752(17)	2.5345(18)	2.6179(13)	2.537(2)	2.444(5)
Sn1–N2	3.5174(19)	3.2736(19)	2.6179(13)[b]	2.648(2)	w
X1–Sn1–X2	93.63(6)	94.58(6)	89.794(18)	88.807(8)	96.15(5)
X1–Sn1–C10	92.73(6)	95.68(6)	101.86(4)[a]	95.11(7)	96.30(9)
X2–Sn1–C10	113.86(8)	115.28(8)	97.56(4)[a]	99.82(8)	106.00(9)
X1–Sn1–C1	94.45(6)	95.10(6)	97.56(4)	99.81(8)	94.3(2)
X2–Sn1–C1	114.28(8)	108.05(8)	101.86(4)	96.62(8)	112.2(2)
C10–Sn1–C1	130.66(8)	134.15(8)	152.47(7)[a]	157.98(11)	138.88(17)
X1–Sn1–N1	169.76(4)	168.60(5)	166.30(3)	170.41(6)	168.15(12)
X2–Sn1–N1	92.19(7)	92.48(7)	81.75(3)	84.04(6)	87.83(12)
C10–Sn1–N1	92.61(7)	89.35(7)	89.98(6)	92.41(9)	93.31(16)
C1–Sn1–N1	75.46(7)	74.18(7)	73.87(5)	74.77(10)	73.9(2)
X1–Sn1–N2	95.82(3)	178.97(7)	81.75(3)[b]	84.27(5)	—
X2–Sn1–N2	169.97(6)	86.42(4)	166.30(3)[b]	169.59(5)	—
C10–Sn1–N2	62.39(6)	72.05(6)	89.98(6)[b]	73.17(9)	—
C1–Sn1–N2	68.33(6)	64.36(7)	73.87(5)[b]	92.23(9)	—
N1–Sn1–N2	78.69(5)	86.56(6)	108.47(4)[b]	103.65(7)	—

[a] C10 is C1a.

[b] N2 is N1a, where a is: x, y, z; $-x, y, -z + 1/2$; $x + 1/2, y + 1/2, z$; $-x + 1/2, y + 1/2, -z + 1/2$; $-x, -y, -z$; $x, -y, z - 1/2$; $-x + 1/2, -y + 1/2, -z$; $x + 1/2, -y + 1/2, z - 1/2$.

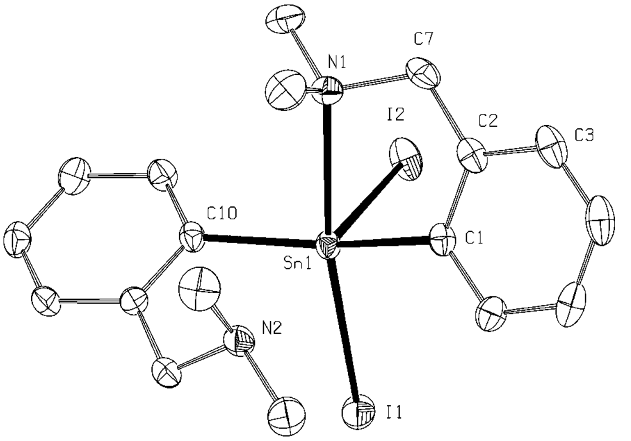


Figure 4. The molecular structure of **4** (ORTEP, 50% probability level); hydrogen atoms are omitted for clarity.

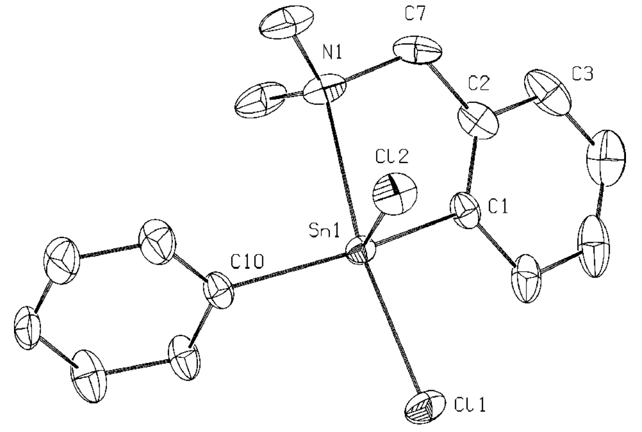
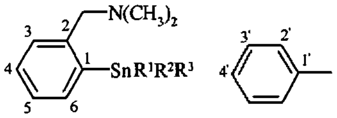


Figure 5. The molecular structure of **5** (ORTEP, 30% probability level); hydrogen atoms are omitted for clarity.

The variations in interatomic distances and angles in **1** and the naphthyl analogue are probably caused by differences in the rigidity of the ligands. The torsion angles (Φ(C1, C2, C7, N)) indicating the deviation of nitrogen donor atom from the plane of the parent aromatic ring are significantly higher (36.8° for N1a, 59.3° for N2a, 30.8° for N1b, and 68.5° for N2b) than in the rest of the known *C*,*N*-chelated triorganotin compounds (20–33°).[16] The differences in the C_{ligand}–Sn–C_{ligand} angles (130.66(8) and 134.15(8)° for the two different molecules in the unit cell of **1** and 140.0° for the naphthyl analogue) deviated considerably from the ideal octahedral value of 180°; and there is a significant elongation of the Sn–N2 distance in **1** (3.5174(19) and 3.2736(19) Å) compared with the naphthyl

Compound	R^1	R^2	R^3
1	L^{CN}	Ph	Cl
2	L^{CN}	Cl	Cl
3	L^{CN}	Br	Br
4	L^{CN}	I	I
5	Ph	Cl	Cl



Scheme 1.

analogue (3.10(1) Å) and the diphenyltin dichloride pyrazine complex (2.965(11) Å), the longest Sn–N bond length so far, that has been ascribed to Sn–N coordination.[17] This leads us to describe the geometry of the first molecule of **1** more likely as distorted octahedral, similar to the naphthyl analogue, and distorted trigonal bipyramidal for the second molecule. We tested **1** by the structural-correlation method originally given by Bürgi[18] and elaborated for tin compounds by Britton and Dunitz.[19] This maps the pathways for the S_N2 reaction of triorganotin halides SnC_3XY and S_N3 and $(S_N2)^2$ reactions of diorganotin $SnC_2X_2Y_2$ ensembles having *C,C*-transoid arrangement 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 and C–Sn–N or C–Sn–C bond angles, do not match well with the theoretical curves deduced from crystallographic evidence.[19] The real geometry of both molecules of **1** is on the boundary between octahedral and trigonal bipyramidal extremes.

The tin atoms in **2** and **4** are pseudo octahedrally coordinated as a result of the *C,N*-chelate bonding of two L^{CN} groups and two cis-bonded halides. The C1 and C10 atoms are mutually in trans positions and the coordinated nitrogen atoms are bonded in cis fashion (Figs 3 and 4, Table 1). The molecular structures of **2** and **4** reveal some very close similarities to the previously described bis[8-(dimethylamino)-1-naphthyl]methyltin iodide,[15] bis[8-(dimethylamino)-1-naphthyl]tin dibromide,[20] and quinoline-substituted dialkyltin dihalides.[21] The main deviations from the ideal octahedral geometry are the C–Sn–C (152.47(7)° for **2** and 157.97(11)° for **4**; ideal 180°) and N–Sn–N angles (108.47(4)° for **2** and 103.65(7)° for **4**; ideal 90°). The Sn–N distances are even longer (2.6179(13) for **2**; 2.537(2) and 2.648(2) Å for **4**) than found for triorganotin *C,N*-chelated compounds (~2.5 Å)[16] and **1** (coordinated arms). The average value of this parameter for chloride (**2**) and is greater than for iodide (**4**). On the other hand, these values, the values for the tin–halide distance and the appropriate angles match perfectly well with the theoretical curves deduced from crystallographic evidence for $SnC_2X_2Y_2$ ensembles having a *C,C*-transoid arrangement.[19] The values of the Φ angles are in line with previous findings (32.7° for **2**, 29.0° for N1 and 26.4° for N2 in **4**). The angles between the planes of aromatic rings (Ψ) are 37.7° for **2** and 40.4° for **4**.

The molecular structure determination of compound **5** (Fig. 5, Table 1) confirmed the prediction of a distorted trigonal bipyramidal structure with organic groups and one of the halides in the equatorial and second halide and nitrogen donor in axial positions previously predicted by van Koten *et al.*[22] The nitrogen atom is more strongly bonded to tin than in the corresponding diorganotin dihalides **2** and **4**. The Sn–N bond distance (2.444(5) Å) is comparable to the same type distances in triorganotin compounds having this or similar types of ligand[16] and **1**. The expected differences in Sn–Cl bond lengths (2.4481(11) and 2.3547(11) Å) were observed. This longer distance belonging to the chlorine atom in trans position to nitrogen is a bit shorter than in **1** (2.5196(5) and 2.5035(6) Å) and comparable to the same type distance in **2** (2.4390(3) Å). The interatomic angles N1–Sn–Cl1 and Cl1–Sn–Cl2 are similar to similar types of angle found previously for *C,N*-chelated triorganotin compounds.[1] This is caused by a significant electronic influence of the equatorial Cl2 atom (Sn–Cl2 distance is very close to the sum of the van der Waals' radii).[23]

The structure of **1** in chloroform and toluene solution was studied by NMR techniques in the temperature range 220–330 K. The ^{119}Sn NMR spectra reveal a singlet resonance with chemical shifts (−185.7 ppm) comparable to the five-coordinated triorganotin analogue containing only one *C,N*-chelating ligand $L^{CN}SnPh_2Cl$ (−176.2 ppm)[12] in both solvents and over the whole temperature range. The ^{1}H NMR spectra in toluene reveal similar patterns to those previously reported for $(L^{CN})_2SnMeBr$,[5] i.e. two AB patterns for methylene protons and one doublet and one singlet resonance in integral ratio (1 : 1) for NMe_2 groups at lower temperature (below 305 K), thus indicating a structure with only one coordinated nitrogen donor atom and rapid exchange of donor atoms on the NMR time scale at higher temperature (Fig. 1A). The spectra in chloroform have similar decoalescence trends, but the activation energy of the exchange process should be lower, because the pattern of the spectrum at 295 K reveals that only broadening of the signals for the CH_2 and CH_3 groups was detected and also the spectrum at 225 K reveals four broad signals for methylene and two broad singlets for methyl protons.

The values of $\delta(^{119}Sn)$ for **2**–**4** are typical for a [4 + 2] coordinated tin atom and comparable in terms of trend observed and $\delta(^{119}Sn)$ values (−252.8 ppm for **2**, −271.2 ppm for **3** and −347.5 ppm for **4**) to a series of quinoline-substituted dialkyltin dihalides (−248.2 ppm for Cl, −302.3 ppm for Br and −434.2 ppm for I analogues) reported recently.[21] The values of $\delta(^{119}Sn)$ for **2**–**4** in chloroform changed only slightly (1–5 ppm) in the temperature range 190–330 K from the values obtained at room temperature. On the other hand, **2** and **4** in chloroform reveal similar ^{1}H spectral patterns to **3**, which was previously described by van Koten *et al*,[4] i.e. an AB pattern for NCH_2 groups and two singlets for $N(CH_3)_2$ groups at lower temperature. Although the strong broadening appeared for NCH_2 signals (resolved below 310 K for **2**, 320 K for **3** and 275 K for **4**), no coalescence was observed at 330 K (the highest temperature measured). The differences in signals frequency are 410 Hz for **2**, 462 Hz for **3** and 558 Hz for **4**. The coalescence temperature for $N(CH_3)_2$ groups is much lower (297 K for **2**, 287 K for **3** and 274 K for **4**) than for benzylic protons. All aromatic protons become broad without decoalescence at lower temperatures. The previously calculated[7] C1–Sn–C10 angle for **3** (from $^1J(^{119}Sn, ^{13}C)$), i.e. 152°, is similar to the analogous angles found in the solid state for **2** and **4**. These observations support the premise that **2**–**4** have similar structures both in solution and the solid state (for a description see above).

The NMR study for compound **5**, including the study of adduct of **5** with pyridine, has already been done.[6] The ^1H and ^{119}Sn NMR spectra reveal only minimal changes in chemical shifts going from toluene[6] to chloroform (see Experimental section).

The values of the chemical shifts in the ^{13}C NMR spectra for **1**, **2**, **4** and **5** are similar to previously published analogous compounds,[7,12] but the broadening of the signals and the lower solubility of compounds studied means that no additional information about the structure was obtained.

The structures and the purity of the compounds studied were confirmed by electrospray ionization (ESI) mass spectrometry (MS) in the positive-ion mode. In the early studies of organotin compounds[24] the typical feature of the ESI mass spectra is the cleavage of the most labile bond in the molecules to yield two complementary ions, where the cationic part of the molecule can be measured in the positive-ion mode and the anionic part in the negative-ion mode. When the tin–halogen bond was present in the structure the bond was primarily cleaved and $[M - halogen]^+$ ions were observed in the positive-ion mode ESI mass spectra. A different situation was mainly observed in the case of the diorganotin compounds with two L^{CN} ligands. Compounds **2** and **3** reveal an isotopic cluster centre at $m/z = 522$ belonging to the $[(L^{CN})_3Sn]^+$ species; on the other hand, in the spectrum of **4** the $[M - halogen]^+$ signal was observed as a major product of fragmentation.

CONCLUDING REMARKS

Tri- and di-organotin(IV) compounds containing one or two L^{CN} chelating ligands were prepared by reactions of the lithium compound $L^{CN}Li$ with an appropriate amount of (organo)tin halide. The geometry of tin in **1** can be described as on the boundary between octahedral and trigonal bipyramidal. The diorganotin compounds **2**–**4** have a distorted octahedron structure in the solid state and show a dynamic process in solution with a lowering of the activation energy of the dynamic process on going from the diiodide (**4**) to the dichloride derivative (**2**). Compound **5** has a trigonal bipyramidal structure with non-equivalent chlorine atoms.

EXPERIMENTAL

General remarks

All experiments were carried out in an argon atmosphere. (*N*,*N*-Dimethylaminomethyl)benzene, *n*-butyllithium, phenyltin(IV) trichloride, tin(IV) chloride, bromide and iodide were obtained from commercial sources (Sigma–Aldrich). Toluene, benzene, *n*-hexane and *n*-pentane were dried over and distilled from potassium alloy, degassed and stored over a potassium mirror. Chloroform and dichloromethane were dried over and distilled from P_2O_5 and CaH_2.

Bis-{2-[(*N*,*N*-dimethylaminomethyl)phenyl]} phenyltin chloride (1)

To a solution of 2.66 g of phenyltin(IV) trichloride (8.8 mmol) in 30 ml of benzene was dropwise added 2.5 g of $(L^{CN})Li$ (17.6 mmol) in 50 ml of benzene in 30 min at room temperature. The reaction mixture was stirred for an additional 30 min and then filtration of the resulting LiCl was carried out in air. The filtrate was concentrated *in vacuo* to 5 ml and hexane was added to provide a white solid, which was recrystallized from mixture of dichloromethane and pentane. Yield: 1.68 g (38.4%). M.p.: 123–125 °C. ^1H NMR (500.13 MHz, $CDCl_3$, 300 K, ppm): 8.15 (bs, 2H, H(6)), 7.41 (m, 4H, H(4,5)), 7.17 (bs, 2H, H(3)), 3.68 (bs, 4H, NCH_2), 1.96 (s, 12H, $N(CH_3)_2$), 7.67 (d, 2H, H(2′), $^3J(^1H(2'), ^1H(3')) = 9.8$ Hz), 7.36 (m, 3H, H(3′, 4′)). ^{13}C NMR: 141.0 (C(1), $^1J(^{119}Sn, ^{13}C = 865.9$ Hz)), 143.9 (C(2), broad signal), 129.0 (C(4), $^4J(^{119}Sn, ^{13}C = 14.8$ Hz)), 128.5 (C(3), $^3J(^{119}Sn, ^{13}C = 60.1$ Hz)), 127.2 (C(5), $^3J(^{119}Sn, ^{13}C = 76.0$ Hz)), 136.6 (C(6); $^2J(^{119}Sn, ^{13}C = 47.9$ Hz)), 65.6 (C(7), $^nJ(^{119}Sn, ^{13}C = 29.3$ Hz)), 46.0 (C(8)), 144.5 (C(1′), broad signal), 142.8 (C(2′), $^2J(^{119}Sn, ^{13}C = 42.3$ Hz)), 128.9 (C(3′), $^3J(^{119}Sn, ^{13}C = 69.5$ Hz)), 128.7 (C(4′), $^4J(^{119}Sn, ^{13}C = 12.2$ Hz)). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −185.67. ESI-MS: molecular weight (MW) = 500. MS: m/z 465, $[M - Cl]^+$, 100%. Elemental analysis (%). Found: C, 57.62; H, 5.73; N, 5.55. Calc. for $C_{24}H_{29}ClN_2Sn$ (499.66): C, 57.69; H, 5.85; N, 5.61.

Bis-{2[(*N*,*N*-dimethylaminomethyl)phenyl]}tin dichloride (2)

To a solution of 1.6 g of $SnCl_4$ (6 mmol) in 30 ml of benzene was dropwise added 1.7 g of $(L^{CN})Li$ (12.1 mmol) in 30 ml of benzene over 1 h at room temperature. The reaction mixture was stirred for 48 h, and then filtration of the resulting LiCl was carried out. The filtrate was concentrated *in vacuo* to 80% and hexane was added to provide a white precipitate of crude product, which was purified using pentane. Yield: 1.43 g (52%). M.p.: 251–255 °C. ^1H NMR (500.13 MHz, $CDCl_3$, 300 K, ppm): 8.19 (d, 2H, H(6), $^3J(^1H(5), ^1H(6)) = 6.7$ Hz, $^3J(^{119}Sn, ^1H) = 107.1$ Hz), 7.41 (m, 4H, H(4,5)), 7.18 (d, 2H, H(3), $^3J(^1H(4), ^1H(3)) = 7.2$ Hz), 4.07 (d, 2H, NCH_2, $^2J(^1H(A), ^1H(X)) = 14.0$ Hz), 3.37 (d, 2H, NCH_2, $^2J(^1H(A), ^1H(X)) = 14.0$ Hz), 2.24 (bs, 12H, $N(CH_3)_2$). ^{13}C NMR: 140.7 (C(1)), broad signal), 140.8 (C(2), $^2J(^{119}Sn, ^{13}C = 58.3$ Hz)), 130.2 (C(4), $^4J(^{119}Sn, ^{13}C =$

23.8 Hz)), 128.1 (C(3), $^3J(^{119}\text{Sn}, ^{13}\text{C} = 92.1\ \text{Hz})$), 129.2 (C(5), $^3J(^{119}\text{Sn}, ^{13}\text{C} = 102.0\ \text{Hz})$), 135.3 (C(6), $^2J(^{119}\text{Sn}, ^{13}\text{C} = 61.3\ \text{Hz})$), 63.6 (C(7), $^nJ(^{119}\text{Sn}, ^{13}\text{C} = 43.1\ \text{Hz})$), 43.7 (C(8), broad signal). $^{119}\text{Sn}\{^1\text{H}\}$ NMR ($CDCl_3$, 300 K, ppm): −252.84. ESI-MS: MW = 458. MS: *m/z* 522, $[(\text{L}^{\text{CN}})_3\text{Sn}]^+$, 100%; *m/z* 459, $[\text{M} + \text{H}]^+$, 6%; *m/z* 423, $[\text{M} - \text{Cl}]^+$, 18%; *m/z* 136, $[\text{HL}^{\text{CN}} + \text{H}]^+$, 20%; *m/z* 91, $[C_6H_5CH_2]^+$, 4%. Elemental analysis (%). Found: C, 46.98; H, 5.17; N, 6.21. Calc. for $C_{18}H_{24}Cl_2N_2Sn$ (458): C, 47.21; H, 5.28; N, 6.12.

Bis-{2-[(*N*,*N*-dimethylaminomethyl)phenyl]}tin dibromide (3)[7]

ESI-MS: MW = 546. MS: *m/z* 522, $[(\text{L}^{\text{CN}})_3\text{Sn}]^+$, 100%; *m/z* 467, $[\text{M} - \text{Br}]^+$, 8%.

Bis-{2-[(*N*,*N*-dimethylaminomethyl)phenyl]}tin diiodide (4)

As for **2**, to a solution of 2 g of SnI_4 (3.2 mmol) in 30 ml of benzene was dropwise added 0.9 g of $(\text{L}^{\text{CN}})\text{Li}$ (6.4 mmol) in 30 ml of benzene. Yield: 0.86 g (42%). M.p.: 258–262 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, 300 K, ppm): 8.18 (d, 2H, H(6), $^3J(^1H(5), ^1\text{H}(6)) = 7.75$ Hz, $^3J(^{119}\text{Sn}, ^1\text{H}) = 112.9$ Hz), 7.47 (t, 2H, H(4), $^3J(^1\text{H}(5), ^1\text{H}(4)) = 7.4$ Hz), 7.37 (t, 2H, H(5), $^3J(^1\text{H}(4), ^1\text{H}(5)) = 7.4$ Hz), 7.14 (t, 2H, H(3), $^3J(^1\text{H}(4), ^1\text{H}(3)) = 7.2$ Hz), 4.17 (bs, 2H, NCH_2), 3.21 (bs, 2H, NCH_2), 2.23 (bs, 12H, $N(CH_3)_2$). ^{13}C NMR: 138.0 (C(1)), broad signal), 140.2 (C(2), broad signal), 130.2 (C(4), $^4J(^{119}\text{Sn}, ^{13}\text{C} = 18.7\ \text{Hz})$), 128.2 (C(3), $^3J(^{119}\text{Sn}, ^{13}\text{C} = 84.0\ \text{Hz})$), 128.0 (C(5), $^3J(^{119}\text{Sn}, ^{13}\text{C} = 103.3\ \text{Hz})$), 135.5 (C(6), $^2J(^{119}\text{Sn}, ^{13}\text{C} = 67.0\ \text{Hz})$), 63.6 (C(7), $^nJ(^{119}\text{Sn}, ^{13}\text{C} = 36.8\ \text{Hz})$), 43.7 (C(8)). $^{119}\text{Sn}\{^1\text{H}\}$ NMR ($CDCl_3$, 300 K, ppm): −347.46. ESI-MS: MW = 642. MS: *m/z* 919, $[(\text{L}^{\text{CN}})_2\text{SnOSn}(\text{L}^{\text{CN}})_2\text{I}]^+$, 2%; *m/z* 643, $[\text{M} + \text{H}]^+$, 15%; *m/z* 515, $[\text{M} - \text{I}]^+$, 100%; *m/z* 405, $[(\text{L}^{\text{CN}})_2\text{SnOH}]^+$, 4%. Elemental analysis (%). Found: C, 33.7; H, 3.72; N, 4.45. Calc. for $C_{18}H_{24}I_2N_2Sn$ (640.9): C, 33.73; H, 3.77; N, 4.37.

2-[(*N*,*N*-Dimethylaminomethyl)phenyl] phenyltin dichloride (5)

As for **1**, to a solution of 2.3 g of phenyltin(IV) trichloride (7.61 mmol) in 30 ml of benzene was added 1.1 g (7.61 mmol) of $(\text{L}^{\text{CN}})\text{Li}$ in 50 ml of benzene. Yield: 2.1 g (68%); Mp: 145–147 °C. ^{1}H NMR (500.13 MHz,$CDCl_3$, 300 K, ppm): 8.33 (d, 1H, H(6), $^3J(^1\text{H}(5), ^1\text{H}(6)) = 6.4$ Hz, $^3J(^{119}\text{Sn}, ^1\text{H}) = 101.0$ Hz), 7.46 (m, 2H, H(4,5), 7.25 (d, 1H, H(3)), 3.71 (s, 2H, NCH_2), 2.19 (s, 6H, $N(CH_3)_2$), 7.67 (d, 2H, H(2′), $^3J(^1\text{H}(2'), ^1\text{H}(3')) = 8.0$ Hz, $^3J(^{119}\text{Sn}, ^1\text{H}) = 96.0$ Hz), 7.44 (m, 3H, H(3′,4′)). ^{13}C NMR: 141.7 (C(1)), broad signal), 141.68 (C(2), broad signal)), 129.1 (C(4), broad signal), 127.9 (C(3), broad signal), 128.2 (C(5), broad signal), 131.7 (C(6), broad signal), 63.3 (C(7), broad signal), 45.5 (C(8)), 138.1 (C(1′), broad signal), 133.9 (C(2′), $^2J(^{119}\text{Sn}, ^{13}\text{C} = 68.4\ \text{Hz})$), 129.5 (C(3′), $^3J(^{119}\text{Sn}, ^{13}\text{C} = 100.3\ \text{Hz})$), 130.6 (C(4′)). $^{119}\text{Sn}\{^1\text{H}\}$ NMR ($CDCl_3$, 300 K, ppm): −170. ESI-MS: MW = 401. MS: *m/z* 825, $[2\text{M} + \text{Na}]^+$, 6%; *m/z* 593, *m/z* 537, $[\text{M} + \text{H} + \text{HL}^{\text{CN}}]^+$, 46%; *m/z* 459, $[(\text{L}^{\text{CN}})_2\text{SnCl}_2 + \text{H}]^+$, 17%; *m/z* 423, $[(\text{L}^{\text{CN}})_2\text{SnCl}]^+$, 7%; *m/z* 402, $[\text{M} + \text{H}]^+$, 5%; *m/z* 136, $[\text{HL}^{\text{CN}} + \text{H}]^+$, 100%; *m/z* 91, $[C_6H_5CH_2]^+$, 27%. Elemental analysis (%). Found: C, 44.7; H, 4.21; N, 3.52. Calc. for $C_{15}H_{17}Cl_2NSn$ (400.91): C, 44.94; H, 4.27; N, 3.49.

NMR spectroscopy

The solution-state ^{1}H (500.13 MHz), ^{13}C (125.76 MHz) and $^{119}\text{Sn}\{^1\text{H}\}$ (186.50 MHz) NMR spectra of the compounds studied were measured on a Bruker Avance 500 spectrometer equipped with 5 mm probes with *z*-gradient in the temperature range 170–360 K. The solutions were obtained by dissolving 20 mg of each compound in 0.5 ml of deuterated solvents. The ^{1}H chemical shifts were calibrated relative to the signal of residual $CHCl_3$ ($\delta = 7.25$), benzene (7.16) and methanol ($\delta = 3.31$), and the ^{13}C chemical shifts to the signal of $CDCl_3$ ($\delta(^{13}\text{C}) = 77.0$). The ^{119}Sn chemical shifts are referred to external neat tetramethylstannane ($\delta = 0.0$). Positive chemical shift values denote shifts to higher frequencies relative to the standards. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. The ^{1}H and ^{13}C chemical shifts were assigned from standard gradient-selected (gs)-H,H-COSY, gs-^{1}H–^{13}C, gs-^{1}H–^{13}C-HMBC spectra (optimized for $^1J(^{13}\text{C}, ^1\text{H}) \approx 150$ Hz and $^3J(^{13}\text{C}, ^1\text{H}) \approx 8$ Hz respectively), and ^{13}C APT spectra.

Mass spectrometry

Positive-ion ESI mass spectra were measured on an Esquire3000 ion-trap analyser (Bruker Daltonics, Bremen, Germany) in the range *m/z* 50–1500. The ion trap was tuned to give an optimum response for *m/z* 400–600. The samples were dissolved in acetonitrile or methanol and analysed by direct infusion at a flow rate of 3 μl min^{-1}. The ion source temperature was 300 °C, and the flow rate and the pressure of nitrogen were 4 l min^{-1} and 10 psi respectively. The isolation width for MS^n experiments was $m/z = 8$, and the collision amplitude was selected depending on the stability of the particular fragment ion in the range 0.6–1 V.

X-ray crystallography

Single crystals of **1**, **2**, **4**, and **5** were grown from an ∼5% CH_2Cl_2 solution of the appropriate compound, into which hexane was charged via slow vapour diffusion. The relevant crystallographic parameters are given in Table 2.

Data for all colourless crystals were collected at 150(2) K on a Nonius KappaCCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SIR92[25]). All reflections were used in the structure refinement based on F^2 by the full-matrix least-squares technique (SHELXL97[26]). Hydrogen atoms were mostly localized on a difference Fourier map; however, to ensure uniformity of treatment of all crystals, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $\text{H}_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ (pivot atom) or of $1.5U_{\text{eq}}$ for the methyl moiety. Absorption corrections were carried

Table 2. Crystal data and structure refinement for **1**, **2**, **4**, and **5**

	1	**2**	**4**	**5**
Empirical formula	$C_{24}H_{29}ClN_2Sn$	$C_{18}H_{24}Cl_2N_2Sn$	$C_{18}H_{24}I_2N_2Sn$	$C_{15}H_{17}Cl_2NSn$
Formula weight	499.63	457.98	640.88	400.89
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$C2/c$	$P2_1/n$	*Pnma*
Unit cell dimensions				
a (Å)	18.2860(2)	16.9980(3)	10.0360(2)	12.6640(2)
b (Å)	10.1820(1)	8.0690(1)	13.6440(2)	13.9740(3)
c (Å)	24.0670(3)	14.5760(3)	15.0660(3)	9.0960(2)
β (°)	93.6580(6)	105.9530(7)	96.9070(8)	
Volume (Å^3)	4471.86(9)	1922.20(6)	2048.03(7)	1609.69(6)
Z	8	4	4	4
Density (calculated) (Mg m^{-3})	1.484	1.583	2.079	1.654
Absorption coefficient (mm^{-1})	1.274	1.608	4.264	1.906
F(000)	2032	920	512	792
Crystal size (mm^3)	0.25 × 0.175 × 0.15	0.5 × 0.3 × 0.15	0.25 × 0.25 × 0.15	0.26 × 0.2 × 0.2
θ range (°) for data collection	1.0 to 27.49	1 to 27.5	1 to 27.48	1 to 27.5
h range	−23 to 23	−22 to 23	−13 to 13	−16 to 16
k	−13 to 13	−13 to 13	−17 to 17	−18 to 17
l	−31 to 31	−31 to 31	−19 to 19	−11 to 11
Reflections collected	62 782	11 721	29 962	20 594
$T_{\min}$, $T_{\max}$	0.771, 0.815	0.571, 0.767	0.383, 0.646	0.597, 0.716
Independent/observed reflections[a]	10 231/8656	2203/2125	4696/4282	1923/1694
R_{int}[b]	0.045	0.038	0.048	0.038
Absorption correction	Multi-scans[e]	Integration	Integration	Integration
No. of parameters	173	108	213	134
S all data[c]	1.026	1.031	1.129	1.068
R_1, wR_2 [$I > 2\delta(I)$][d]	0.069, 0.195	0.016, 0.040	0.025, 0.057	0.027, 0.062
R_1, wR_2 (all data)	0.082, 0.209	0.017, 0.041	0.029, 0.059	0.033, 0.066
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e$^-$Å^{-3})	0.843, −0.591	0.379, −0.493	0.761, −1.159	0.761, −1.159
CCCD deposition no.	257 471	257 472	257 473	257 474

[a] $I > 2\delta(I)$.
[b] $R_{\text{int}} = \Sigma|F_o{}^2 - F_{o,\text{mean}}{}^2|/\Sigma F_o{}^2$.
[c] $S = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/(N_{\text{diffrs}} - N_{\text{params}})\}^{1/2}$.
[d] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$.
[e] PLATON.
[f] SORTAV.

using either the multi-scans procedure (PLATON[27] or SORTAV[28]) or Gaussian integration from the crystal shape (Coppens)[29]. Crystallographic data for individual structures are summarized in Table 2.

Structure solutions and refinement of **1**, **2**, and **4** crystals were unexceptional; determination of **5** is complicated by disorder. The heavy atoms (tin and chlorine) are placed exactly on a mirror plane of space group *Pnma* (solution in space group $Pna2_1$ was unstable during refinement). On the other hand, the organic ligands are disordered through the mirror plane, which caused the overlapping of aromatic circles. The geometry of the phenyl ligand was, therefore, constrained during refinement into an ideal hexagon and the displacement parameters of C1 and C11 were kept equal. A full list of the 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).

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