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Synthesis of novel terdentate N,C,N′-coordinated butyltin(IV) complexes and their redistribution reactions with $SnCl_4$

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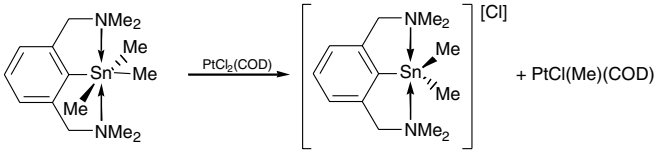
Abstract

The Sn(IV) butyl complexes $[Bu_nSnCl_{3-n}(NCN)]$ (NCN = $[C_6H_3(CH_2NMe_2)_2$-2,6$]^-$, $n = 1$ (**1**), 2 (**2**), 3 (**3**)) were prepared. Spectroscopic analysis of **1**–**3** by ^1H and ^{119}Sn NMR gave evidence for the presence of intramolecular N → Sn interactions in solution. The molecular structure of **1**, as determined by a single-crystal X-ray diffraction study, revealed that it contained a six-coordinate Sn(IV) center with intramolecular N → Sn coordination of both *ortho*-amine substituents. Addition of $SnCl_4$ to **1** resulted in the isolation of the HCl adduct $[BuSnCl_3(NCN^+H)]$ (**6**). Reactions of **2** and **3** with $SnCl_4$ each resulted in the HCl salt $[SnCl_4(NCN^+H)]$ (**8**) and the corresponding butyltin chloride, Bu_2SnCl_2 and Bu_3SnCl, respectively. The formation of HCl adducts **6** and **8** was ascribed to transfer of the NCN ligand to $SnCl_4$ and the presence of HCl (from partial hydrolysis of the product or $SnCl_4$ during the work up procedure). The molecular structures of **6** and **8** have been determined through single-crystal X-ray diffraction and revealed the presence of a $[BuSnCl_3(aryl)]^-$ or $[SnCl_4(aryl)]^-$ stannate anion, respectively, with in each case one coordinated *ortho*-amine function and one protonated amine moiety involved in N–H···Cl–Sn hydrogen bonding in both compounds (2.14 Å for **6** and 2.18 Å for **8**).

Keywords: Pincer; Sn; Aryltin; Redistribution; Hydrogen bonding; Butyltin; NCN ligand

1. Introduction

Tetraorganotins have a proven value as mild alkylating and arylating agents. In the Stille coupling reaction, for example, trialkylarylstannes are used to selectively couple an aryl group with an organic halide or triflate [1]. The reaction involves a transmetallation step in which the aryl group of the stannane is transferred to the transition metal center of the catalyst [2]. Such a transfer reaction is also used for the selective monoalkylation [3] and monoarylation [4] of transition metal complexes. Compared to the tetracoordinate tetraorganotins, penta- and hexacoordinate tin(IV) compounds bearing intramolecularly coordinating ligands are more reactive in such aryl- and alkyl-transfer reactions [5]. The difference in reactivity is ascribed to the increase in electron density at the tin(IV) center by the donor substituent [5,6] For example, the single methylation of $PtCl_2$(COD) by $[Me_3Sn(NCN)]$ [5c] (Eq. (1)) requires less forcing conditions than methylation with Me_4Sn [3].



(1)

As part of our interest in new routes for selective tin-alkyl bond formation, we prepared the novel Sn(IV) butyl complexes $[Bu_nSnCl_{3-n}(NCN)]$ ($n = 1$–3) bearing the

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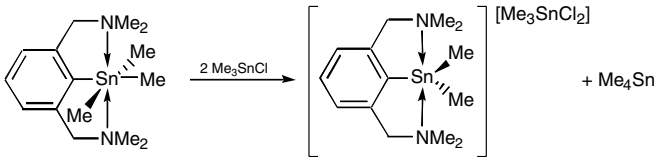
monoanionic aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (NCN) and studied their structure in solution as well as in the solid state [7]. The NCN pincer ligand has been employed for many years in our group to prepare a wide range of organometallic complexes of which some have been applied successfully as catalysts [8], sensors [9], and switches [10].

Since $[Me_3Sn(NCN)]$ reacts with Me_3SnCl to give exclusively Me_4Sn and $[Me_2Sn(NCN)][Me_3SnCl_2]$ (Eq. (2)) [5c] we expected that the novel NCN Sn(IV) butyl compounds could selectively transfer one or more butyl groups to other metal centers. To investigate their use as selective alkylating agents for the synthesis of other alkyltin compounds, reactions of the (NCN)Sn(IV)-butyl complexes $[Bu_nSnCl_{3-n}(NCN)]$ (NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$, $n = 1$ (**1**), 2 (**2**), 3 (**3**)) with $SnCl_4$ were carried out.

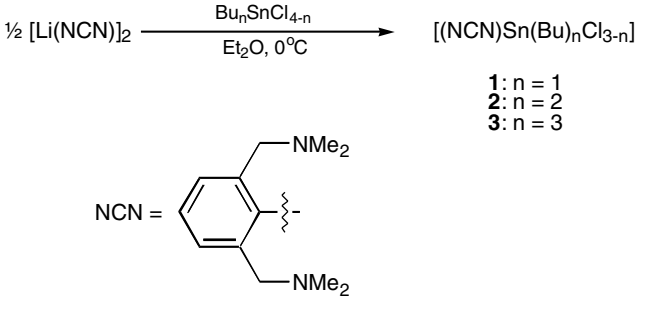


(2)

2. Results and discussion

2.1. Synthesis and spectroscopic analysis of (NCN)Sn(IV)-butyl complexes 1–3

The Sn(IV) butyl complexes $[Bu_nSnCl_{3-n}(NCN)]$ ($n = 1$ (**1**), 2 (**2**), 3 (**3**)) were prepared by reacting the butyltin chlorides Bu_nSnCl_{3-n} with $[LiC_6H_3(CH_2NMe_2)_2\text{-}2,6]_2$ in Et_2O at 0 °C (Eq. (3)).



(3)

Complexes **1**–**3** were isolated in 67–98% yield as white solids. All three complexes were examined by ^1H and ^{119}Sn NMR spectroscopy in $CDCl_3$ solutions. Since both NMe_2 substituents of the NCN-pincer ligand are in principle available for intramolecular N → Sn coordination, the presence of such interactions was studied by comparison of the ^1H and ^{119}Sn NMR data of complexes **1**–**3** with the data of the free arylamine $C_6H_4(CH_2NMe_2)_2$-1,3 and the stannanes $SnCl_2(Bu)(C_6H_5)$, $SnCl(Bu)_2(C_6H_5)$ and $SnBu_3(C_6H_5)$ (Table 1).

Both the CH_2N and the NMe_2 resonances of complexes **1**–**3** appear as one singlet in the ^1H NMR spectrum, indicating the chemical equivalence of the two CH_2NMe_2 substituents of the NCN-pincer ligand on the NMR time scale. The non-aromatic ^1H resonances of the NCN ligand in **1**–**3** are shifted 0.3–0.8 ppm downfield compared to those of the free $C_6H_4(CH_2NMe_2)_2$-1,3 (Table 1). The magnitude of these shifts is dependent on the number of butyl substituents. The largest downfield shifts are observed for **1** with only one butyl substituent, while the smallest downfield shifts are observed for **3** containing three butyl substituents. Since the change in the chemical shift for the NMe_2 resonance is relatively large (0.3–0.8 ppm), the tin center is most likely involved in a direct N → Sn interaction.

The ^{119}Sn NMR chemical shift of **1** (δ −215.3), **2** (δ −44.2) and **3** (δ −73.9), respectively, are significantly more upfield than those of the stannanes $SnCl_2(n\text{-}Bu)(C_6H_5)$ (δ +22.2) [11], $SnCl(n\text{-}Bu)_2(C_6H_5)$ (δ +90.0) [12] and $Sn(n\text{-}Bu)_3(C_6H_5)$ (δ +41.7) [13] (Table 1). The upfield shift points towards an, at least partial, coordination of the CH_2NMe_2 donor to the tin center. The largest upfield ^{119}Sn NMR chemical shift observed for **1** is consistent with a six-coordinate tin center. If only one N → Sn interaction was involved, a value close to δ −94 would have been expected [14]. For **1**, the presence of two N → Sn dative interactions in the solid state was established by a single-crystal X-ray crystallographic study (Fig. 1, vide infra).

The ^{119}Sn NMR chemical shift of **2** is in close agreement with that of five-coordinate triorganotin chloride $[Me_2SnCl\{C_6H_4(CH_2NMe(CH_2)_2NMe_2)\text{-}2\}]$ (δ −45 in $CDCl_3$) [15]. Like closely related $[Me_2SnBr(NCN)]$ [16], **2** is expected to be present as a five-coordinate species in which the aryl moiety only serves as a bidentate C,N-coordinated ligand. The fluxionality of the CH_2NMe_2 substituents in such complexes has been demonstrated for several NCN-pincer metal complexes [7a,16,17]. At room temperature, the ^1H NMR spectrum of the NCN-pincer ligand of **2** displayed only one set of singlet CH_2 and NMe_2 resonances,

Table 1
Selected ^1H and ^{119}Sn NMR data for stannanes **1**–**3**, their free ligand precursor $C_6H_4(CH_2NMe_2)_2$-1,3 and stannanes $SnCl_2(Bu)(C_6H_5)$, $SnCl(Bu)_2(C_6H_5)$ and $Sn(Bu)_3(C_6H_5)$[a]

Compound	$\delta(^1H)$		$\delta(^{119}Sn)$
	CH_2	NMe_2	
(NCN)H[b]	3.12	1.94	–
$SnCl_2(Bu)(C_6H_5)$	–	–	+22.2
$SnCl(Bu)_2(C_6H_5)$	–	–	+90.0
$Sn(Bu)_3(C_6H_5)$	–	–	+41.7
$[BuSnCl_2(NCN)]$ (**1**)	3.91	2.75	−215.3
$[Bu_2SnCl(NCN)]$ (**2**)	3.73	2.24	−44.2
$[Bu_3Sn(NCN)]$ (**3**)	3.44	2.10	−73.9
$[Bu_2Sn(NCN)][B(C_6H_5)_4]$ (**4**)	3.72	2.51	+56.5
$[Bu_2Sn(NCN)][CF_3SO_3]$(**5**)	3.83	2.58	+60.3
$[BuSnCl_2(NCN)(HCl)]$ (**6**)	3.98	2.65	−294.9
	4.78 (CH_2N^+)	2.85 (N^+Me_2)	
$[SnCl_3(NCN)]$ (**7**)	4.17	2.83	−265.3
$[SnCl_3(NCN)(HCl)]$ (**8**)	4.09	2.84	−258.0
	5.01 (CH_2N^+)	2.94 (N^+Me_2)	

[a] In $CDCl_3$ at 298 K.
[b] NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$.

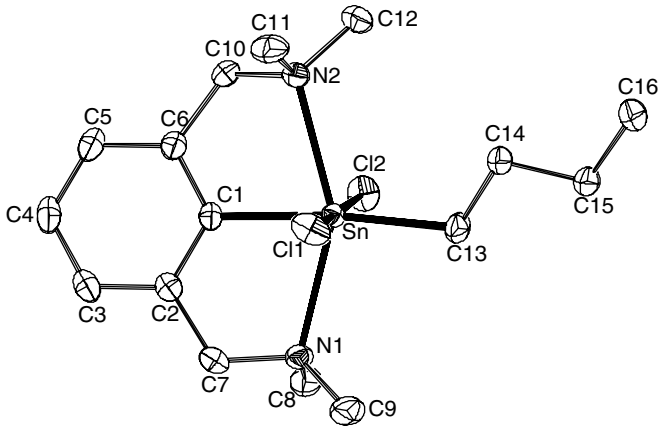
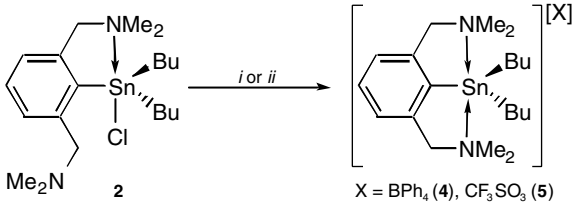


Fig. 1. Displacement ellipsoid plot (50% probability) of [*n*-BuSnCl$_2$-{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}] (**1**). Hydrogen atoms have been omitted for clarity.

indicating a fast interchange of the two CH_2NMe_2 groups. These resonances did not de-coalesce at lower temperatures, not even at −80 °C (CD_2Cl_2) indicating that the fluxional process is fast and low in energy. The mechanism of this process (associative or dissociative) remains unestablished.

It was observed previously that complexes of the type [$R_2SnX(NCN)$] are able to dissociate into the ionic complexes [$R_2Sn(NCN)$][X] (R = Me, X = Cl, Br; R = Ph; X = Cl, Br) [5c,17,18]. To exclude this possibility, we prepared ionic [$Bu_2Sn(NCN)$][X] (X = BPh_4 (**4**) and CF_3SO_3 (**5**)) (Eq. (4)) and compared their ^{119}Sn NMR data with that of **2** (Table 1). The ionic character of **4** in the solid state was confirmed by an X-ray crystallographic study (vide infra). The large difference in the ^{119}Sn NMR data of **4** and **5** (δ +56.5 and δ +60.3, respectively) compared to that of **2** (δ −44.2), ruled out [$Bu_2Sn(NCN)$][Cl] as a possible structure of **2**.



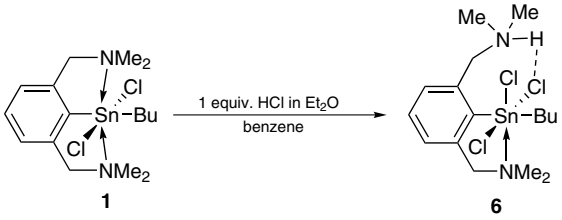
(4)

(i) $NaBPh_4$, THF (ii) $AgCF_3SO_3$, C_6H_6

The ^{119}Sn NMR chemical shift of **3** (δ −73.9) is in good agreement with that of closely related hexa-coordinate [$Me_3Sn(NCN)$] (δ −86.9) [5c]. Because of the strong structural similarity as well as the comparable ^{119}Sn NMR data, we conclude that the tin center in **3** is six-coordinate as well, albeit that the N → Sn interactions are relatively weak.

2.2. Reactions of *1–3* with $SnCl_4$

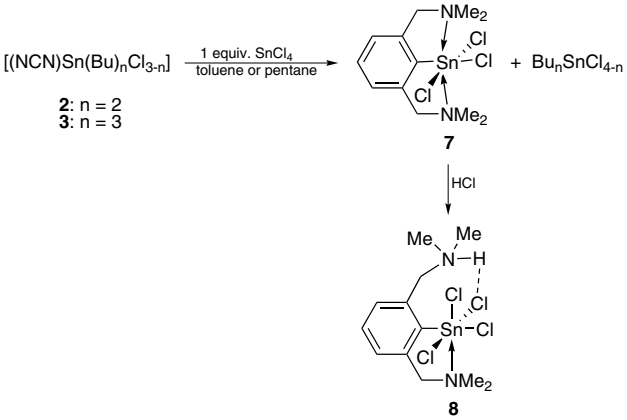
Addition of one equivalent of $SnCl_4$ to **1**–**3** at room temperature resulted in the unexpected isolation of [$BuSnCl_2(NCN)(HCl)$] (**6**) for **1** and [$SnCl_3(NCN)(HCl)$] (**8**) for **2** and **3**. In the reaction of **2** and **3**, also the formation of the corresponding butyltin chlorides, *n*-Bu_2SnCl_2 (>95%) and *n*-Bu_3SnCl (87%) (^{1}H NMR), respectively, was observed (Scheme 1). To confirm the identity of the product, an independent sample of **6** was prepared by reacting **1** with one equivalent of HCl (Eq. (5)). Complexes **6** and **8** are most likely the result of partial hydrolysis of **1** and putative [$SnCl_3(NCN)$] (**7**), respectively, affording HCl that reacts with **1** or **7** to form the final product. Formation of **6** and **8** is so predominant, despite the special care that was taken to exclude water, that it cannot be dismissed as a mere artifact of sub-optimal experimental conditions.



(5)

The ^{1}H NMR spectrum of **6** (25 °C, $CDCl_3$) displayed a singlet and a doublet for the NMe resonances (δ 2.51 and 2.85, respectively), indicating the chemical disparity of the two CH_2NMe_2 donor substituents. Furthermore, a broad low-field resonance at δ 10.91 was assigned to the ammonium proton. The ^{119}Sn NMR chemical shift (δ −294.9) had shifted about 90 ppm upfield compared to **1**, in line with the sixfold coordination of the Sn center and replacement of the –NMe_2 donor by a chloride ion. The geometry around the tin center was confirmed in the solid state by a single-crystal X-ray crystallographic structure determination (Fig. 4, vide infra).

For **8**, one singlet (δ 2.84) and one doublet (δ 2.94) were noticed for the NMe resonances in the ^{1}H NMR spectrum. The broad signal at δ 9.78 is ascribed to the N^+H resonance. The resonances of the CH_2NMe_2 donor substituents of **8** are all shifted 0.1–0.2 ppm downfield compared to those of **6**. This can be explained by the stronger electron withdrawing tin center of **8**. The molecular structure of **8** in the solid state was confirmed by an X-ray crystallographic structure determination (Fig. 6, vide infra).



Scheme 1. Reaction of **2** and **3** with $SnCl_4$.

The reaction of **2** with one equiv. of $SnCl_4$ was also performed in $CDCl_3$ at room temperature and monitored by ^1H and ^{119}Sn NMR spectroscopy. After addition of $SnCl_4$, immediate formation of equimolar amounts of *n*-Bu_2SnCl_2 and **7** along with traces of **8** (<5%) was observed. The ^{119}Sn and ^1H NMR data of **7** (Table 1) are in close agreement with hexa-coordinate **1**. Next to *n*-Bu_2SnCl_2, no other butyltin species were observed. The reaction of **3** with $SnCl_4$ is believed to involve intermediate **7** as well.

The reactions of **2** and **3** with $SnCl_4$, either involve butyl group transfer or transfer of the NCN-pincer ligand to $SnCl_4$. Butyl group transfer from **2** and **3** would initially result in **1** and **2** as intermediates, respectively, along with *n*-$BuSnCl_3$ for **2** and *n*-Bu_2SnCl_2 for **3**. As none of these intermediates were observed, reaction of **2** and **3** with $SnCl_4$ appears to involve direct NCN ligand/Cl exchange. This is remarkable given the chelating nature of the NCN ligand and its general resistance to undergo transfer reactions. However, initial complexation of the strong Lewis acid $SnCl_4$ with one of the NMe_2 moieties, followed by intramolecular aryl/Cl exchange – the latter being generally facile for regular aryl groups – may very well offer a low activation energy pathway for this process.

2.3. Solid state structures of complexes *1, 4, 6* and *8*

To investigate the N → Sn interactions of complexes **1**, **4**, **6** and **8** in the solid state, X-ray crystal structure determinations have been carried out (Figs. 1–6, respectively). Selected bond distances and bond angles of **1**, **4**, **6** and **8** are presented in Table 2.

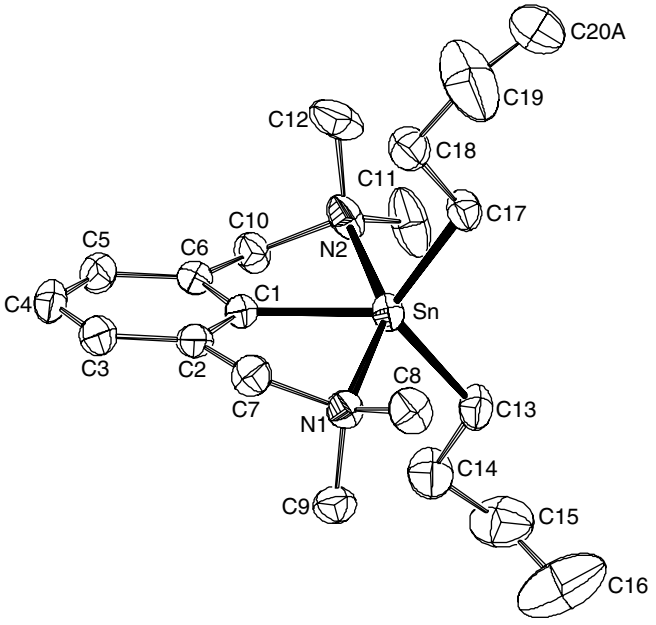


Fig. 2. Displacement ellipsoid plot (50% probability) of [*n*-$Bu_2Sn\{C_6H_3(CH_2NMe_2)_2$-2,6$\}$][$B(C_6H_5)_4$] (**4**). Hydrogen atoms, the tetraphenyl boron anion, and the CH_2Cl_2 solvent molecule have been omitted for clarity. Only the major conformation of the disordered atom C20 is shown.

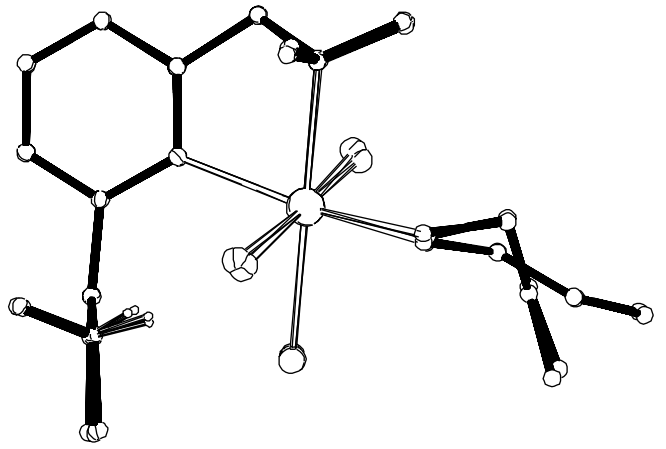


Fig. 3. Quaternion fit [28] of the four independent molecules in the crystal structure of [*n*-$BuSnCl_2\{C_6H_3(CH_2NMe_2)_2$-2,6$\}$(HCl)] (**6**). CH hydrogen atoms are omitted for clarity.

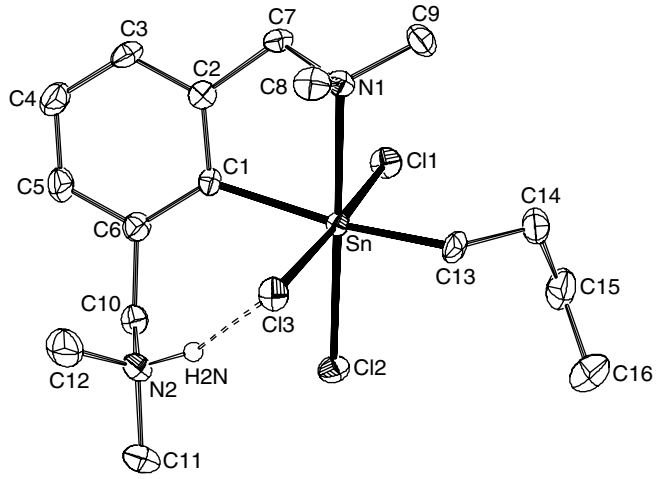


Fig. 4. Displacement ellipsoid plot (50% probability) of [*n*-$BuSnCl_2$-$\{C_6H_3(CH_2NMe_2)_2$-2,6$\}$(HCl)] (**6**). CH hydrogen atoms are omitted for clarity.

The molecular geometry of triorganotin **1** (Fig. 1) shows a six-coordinated tin center with both CH_2NMe_2 donor substituents involved in intramolecular N → Sn interactions. The distortion of the octahedral ligand array around the tin(IV) center arises from the large deviation in the N(1)–Sn–N(2) bond angle (151.09(4)°) due to the chelation of the pincer ligand. The Sn–N bond distances are similar in length, indicating that the two CH_2NMe_2 donor substituents have N → Sn interactions of the same strength. The bond distance between the C_{ipso} atom (C(1)) of the NCN-pincer ligand and the tin center (2.0967 (15) Å) is comparable to those of related [(4-tolyl)SnI_2-$\{C_6H_3(CH_2NMe_2)_2$-2,6$\}$] (2.109(9) Å) [19] and [$PhSnCl_2$-$\{C_6H_3(CH_2NMe_2)_2$-2,6$\}$] (2.092(10) Å) [17]. The Sn–C(13) bond length (2.1355(16) Å) is in close agreement with the length found for the methyl substituent in *trans* position to the C_{ipso} atom of the C_2N_4 ligand in [$(SnMe_3)_2$-$\{C_6(CH_2NMe_2)$-2,3,5,6$\}$] (2.139(3) Å) [18b]. The bond

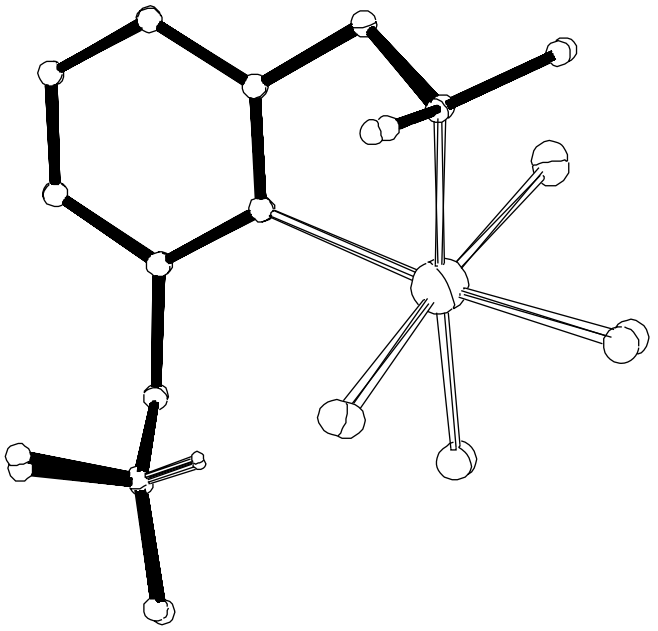


Fig. 5. Quaternion fit [28] of the two independent molecules in the crystal structure of $[SnCl_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(HCl)]$ (**8**). CH hydrogen atoms have been omitted for clarity.

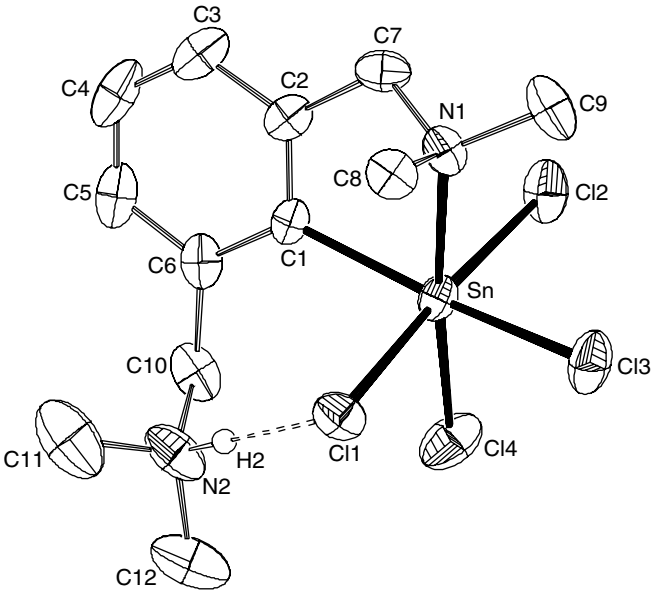


Fig. 6. Displacement ellipsoid plot (50% probability) of $[SnCl_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(HCl)]$ (**8**). CH hydrogen atoms and disordered solvent molecules have been omitted for clarity.

distances as well as the bond angles of the NCN-pincer moiety are unexceptional.

The molecular geometry of ionic triorganotin **4** (Fig. 2) is distorted trigonal bipyramidal and is formed by the three C atoms in the equatorial plane and the two N atoms. The distortion of the trigonal bipyramidal geometry results from the small N(1)–Sn–N(2) angle of 150.72(6)°. The sum of the C–Sn–C angles in the equatorial plane equals 360.00(8)°. The tin–nitrogen distances of

Table 2
Selected bond distances and bond angles for **1**, **4**, **6**, and **8**

Bond distance (Å)		Bond angles (°)	
*Compound **1***			
Sn–C(1)	2.0967(15)	Cl(1)–Sn–Cl(2)	175.649(14)
Sn–C(13)	2.1355(16)	N(1)–Sn–N(2)	151.09(4)
Sn–N(1)	2.4564(13)	C(1)–Sn–C(13)	173.87(6)
Sn–N(2)	2.4441(13)	N(1)–Sn–C(1)	75.26(5)
Sn–Cl(1)	2.5695(4)	N(2)–Sn–C(1)	75.82(5)
Sn–Cl(2)	2.5513(4)	Cl(1)–Sn–C(1)	91.38(4)
		Cl(2)–Sn–C(1)	91.69(4)
*Compound **4***			
Sn–C(1)	2.101(2)	N(1)–Sn–N(2)	150.72(6)
Sn–C(13)	2.134(3)	N(1)–Sn–C(13)	99.10(8)
Sn–C(17)	2.136(2)	N(1)–Sn–C(17)	97.51(7)
Sn–N(1)	2.4173(17)	N(1)–Sn–C(1)	75.33(7)
Sn–N(2)	2.4393(18)	C(1)–Sn–C(13)	126.50(8)
		C(1)–Sn–C(17)	120.44(8)
		C(13)–Sn–C(17)	113.06(8)
*Compound **6***[a]			
Sn–C(1)	2.179(4)	N(1)–Sn–C(1)	77.42(14)
Sn–C(13)	2.129(4)	N(1)–Sn–C(13)	89.09(14)
Sn–N(1)	2.419(4)	N(1)–Sn–Cl(1)	86.60(8)
Sn–Cl(1)	2.4811(9)	N(1)–Sn–Cl(2)	178.90(9)
Sn–Cl(2)	2.5182(12)	N(1)–Sn–Cl(3)	94.26(8)
Sn–Cl(3)	2.8015(10)	C(1)–Sn–C(13)	160.99(15)
N(2)–H(2N)	1.03(4)	C(1)–Sn–Cl(1)	92.34(10)
H(2N)···Cl(3)	2.14(4)	C(1)–Sn–Cl(2)	101.91(11)
N(2)···Cl(3)	3.109(4)	C(1)–Sn–Cl(3)	84.54(10)
		N(2)–H(2N)···Cl(3)	155(3)
*Compound **8***[b]			
Sn–C(1)	2.169(3)	N(1)–Sn–C(1)	78.70(9)
Sn–N(1)	2.351(2)	N(1)–Sn–Cl(1)	95.63(6)
Sn–Cl(1)	2.5513(7)	N(1)–Sn–Cl(2)	84.98(6)
Sn–Cl(2)	2.4515(8)	N(1)–Sn–Cl(3)	86.77(6)
Sn–Cl(3)	2.4073(8)	N(1)–Sn–Cl(4)	172.73(6)
Sn–Cl(4)	2.4349(8)	C(1)–Sn–Cl(1)	88.66(7)
N(2)–H(2)	0.91	C(1)–Sn–Cl(2)	95.78(7)
H(2)···Cl(1)	2.18	C(1)–Sn–Cl(3)	162.48(7)
N(2)···Cl(1)	3.091(3)	C(1)–Sn–Cl(4)	104.44(8)
		Cl(1)–Sn–Cl(2)	175.55(3)
		N(2)–H(2)···Cl(1)	179

[a] Only the first of four independent molecules is considered.
[b] Only the first of two independent molecules is considered.

2.4173(17) and 2.4393(18) Å, respectively, are similar to those reported for $[Me_2Sn\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}][Br]$ (2.41 and 2.56 Å) [18a], $[Ph_2Sn\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}\text{-}[Br(H_2O)]$ (2.4398(14) Å) [18b] and $[Me_2Sn\{C_6H_3(CH_2N\text{-}Me_2)_2\text{-}2,6\}][Li(H_2O)_4][Br][Cl]$ (2.36(2) and 2.45(2) Å) [20]. Also the Sn–C bond distances are essentially comparable to those of the strongly related $[Me_2Sn\{C_6H_3(CH_2N\text{-}Me_2)_2\text{-}2,6\}][Br]$ complex [18a]. Because of the flexible butyl moiety, some disorder in the position of the δ-C atom is found. The bond angles and the bond distances found for the tetraphenyl boron anion are as expected.

The zwitterionic diorganotin complex **6** crystallizes in the chiral space group $P2_1$ with four independent molecules in the asymmetric unit. The independent molecules essentially differ only in the conformation of the *n*-butyl ligand (Fig. 3). We therefore discuss only the geometry of the first

independent molecule. The molecular geometry, depicted in Fig. 4, shows a distorted octahedral arrangement of the six ligands (one N atom, two C atoms and three Cl atoms) around the tin(IV) center. The distortion of the geometry coordination sphere arises from the C(1)–Sn–C(2) bond angle (160.99(15)°) which deviates significantly from the ideal 180°. As was concluded from the ^{1}H NMR data, one CH_2NMe_2 donor substituent is coordinated to the tin center via an N → Sn interaction while the other has accepted a proton and is present as CH_2-N^+HMe_2.

The Sn–Cl(3) bond (2.8015(10) Å) is significantly longer than the other two Sn–Cl bonds (2.5182(12) and 2.4811(9) Å). This can be explained by the intramolecular H···Cl(3) bond interaction of 2.15(4) Å. Such an increase of the Sn–Cl bond distance was not observed for $[C_2H_5SnCl_4(pyridine)](pyridineH)$ [21]. with intermolecular H···Cl bonds. Except for the Sn–Cl(3) bond of **6**, all other tin–ligand bond distances are comparable to those found for **1**.

The mono-organotin complex **8** crystallizes with two independent molecules in the asymmetric unit. The independent molecules have a very similar conformation (Fig. 6). We therefore discuss only the geometry of the first independent molecule. The molecular geometry is similar to that of **6**, also shows a hexa-coordinated tin center with one CH_2NMe_2 donor substituent coordinated to the tin center via a N → Sn interaction (Fig. 6). The tin(IV) center has a distorted octahedral ligand array that arise from bonding interactions with C(1), the four chloride substituents and the N-donor atom of the CH_2NMe_2 substituent. The distortion in the octahedral ligand array is the result of the five membered ring (Sn, C(1), C(2), C(7), N(1)) with a N(1)–Sn–C(1) bond angle of 78.70(9)°. As was observed for **6**, the Cl atom involved in the intramolecular H···Cl interaction shows a longer Sn–Cl bond distance (2.5513(7)°) than the other three Sn–Cl bonds (2.4515(8), 2.4073(8) and 2.4349(8)°). The difference was smaller than in complex **6**. Except for the Cl atom involved in the H···Cl interaction, all parameters for the ligands around the tin center are similar. The bond distances as well as the bond angles of the NCN-pincer moiety are in agreement with those of closely related zwitterionic $[SnBr_3\{C_6H_3(CH_2NMe_2)_2$-2,6$\}(H_2O)]$ with intra- and intermolecular hydrogen bonds [22].

3. Conclusion

Analysis by ^{1}H and ^{119}Sn NMR spectroscopy indicates that [*n*-BuSnCl$_2$(NCN)] (**1**) and [*n*-Bu$_3$Sn(NCN)] (**3**) are hexa-coordinate tin species in solution with both CH_2NMe_2 donor substituents involved in N → Sn coordination. On the other hand, [*n*-Bu$_2$SnCl(NCN)] (**2**) is present as a penta-coordinate species with only one of the CH_2NMe_2 donor substituents coordinated to the tin center. Reactions of **2** and **3** with $SnCl_4$, demonstrate that not the butyl group but the NCN pincer ligand is transferred which results in the formation of [$SnCl_3$(NCN)] (**7**) and the corresponding butyltin chloride. Due to undesired hydrolysis of **7** or the presence of remaining $SnCl_4$ during the work-up procedure, **7** was isolated as its HCl adduct **8**. These results demonstrate that the *ortho*-CH_2NMe_2 donor substituents have no influence on the transfer reactions of **2** and **3** with $SnCl_4$ since these species react in the same way with $SnCl_4$ as the tetrahedral stannanes $SnCl_{3-n}(n\text{-}Bu_n)(C_6H_5)$ that lack intramolecular donor substituents.

4. Experimental

4.1. General comments

All reactions and manipulations were carried out under an inert N_2 atmosphere using standard Schlenk techniques. All solvents were dried and distilled prior to use. $[LiC_6H_3(CH_2NMe_2)_2$-2,6$]_2$ was prepared according to the literature procedures [23]. Commercial anhydrous $SnCl_4$, *n*-BuSnCl$_3$, *n*-Bu$_2$SnCl$_2$ and *n*-Bu$_3$SnCl were used as supplied. ^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H} and ^{119}Sn{^{1}H} NMR spectra were recorded at 298 K on a Varian Mercury 200 MHz spectrometer. ^{11}B{^{1}H} NMR spectra was externally referenced against $BF_3 \cdot Et_2O$ and ^{119}Sn{^{1}H} NMR spectra against Me_4Sn ($\delta = 0$ ppm). GC analysis were carried out on a Perkin–Elmer instrument consisting of a Autosystem XL GC. Elemental analyses were carried out by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim am Ruhr, Germany.

4.2. Synthesis of [*n*-BuSnCl$_2${$C_6H_3(CH_2NMe_2)_2$-2,6}] (*1*)

A solution of *n*-BuSnCl$_3$ (3.92 g, 13.5 mmol) in Et_2O (30 mL) was cooled to 0 °C. Next, a solution of $[LiC_6H_3(CH_2NMe_2)_2$-2,6$]_2$ (2.67 g, 13.5 mmol) in Et_2O (50 mL) was added drop-wise within 1.5 h under formation of a white precipitate. The resulting reaction mixture was stirred for an additional 2.5 h at room temperature after which the Et_2O was evaporated in vacuo. The residue was dissolved in toluene (50 mL) and filtered. Addition of hexane (25 mL) to the toluene solution and storage for 4 days at −30 °C resulted in the formation of colorless needles in 67% yield. ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.97 (3H, t, $^3J_{HH} = 7.2$ Hz, Sn*Bu*), 1.43 (2H, m, $^3J_{HH} = 7.4$ H, Sn*Bu*), 1.93 (2H, m, Sn*Bu*), 2.20 (2H, t, Sn*Bu*), 2.75 (12H, s, N*Me*$_3$), 3.91 (4H, s, Ar*CH*$_2$N), 7.09 (2H, d, $^3J_{HH} = 7.6$ Hz, Ar*H*), 7.26 (t, 1H, $^3J_{HH} = 6.6$ Hz, Ar*H*). ^{13}C NMR ($CDCl_3$, 25 °C): δ 13.7, 26.3, 28.7, 40.1, 47.6, 63.2, 126.1, 130.0, 137.3. ^{119}Sn NMR ($CDCl_3$, 25 °C): δ −215.3. Anal. Calc. for $C_{16}H_{28}Cl_2N_2Sn$: C, 43.87; H, 6.44; N, 6.40. Found: C, 43.97; H, 6.40; N, 6.36%.

4.3. Synthesis of [*n*-Bu$_2$SnCl{$C_6H_3(CH_2NMe_2)_2$-2,6}] (*2*)

A solution of *n*-Bu$_2$SnCl$_2$ (3.15 g, 10.0 mmol) in Et_2O (50 mL) was cooled to 0 °C. Next, a solution of

$[LiC_6H_3(CH_2NMe_2)_2\text{-}2,6]_2$ (2.08 g, 10.5 mmol) in Et_2O (50 mL) was added drop-wise within 0.5 h under formation of a white precipitate. After the reaction mixture had stirred overnight at room temperature, it was filtered and washed with Et_2O (10 mL). The solvent was evaporated in vacuo. Traces off Et_2O and other volatiles were removed in vacuo at 100 °C. The resulting brown oil was dissolved in 15 mL of CH_2Cl_2 and centrifuged at 2400 T/min. The CH_2Cl_2 layer was carefully decantated and evaporated till dryness. The product was isolated as a orange/brown oil (4.13 g, 90%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.88 (6H, t, $^3J_{HH} = 7.0$ Hz, Sn*Bu*), 1.34 (8H, m, Sn*Bu*), 1.69 (4H, m, Sn*Bu*), 2.24 (12H, s, N*Me*$_3$), 3.73 (4H, s, Ar*CH*$_2$N), 7.05 (2H, d, $^3J_{HH} = 7.4$ Hz, Ar*H*), 7.21 (1H, t, $^3J_{HH} = 7.0$ Hz, Ar*H*). ^{13}C NMR ($CDCl_3$, 25 °C): δ 13.8, 19.3, 27.4, 28.8, 45.4, 64.8, 127.5, 129.6, 140.3, 145.2 ($^1J_{CSn} = 33$Hz). ^{119}Sn NMR ($CDCl_3$, 25 °C): δ −44.2. Anal. Calc. for $C_{20}H_{37}ClN_2Sn$: C, 52.26; H, 8.11; Cl, 7.71; N, 6.09; Sn, 25.82. Found: C, 52.38; H, 7.99; Cl, 7.66; N, 6.09; Sn, 25.91%.

4.4. Synthesis of [n-Bu$_3$Sn{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}] (3)

A solution of $[LiC_6H_3(CH_2NMe_2)_2\text{-}2,6]_2$ (2.62 g, 13.2 mmol) in Et_2O (40 mL) was cooled to 0 °C. Next, *n*-Bu_3SnCl (4.31 g, 13.2 mmol) dissolved in Et_2O (20 mL) was added drop-wise to the solution. The reaction mixture was stirred for 15 h at room temperature and H_2O (10 mL) was added. The precipitate was removed by filtration and the ether layer was washed with H_2O (3 × 20 mL). The Et_2O phase was dried on $MgSO_4$. Evaporation of the solvent gave a slightly yellow oil. Yield 6.20 g (98%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.91 (9H, t, $^3J_{HH} = 7.2$ Hz, Sn*Bu*), 1.05 (6H, m, Sn*Bu*), 1.35 (6H, sextet, $^3J_{HH} = 7.1$ Hz, Sn*Bu*), 1.49 (6H, m, Sn*Bu*), 2.10 (12H, s, N*Me*$_3$), 3.44 (4H, s, Ar*CH*$_2$N), 7.13 (m, 3H, Ar*H*). ^{119}Sn NMR ($CDCl_3$, 25 °C): δ −73.9. Anal. Calc. for $C_{24}H_{46}N_2Sn$: C, 59.89; H, 9.63; N, 5.82. Found: C, 59.69; H, 9.56; N, 5.71%.

4.5. Synthesis of [n-Bu$_2$Sn{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}][B(C$_6$H$_5$)$_4$] (4)

A solution of **2** (1.50 g, 3.3 mmol) in THF (20 mL) was cooled to 0 °C. Next, $NaB(C_6H_5)_4$ (1.13 g, 3.3 mmol) dissolved in THF (20 mL) was added dropwise to this solution and it was stirred for 2 h at room temperature to give a white precipitate. The reaction mixture was centrifuged and the THF phase was carefully decanted and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and the product was precipitated upon addition of hexane to the solution at −30 °C. The product was isolated by filtration, washed with hexane (2 × 10 mL) and dried in vacuo to give 1.95 g (79%) of a white powder. ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.97 (6H, t, $^3J_{HH} = 5.0$ Hz, Sn*Bu*), 1.45 (8H, m, Sn*Bu*), 1.61 (3H, m, Sn*Bu*), 2.51 (12H, s, N*Me*$_3$), 3.72 (4H, s, Ar*CH*$_2$N), 6.91 (t, 4H, $^3J_{HH} = 4.8$ Hz, BC$_6$*H*$_5$), 7.06 (8H, t, $^3J_{HH} = 4.8$ Hz, BC$_6$*H*$_5$), 7.25 (2H, d, $^3J_{HH} = 5.0$ Hz, Ar*H*), 7.39 (8H, b, BC$_6$*H*$_5$), 7.50 (1H, t, $^3J_{HH} = 5.0$ Hz, Ar*H*). ^{11}B NMR ($CDCl_3$, 25 °C): δ −6.37 (s). ^{13}C NMR ($CDCl_3$, 25 °C): 13.5, 14.8, 27.2, 28.3, 46.3, 64.7, 121.8, 125.6, 126.5, 128,3, 132.0, 136.4, 142.5. ^{119}Sn NMR ($CDCl_3$, 25 °C): δ +56.5. Anal. Calc. for $C_{48}H_{57}BN_2Sn$: C, 71.08; H, 7.73; B, 1.45; N, 3.77. Found: C, 68.49; H, 7.53; B, 2.73; N, 3.26%.

Crystals were obtained by slow diffusion of hexane into a solution of **4** in CH_2Cl_2.

4.6. Synthesis of [n-Bu$_2$Sn{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}][CF$_3$-SO$_3$] (5)

To a solution of **2** (0.5 g, 1.1 mmol) in benzene (10 mL), silver triflate (0.28 g, 1.1 mmol) dissolved in benzene (10 mL) was added slowly within 15 min. The reaction mixture was stirred for 3 h at room temperature and was subsequently filtered. The filtrate was evaporated to dryness to give a light brown colored powder, which was re-dissolved in dichloromethane (10 mL) and precipitated with hexane (25 mL). The suspension was stored overnight at −30 °C after which it was filtered. The product was isolated as a light brown powder (0.48 g, 77%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.92 (6H, t, $^3J_{HH} = 7.0$ Hz, Sn*Bu*), 1.43 (8H, m, Sn*Bu*), 1.77 (3H, m, Sn*Bu*), 2.58 (12H, s, N*Me*$_3$), 3.83 (4H, s, Ar*CH*$_2$N), 7.21 (2H, d, $^3J_{HH} = 5.0$ Hz, Ar*H*), 7.42 (1H, t, $^3J_{HH} = 5.0$ Hz, Ar*H*). ^{13}C NMR ($CDCl_3$, 25 °C): 13.5, 15.1, 27.1, 28.4, 46.7, 65.3, 126.4, 131.9, 138.5, 142.8 ^{119}Sn NMR ($CDCl_3$, 25 °C): δ +60.3.

4.7. Synthesis of [n-BuSnCl$_2$C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}-(HCl)] (6)

To a solution of **2** (0.5 g, 1.1 mmol) in benzene (10 mL), 0.1 M HCl (10 mL) in Et_2O was added drop-wise in 15 min to give a white precipitate. The reaction mixture was stirred for an additional 0.5 h at room temperature after which it was filtered and the residue was washed with cold benzene (10 mL). The product was dried in vacuo to give 0.39 g (72%) of a white powder. ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.98 (3H, t, $^3J_{HH} = 6.8$ Hz, Sn*Bu*), 1.46 (2H, se, $^3J_{HH} = 7.4$ Hz, Sn*Bu*), 2.05 (4H, m, Sn*Bu*), 2.61 (6H, s, N*CH*$_3$), 2.85 (6H, d, $^3J_{HH} = 4.4$ Hz, N$^+$C*H*$_3$), 3.98 (2H, b, *CH*$_2$N), 4.78 (2H, br, *CH*$_2$N$^+$), 7.21 (3H, m, Ar*H*), 10.91 (1H, b, N$^+$*H*). ^{13}C NMR ($CDCl_3$, 25 °C): 14.2, 26.1, 29.0, 44.1, 42.6, 46.5, 62.1, 64.2, 129.1, 134.0, 134.5 140.8. ^{119}Sn NMR ($CDCl_3$, 25 °C): δ −304.0. Anal. Calc. for $C_{12}H_{20}Cl_4N_2Sn$: C, 40.50; H, 6.16; N, 5.99. Found: C, 39.88; H, 6.03; N, 5.63%.

4.8. Reaction of 1 with SnCl$_4$

To a solution of **1** (0.70 g, 1.60 mmol) in hexane (30 mL), $SnCl_4$ (0.19 mL, 1.60 mmol) was added. The reaction mixture was stirred for 16 h at room temperature during which a white precipitate was formed. Next, the precipitate was isolated by filtration, dissolved in CH_2Cl_2

(10 mL) and the solution was filtered again. The product was precipitated with pentane (10 mL), isolated by filtration and dried in vacuo to give 0.74 g (66%) of a white powder. ^{1}H, ^{13}C and ^{119}Sn NMR data of the product were identical to those of **6**.

4.9. Reaction of 2 with $SnCl_4$

To a solution of **2** (0.75 g, 1.63 mmol) in toluene (10 mL), $SnCl_4$ (0.19 mL, 1.63 mmol) was added. The reaction mixture was stirred for 1 h at room temperature during which a slightly yellow oil was formed. Next, the upper toluene layer was decanted and all volatiles were removed in vacuo to give 0.20 g of a white solid which was found to be a mixture of *n*-Bu_2SnCl_2 (84%) and **8** (16%) (^{1}H NMR). The yellow oil (1.00 g) was characterized by ^{1}H NMR as a mixture of *n*-Bu_2SnCl_2 (41%) and **8** (59%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.84 (6H, s, NCH_3), 2.94 (6H, d, $^3J_{HH} = 4.8$ Hz, N^+CH_3), 4.09 (2H, s, CH_2N), 5.01 (2H, br, CH_2N^+), 7.27 (3H, m, Ar*H*), 9.78 (1H, b, N^+H); ^{119}Sn NMR ($CDCl_3$, 25 °C): δ −258.0 (**8**). The ^{1}H NMR data of *n*-Bu_2SnCl_2 were in good agreement with the literature values [24].

The same reaction was also performed in NMR tube with $CDCl_3$ as solvent and monitored by ^{1}H and ^{119}Sn NMR spectroscopy. To a solution of **2** (30 mg, 0.065 mmol) in $CDCl_3$ (0.5 mL), $SnCl_4$ (7.5 μL, 0.065 mmol) was added. After 10 min at room temperature, NMR spectra displayed the formation of equimolar amounts **7** and *n*-Bu_2SnCl_2 and traces of **8** (<5%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.83 (12H, s, NCH_3), 4.17 (4H, s, CH_2N), 7.47 (2H, d, $^3J_{HH} = 7.2$ Hz, Ar*H*), 7.36 (1H, t, $^3J_{HH} = 7.8$ Hz, Ar*H*); ^{119}Sn NMR ($CDCl_3$, 25 °C): δ −295.3 (**7**). The ^{1}H NMR data of *n*-Bu_2SnCl_2 were in good agreement with the literature values [24].

4.10. Reaction of 3 with $SnCl_4$

To a solution of **3** (1.06 g, 2.20 mmol) in pentane (20 mL), $SnCl_4$ (0.25 mL, 2.20 mmol) dissolved in pentane (20 mL) was added. The reaction mixture was stirred for 16 h at room temperature during which a white precipitate was formed. The product was isolated by filtration, washed with pentane (5 mL) and dried in vacuo. Yield: 0.91 g of a white powder. The ^{1}H and ^{119}Sn NMR spectra displayed the presence of **8** and *n*-Bu_3SnCl (11%). All volatiles were removed in vacuo to afford 0.62 g of a colorless oil (87%). The oil was identified by ^{1}H NMR spectroscopy as *n*-Bu_3SnCl [25]. Single crystals of **8** were obtained by storing a concentrated CH_2Cl_2 solution of **8** for one week at −25 °C.

5. X-ray crystal structure determinations

X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode and graphite monochromator ($\lambda = 0.71073$ Å) up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1} at a temperature of 150(2) K. The structures were solved with automated Patterson methods [26] and refined with SHELXL-97 [27] on F^2 of all reflections. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON package [28].

5.1. Compound 1

$C_{16}H_{28}Cl_2N_2Sn$, formula weight = 437.99, colorless needle, $0.61 \times 0.20 \times 0.09$ mm^3, orthorhombic, *Pbca* (no. 61), $a = 10.2522(2)$ Å, $b = 12.3622(2)$ Å, $c = 30.3866(5)$ Å, $V = 3851.19(12)$ Å^3, $Z = 8$, $D_{calc} = 1.511$ g/cm^3. 54 404 reflections were measured. An absorption correction based on multiple measured reflections was applied ($\mu = 1.601$ mm^{-1}, 0.72–0.86 correction range). 4405 reflections were unique ($R_{int} = 0.048$). Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and refined freely with isotropic displacement parameters. The methyl group at C20 was disordered over two positions. 302 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0179/0.0443. R_1/wR_2 [all reflections]: 0.0226/0.0462. $S = 1.065$. Residual electron density between −0.42 and 0.38 e/Å^3.

5.2. Compound 4

$[C_{20}H_{37}N_2Sn][C_{24}H_{20}B] \cdot CH_2Cl_2$, formula weight = 828.34, colorless block, $0.39 \times 0.27 \times 0.27$ mm^3, monoclinic, $P2_1/c$ (no. 14), $a = 14.6597(1)$ Å, $b = 16.6642(2)$ Å, $c = 22.4244(1)$ Å, $\beta = 128.2072(5)°$, $V = 4304.58(7)$ Å^3, $Z = 4$, $D_{calc} = 1.278$ g/cm^3. 79 503 reflections were measured. An absorption correction based on multiple measured reflections was applied ($\mu = 0.750$ mm^{-1}, 0.72–0.81 correction range). 9865 reflections were unique ($R_{int} = 0.054$). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in geometrically idealized positions and refined with a riding model. 487 parameters were refined with 45 restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0303/0.0697. R_1/wR_2 [all reflections]: 0.0425/0.0744. $S = 1.034$. Residual electron density between −0.50 and 0.65 e/Å^3.

5.3. Compound 6

$C_{16}H_{29}Cl_3N_2Sn$, formula weight = 474.45, colorless block, $0.36 \times 0.27 \times 0.24$ mm^3, monoclinic, $P2_1$ (no. 4), $a = 10.4185(1)$ Å, $b = 13.2394(2)$ Å, $c = 29.5834(4)$ Å, $\beta = 89.9920(5)°$, $V = 4080.58(9)$ Å^3, $Z = 8$, $D_{calc} = 1.545$ g/cm^3. 83 300 reflections were measured. An absorption correction based on multiple measured reflections was applied ($\mu = 1.644$ mm^{-1}, 0.63–0.68 correction range). 18 317 reflections were unique ($R_{int} = 0.042$). The crystal appeared to be pseudo-merohedrally twinned with a two-fold rotation about the reciprocal a^* axis as twin operation (pseudo-orthorhombic twinning). The twin fraction refined to 0.5070(4). Non-hydrogen atoms were refined with aniso-

tropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. The NH hydrogen atoms were refined freely with isotropic displacement parameters; all other hydrogen atoms were refined with a riding model. 830 parameters were refined with one restraint. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0217/0.0482. R_1/wR_2 [all reflections]: 0.0229/0.0487. $S = 1.028$. Flack parameter $x = -0.028(8)$. Residual electron density between -0.60 and 0.50 e/Å^3.

5.4. Compound 8

$C_{12}H_{20}Cl_4N_2Sn$, formula weight = 452.79, colorless needle, $0.30 \times 0.06 \times 0.06$ mm^3, tetragonal, $I4_1/a$ (no. 88), a = b=27.3794(3) Å, c = 19.4629(2) Å, V = 14590.0(3) Å^3, $Z = 32$, $D_{calc} = 1.649$ g/cm^3. 91185 reflections were measured. An analytical absorption correction was applied ($\mu = 1.977$ mm^{-1}, 0.77–0.96 correction range). 8377 reflections were unique ($R_{int} = 0.061$). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in geometrically idealized positions and refined with a riding model. The crystal structure contains large voids (1086.4 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the PLATON program [28] resulting in 334 electrons/unit cell. 343 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0305/0.0579. R_1/wR_2 [all reflections]: 0.0503/0.0618. $S = 1.009$. Residual electron density between -0.43 and 0.41 e/Å^3.

6. Supplementary data

CCDC-287817 (compound **1**), -287818 (**4**), -287819 (**6**), and -287820 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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