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Utilization of hypervalently activated organotin compounds in synthesis. Preparation and reactions of $Me_2N(CH_2)_3SnPh_3$

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Abstract

The reaction of $Me_2N(CH_2)_3SnPh_3$ (**1**) with phenol gives $Me_2N(CH_2)_3Sn(OPh)_nPh_{(3-n)}$ (**2**, $n = 1$; **3**, $n = 2$) in good yields. All the phenyl groups are cleaved off when **1** is treated with glycol or pinacol, resulting in the formation of $[Me_2N(CH_2)_3Sn]_2(OC_2H_4O)_3$ (**4**) and $[Me_2N(CH_2)_3Sn]_2(OC_2Me_4O)_3$ (**5**), respectively. Compounds **4** and **5** are transformed almost quantitatively into $Me_2N(CH_2)_3Sn(SPh)_3$ (**6**) and $[Me_2N(CH_2)_3SnCl_4]^-H^+$ (**7**) by reaction with phenyl mercaptan and trimethylchlorosilane, respectively. The reaction of **2** with triethanolamine and nitrilotriacetic acid affords the new stannatrane $Me_2N(CH_2)_3Sn(OCH_2CH_2)_3N$ (**8**) and $Me_2N(CH_2)_3Sn(OCOCH_2)_3N$ (**9**), respectively. However, the N-oxide derivative $Me_2(O)N(CH_2)_3Sn(OCOCH_2)_3N$ (**10**) is obtained by reaction of **1** with $N(CH_2COOH)_3$ in DMF. Compounds **1**-**10** have been characterized by means of ^1H, ^{13}C and ^{119}Sn NMR spectroscopy and mass spectrometry. The crystal structures of $Me_2N(CH_2)_3Sn(SPh)_3$ (**6**) and $Me_2(O)N(CH_2)_3Sn(OCOCH_2)_3N$ (**10**) have been determined by an X-ray diffraction study. The tin atom in **6** is trigonal bipyramidal with an intramolecular Sn-N distance of 2.605(6) Å. Compound **10** contains an octahedral tin with intramolecular Sn-N and Sn-ON distances of 2.231(7) and 2.101(7) Å, respectively.

1. Introduction

Controlled syntheses of oligomeric tin clusters having an Sn-O framework have potential uses as pillaring agents in clays. One group of tin compounds which appear particularly promising are those derived from the hydrolysis of organotin(IV)trihalides. Factors that determine the hydrolysis pathway of $RSnX_3$ are not yet understood. For example, the partial hydrolysis of $^iPrSnCl_3$ leads to a variety of products including $^iPrSn(OH)Cl_2 \cdot H_2O$ [1], $(^iPrSn)_9O_8(OH)_6Cl_5 \cdot DMSO$ [2] and $[(^iPrSn)_{12}O_{14}(OH)_6]^{2+}$ [3].

One common feature of the structure of these compounds is the presence of six- and four-membered rings and at least one hypervalent tin(IV) centre. The nature of the organoyl group R plays some role in determining the reaction pathway as evidenced by the fact that controlled hydrolysis of $BuSnCl_3$ also leads to a well-defined organotin cluster whereas $PhSnCl_3$ does not appear to give similar well-defined products [4].

We have decided to study the influence of an intramolecular donor on the hydrolysis path of $RSnX_3$ in order to investigate the effect on the hydrolysis pathway of the changed Lewis acidity induced by hypervalency at the tin centre. Monoorganotin trihalides $RSnX_3$ (X = halogen) are usually prepared by redistribution between R_4Sn and SnX_4. However, these reactions only give good yields for R = n-alkyl, aryl [5]. For some bulky R substituents, selective halogen cleavage reactions also have been successful for making $RSnX_3$ (X = halogen) [6]. So far there are only a few methods for making functionally substituted compounds $RSnX_3$, such as, for instance, $MeOCOCH_2CH_2SnCl_3$ [7] and o-$SnCl_3$-p-$MeC_6H_3C(:NH)p$-C_6H_4Me [8].

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In this paper, we report the synthesis of $Me_2N(CH_2)_3SnPh_3$ (1) and investigate its synthetic potential as precursor for $Me_2N(CH_2)_3SnX_3$ (X = halogen, OR, OCOR).

2. Results and discussion

2.1. Synthesis of $Me_2N(CH_2)_3SnPh_3$ (1)

3-Dimethylaminopropyl triphenylstannane (**1**) is prepared almost quantitatively from 3-dimethylaminopropylmagnesium chloride and triphenyltin chloride in THF (eqn. (1)).

$$Me_2N(CH_2)_3MgCl + Ph_3SnCl \xrightarrow[-MgCl_2]{THF} \underset{(1)}{Me_2N(CH_2)_3SnPh_3} \quad (1)$$

Compound **1** is a liquid. The ^{119}Sn NMR chemical shift of −102.2 ppm and the $^1J(^{119}Sn-^{13}CH_2)$ and $^1J(^{119}Sn-^{13}C_i)$ couplings of 400 and 487 Hz, respectively, indicate the tin atom in **1** to be tetracoordinated (see Table 2). For Ph_3SnBu, comparable with **1**, a ^{119}Sn chemical shift of −101.5 ppm has been observed [9].

Attempts to cleave all the phenyl groups from **1** by bromine or iodine failed, and resulted in mixtures of compounds which could not be separated. However, the monohalogenated compounds $Me_2N(CH_2)_3Sn(X)Ph_2$ (X = F, Cl, Br, I) could be isolated in good yields but these will be described in a separate paper in connection with their molecular structures [10].

2.2. Reaction of 1 with phenol, glycol and pinacol, respectively

When **1** is treated with the appropriate quantity of phenol in refluxing toluene, one and then two phenyl groups are cleaved off, yielding **2** as a crystalline solid and **3** as a colourless oil (eqn. (2)).

$$Me_2N(CH_2)_3SnPh_3 + nPhOH \xrightarrow[-nPhH]{toluene,\ reflex} \underset{\mathbf{2},\ n=1;\ \mathbf{3},\ n=2}{Me_2N(CH_2)_3Sn(OPh)_nPh_{3-n}} \quad (2)$$

Some cleavage of the tin–alkyl bond also occurs, and this leads to the formation of small amounts of Ph_3SnOPh. The tin atoms in **2** and **3** are pentacoordinate by intramolecular Sn–N coordination, as evidenced by their ^{119}Sn NMR chemical shifts and $^1J(^{119}Sn-^{13}C)$ coupling constants (see Table 2). Attempts to cleave off all the phenyl groups by use of an excess of phenol were not successful.

Difunctional alcohols such as glycol and pinacol do not react with **1** in boiling xylene. However, when the reaction is performed at 150°C with the alcohol itself as solvent, all the phenyl groups of **1** are cleaved off, to give the corresponding organotin alkoxides **4** and **5** (eqns. (3), (4)).

$$2Me_2N(CH_2)_3SnPh_3 \xrightarrow[-6PhH]{HOCH_2CH_2OH,\ 150°C,\ 5\ h} \underset{(4)}{[Me_2N(CH_2)_3Sn]_2(OC_2H_4O)_3} \quad (3)$$

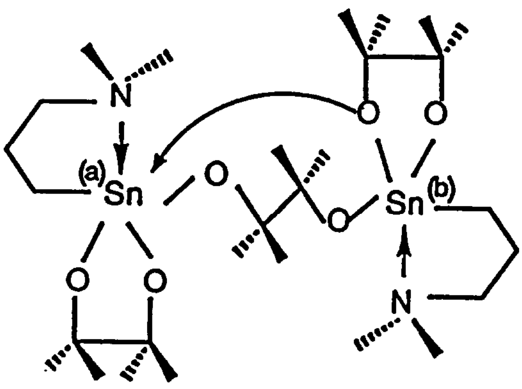
$$2Me_2N(CH_2)_3SnPh_3 \xrightarrow[-6PhH]{HOC_2Me_4OH,\ 150°C,\ 22\ h} \underset{(5)}{[Me_2N(CH_2)_3Sn]_2(OC_2Me_4O)_3} \quad (4)$$

Compound **4** is a viscous liquid whereas **5** is a solid. Both **4** and **5** show good solubility in common organic solvents and are very hygroscopic.

Although the ^1H and ^{13}C NMR spectra are rather complex, they confirm the absence of phenyl groups and show the presence of the $Me_2NCH_2CH_2CH_2$ group. Tetraphenyltin does not react with glycol or pinacol under the same conditions thus indicating the activating role of the dimethylaminopropyl group in **1**.

The ^{119}Sn NMR spectrum of **4** (in CD_2Cl_2) displays sharp resonances at −353, −357, −369 and −387 ppm and broad signals at −454, −469, −563 and −610 ppm indicating that complex structures with hexa- and possibly even hepta-coordinated tin centres build up by intra- and intermolecular Sn–O interactions. Such complex structure has also been found for $MeSn(OCH_2CH_2)_3N$ [11,12]. Despite repeated efforts, it was not possible to isolate analytically pure samples of the intermediate **4**.

The ^{119}Sn NMR spectrum of **5** (in xylene, T = 25°C) is much simpler and displays two signals of equal intensity at −282 ppm ($^2J(^{119}Sn-O-^{117/119}Sn)$ 176 Hz) and −379 ppm ($^2J(^{119}Sn-O-^{117/119}Sn)$ 176 Hz). However, the satellites disappear and the signals become broader ($\delta(^{119}Sn)$ −284, −377 ppm, $W_{1/2}$ = 350 Hz) when the spectrum is recorded at 120°C. The ^{13}C NMR spectrum (in CD_2Cl_2) displays two $SnCH_2$ (19.4, 19.7 ppm), two CH_2 (23.1, 23.5 ppm), two NCH_2 (59.6 ppm, $J(^{119}Sn-^{13}C)$ = 103 Hz; 63.1 ppm, $J(^{119}Sn-^{13}C)$ = 158 Hz) and two NCH_3 (45.4, 46.3 ppm) signals, four signals for the OC carbons at 74.6, 74.9, 75.3 and 77.7 ppm ($^2J(^{119}Sn-^{13}C)$ = 21 Hz) and five signals for the CH_3 carbons at 25.1, 25.2, 26.4, 27.2 and 27.4 ppm. The assignment of the $SnCH_2$ and CH_2 signals remains uncertain as no $J(^{119}Sn-^{13}C)$ couplings are observed, probably owing to superposition with the CH_3 signals. At −80°C, four signals of equal intensity are observed for the N-methyl carbons. Only one signal is observed for these carbons when the spectrum is recorded in xylene at 120°C.



(A)

These data suggest that **5** has structure **A**, which contains both a penta- and a hexacoordinate tin and in which the N-methyl groups are diastereotopic.

Stereomodels show that structure **A** is not strained and that further association via intermolecular Sn–O bridges is prevented by the bulk of the pinacol. The observed $^{2}J(^{119}Sn\text{–O–}^{117/119}Sn)$ couplings of 176 Hz are typical for Sn–O ··· Sn bridges and similar values have been reported for $MeSn(OCH_2CH_2)_3N$ [12] and $^{t}Bu_2Sn(OCH_2CH_2O)$ [13].

The temperature-dependent ^{13}C and ^{119}Sn NMR spectra of **5** can be explained in terms of intramolecular Sn–N and Sn–O dissociation processes. The coalescence of the four N-methyl signals in the ^{13}C NMR spectrum into two resonances of equal intensity at room temperature indicates that Sn–N dissociation is fast on the ^{13}C NMR time scale whereas the intramolecular Sn–O ··· Sn bridge remains intact. At 120°C only one resonance is observed for the N-methyl carbons indicating that Sn–O dissociation becomes fast on the NMR time scale. The collapse of the $^{2}J(^{119}Sn\text{–O–}^{117/119}Sn)$ coupling in the ^{119}Sn NMR spectrum at 120°C also indicates dissociation of the Sn–O ··· Sn bridge. But even at this temperature, the dissociation is still slow on the ^{119}Sn NMR time scale and therefore no coalescence of the two ^{119}Sn NMR signals is observed.

Although the structures of **4** and **5** could not be confirmed by X-ray studies owing to lack of suitable crystals, their composition is also supported by subsequent reactions. Thus **5** reacts almost quantitatively with phenyl mercaptan to yield the trithiolate **6** (eqn. (5)).

$$[Me_2N(CH_2)_3Sn]_2(OC_2Me_4O)_3 + 6PhSH \xrightarrow[-3HOC_2Me_4OH]{C_7H_8} 2Me_2N(CH_2)_3Sn(SPh)_3 \quad (5)$$
$$(\mathbf{6})$$

Compound **6** is a colourless crystalline solid, quite soluble in common organic solvents. Its ^{119}Sn NMR chemical shift of −26.1 ppm is comparable with that for $MeSn(SCH_2CH_2)_3N$ [11], and is in agreement with pentacoordination, as is the $^{1}J(^{119}Sn\text{–}^{13}C)$ coupling of 542 Hz for the equatorial bonded CH_2 carbon (see Table 2).

3-Dimethylaminopropyl trichlorostannane hydrochloride (**7**) is obtained almost quantitatively when **4** is treated with trimethylchlorosilane (eqn. (6)).

$$[Me_2N(CH_2)_3Sn]_2(OC_2H_4)_3 + nMe_3SiCl \xrightarrow[-3(Me_3SiOCH_2)_2]{C_7H_8/HCl} 2[Me_2N(CH_2)_3SnCl_4]^{-}\cdot H^{+} \quad (6)$$
$$(\mathbf{7})$$

The source of hydrogen chloride is hydrolysis of the excess of trimethyl chlorosilane used in the reaction. Thus, the method described here provides a very efficient route for synthesis of γ-functional substituted monoorganotin trihalides.

Compound **7** is a colourless amorphous solid which is only poorly soluble in aprotic organic solvents such as benzene and chloroform but highly soluble in pyridine, methanol and water. The ^{119}Sn NMR chemical shift of −429.8 ppm as well as the $^{1}J(^{119}Sn\text{–}^{13}C)$ coupling of 1230 Hz (Table 2) indicate hexacoordination by intramolecular Sn–N coordination and interaction with chloride.

2.3. Reactions of 1 and 2 with triethanolamine and nitrilotriacetic acid, respectively

When a solution of equimolar quantities of **1** and triethanolamine in xylene is refluxed for 77 h, the ^{119}Sn NMR spectrum shows two signals at −101.5 (70%) and −289.2 ppm (30%). The high frequency ^{119}Sn signal arises from unreacted **1** whereas the low frequency signal is assigned to the stannatrane $Me_2N(CH_2)_3Sn(OCH_2CH_2)_3N$ (**8**). Additionally, some oily precipitate, very likely to be a polymer, was also formed, but was not further analysed. However, **8** was obtained quantitatively and in shorter time from the pentacoordinate $Me_2N(CH_2)_3Sn(OPh)Ph_2$ and $N(CH_2CH_2OH)_3$ (eqn. (7)).

$$Me_2N(CH_2)_3Sn(OPh)Ph_2 + (HOCH_2CH_2)_3N \xrightarrow[-2PhH,\ -PhOH]{\text{xylene, reflux, 15 h}} Me_2N(CH_2)_3Sn(OC_2H_4)_3N \quad (7)$$
$$(\mathbf{8})$$

Compound **8** is a colourless viscous oil, quite soluble in organic solvents as well as in water. Its ^{119}Sn NMR

TABLE 1. ^{1}H NMR data for $\overset{1}{Me}_2N\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2SnX_3$, **1–3** and **6–10**

Compound	Solvent	Chemical shifts δ (ppm) (J(^{119}Sn – ^{1}H) coupling constants, Hz)					
		1	2	3	4	NCH_2	OCH_2
1 [a]	$CDCl_3$	2.09	2.27	1.85	1.48		
2 [b]	$CDCl_3$	1.74	2.27	1.92	1.60		
3 [c]	$CDCl_3$	2.40	2.10	1.80	1.50		
6 [d]	$CDCl_3$	2.40	2.25	1.70	1.25		
7	D_2O	2.67	2.97	1.95	1.32		
8	$CDCl_3$	2.36	2.40	1.77 (160)	1.21 (96)	2.94 (47)	3.95 (24)
9	D_2O	2.70	3.03	2.00 (130)	1.48 (120)	3.73 (40)	
10	D_2O	3.14	3.47	2.25	1.77	3.75 (40)	

[a] *o*-Ph 7.58; *m,p*-Ph 7.32 ppm. [b] *o*-Ph 7.75 ($^2J(^{119}Sn-^1H) = 53$ Hz); *m,p*-Ph 7.40 ppm. [c] Ph, OPh, complex pattern between 6.4 and 7.8 ppm. [d] *o*-Ph 7.35; *m,p*-Ph 7.20 ppm.

spectrum is nearly temperature-independent (Table 2). The ^{1}H NMR spectrum (Table 1) shows a triplet for the $SnCH_2$ protons, a quintet for the CH_2 protons and a complex pattern for the NCH_2 protons superimposed on the singlet for the NCH_3 protons. The NCH_2 and OCH_2 protons of the triethanolamine moiety appear as well resolved triplets. The assignment of the NCH_2 signals follows from both intensity arguments and decoupling experiments. The ^{13}C NMR spectrum (Table 2) displays single resonances for each carbon atom. The spectrum is the same when recorded in CD_2Cl_2 at -80°C.

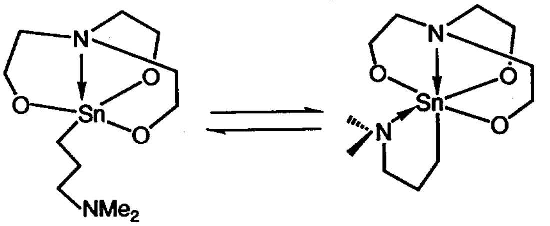
The NMR results can be interpreted in terms of an equilibrium between penta- and hexacoordinated structures **B** and **C** as the ^{119}Sn NMR chemical shift lies between -246 ppm measured for the pentacoordinated $^tBuSn(OCH_2CH_2)_3N$ [11] and -383 ppm of the hexacoordinated tin site of $^nBuSn(OCH_2CH_2)_3N$ [11]. The equilibrium is fast on the ^{13}C NMR time scale, *i.e.* the low temperature spectrum does not show any splitting of the signals of the ring methylene carbons. Furthermore, the position of the equilibrium, *i.e.* the ratio of **B** and **C**, is temperature-independent. Thus, **8** differs from n-butylstannatrane $^nBuSn(OCH_2CH_2)_3N$

TABLE 2. ^{13}C and ^{119}Sn NMR data for $\overset{1}{Me}_2N\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{Sn}X_3$, **1–3** and **6–10**

Compound	Solvent	Chemical shifts δ (ppm) ($J(^{119}Sn-^{13}C)$ coupling constants, Hz)							
		1	2	3	4	5	NCH_2	OCH_2	OCO
1 [a]	$CDCl_3$	45.0	62.8 (63)	23.9 (20)	7.9 (400)	−102.2 [b]			
2 [c]	$CDCl_3$	46.4	61.2 (55)	21.3 (27)	9.2 (595)	−150.4 [b]			
3 [d]	$CDCl_3$	46.1	60.1	21.7	17.2	−233.1 [b]			
6 [e]	$CDCl_3$	46.0	59.7 (76)	21.0 (41)	18.6 (542)	−26.1			
7	CD_3OD	44.5	61.1 (195)	23.2 (50)	41.1 (1230 [f])	−429.8			
8	$CDCl_3$	45.9	60.1 (102)	19.2 (44)	11.4 (990)	−291.2 [g]	57.2 (112)	58.4 (46)	
9	D_2O	41.4	56.9 (175)	18.1 (52)	16.3 (1120)	−425.7	56.8/62.7		169.5/173.0
10	D_2O	58.1	69.1 (104)	19.2 (69)	16.8 (1049)	−403.3	62.8		172.9

[a] C_i 138.6 ($^1J(^{119}Sn-^{13}C) = 487$ Hz), C_o 136.5 ($^2J(^{119}Sn-^{13}C) = 38$ Hz), C_m 128, C_p 128.3 ppm. [b] In CH_2Cl_2. [c] C_i 141.0 ($^1J(^{119}Sn-^{13}C)$ 675 Hz, C_o 136 ($^1J(^{119}Sn-^{13}C)$), C_m 128.3 ($^3J(^{119}Sn-^{13}C)$ 60.2 Hz), C_p 129.0 ppm. [d] Ph, OPh carbons show a complex pattern between 118.7 and 139.4 ppm. [e] C_i 1330, C_o 135.8, C_m 128.4, C_p 126.5 ppm. [f] Only the low frequency side of the couplings is visible. The high frequency part is superimposed by the CD_3OD signals. [g] $T = 55$°C, δ (^{119}Sn) -293.6 ppm; δ (^{119}Sn) -366 ppm (in H_2O).

which shows auto-association *via* intermolecular Sn–O ··· Sn bridges [11]. In fact, the process **A** ⇆ **B** maps the nucleophilic attack at a pentavalent tin centre.



(B) (C)

This attack is very likely to be *cis* as was shown by X-ray studies on naphthylaminosilatrane [14], and bis(naphthylamino)methyl-iodostannane [15].

The reaction of **2** with nitrilotriacetic acid to give **9** proceeds even faster than the tin-phenyl bond cleavage by triethanolamine (eqn. (8)).

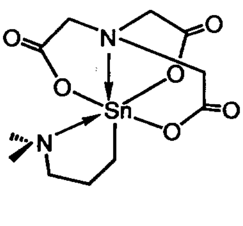
$$Me_2N(CH_2)_3Sn(OPh)Ph_2 + (HOCOCH_2)_3N \xrightarrow[-2PhH,\ -PhOH]{dmf,\ 130°C,\ 1\ h} Me_2N(CH_2)_3Sn(OCOCH_2)_3N \quad (8)$$

(9)

Compound **9** separates as a solid quantitatively from the hot reaction mixture. It melts with decomposition and is soluble only in water. The ^{119}Sn NMR chemical shift of −425.7 ppm and $^1J(^{119}Sn-^{13}C)$ coupling of 1120 Hz (Table 2) indicate that the tin is at least hexacoordinate. Similar values have been observed for $RSn(OCOCH_2)_3N$ (R = Me, ^tBu) [16].

The ^{13}C NMR spectrum of **9** (Table 2) displays single resonances for each carbon of the dimethylaminopropyl chain but two resonances of different intensity for the NCH_2 and OCO carbons, respectively, of the nitrilotriacetic acid part. These resonances become broader at 80°C, whereas the signals for the dimethylaminopropyl chain remain sharp. However, no splitting was observed for the signal of the NCH_2 protons in the ^1H NMR spectrum (Table 1).

The NMR spectroscopic results can be interpreted in terms of structure **D**. The intramolecular Sn–NMe_2 coordination is kinetically stable on the ^{13}C NMR time scale but labile on the ^1H NMR time scale.



(D)

A somewhat surprising result is observed when **1** is treated with nitrilotriacetic acid in DMF at 120–130°C. After 6 h the ^{119}Sn NMR spectrum displays four signals at −110.2(I), −392.5(II), −403.0(III) and −423.7(IV) ppm indicating the presence of **1** (signal I), **9** (signal IV) and two new species (signals II and III). After a further 16 h at 130°C, the solution has turned a deep red colour and the signals I and IV have disappeared. The ^{119}Sn NMR spectrum of this red solution shows resonances II and III with an intensity ratio of about one to four. Work-up of this solution gives colourless crystals of **10** (eqn. (9)).

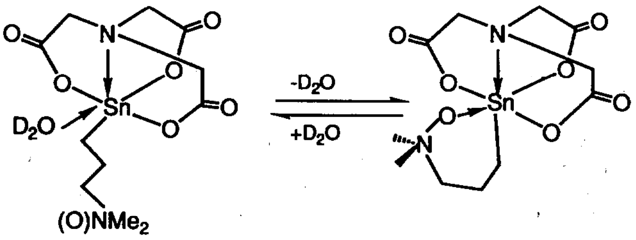
$$Me_2N(CH_2)_3SnPh_3 + (HOCOCH_2)_3N \xrightarrow[-3PhH]{dmf,\ 22\ h} Me_2(O)N(CH_2)_3Sn(OCOCH_2)_3N \quad (9)$$

(10)

In contrast to **9**, compound **10** is not only soluble in water but also in DMF and methanol.

The ^{119}Sn chemical shift and $^1J(^{119}Sn-^{13}C)$ coupling (Table 2) of **10** are only slightly different from **9**, indicating a similar environment around tin. The high frequency shifts for the NCH_3 and NCH_2 carbons and protons of the dimethylaminopropyl chain in the ^{13}C (Table 2) and ^1H (Table 1) NMR spectra are in agreement with structure established for the N-oxide in the solid state by X-ray diffraction (see below).

In contrast to **9**, the ^{13}C NMR spectrum of **10** shows no splitting of the NCH_2 or OCO signals. This indicates the Sn–O dissociation (**E** ⇆ **F**) is fast on the ^{13}C NMR time scale, and reveals the kinetic lability of the six-membered chelate in **10** compared with the relative stability of the five-membered chelate in **9**.



(E) (F)

2.4. *Molecular structure of 6*

The molecular structure of **6** is shown in Fig. 1, selected bond lengths and bond angles are summarized in Table 3. The tin atom in **6** is distorted trigonal bipyramidal coordinated with N(1) and S(1) in axial and C(1), S(2) and S(3) in equatorial positions. The sum of the equatorial bond angles S(2)–Sn–S(3), S(2)–Sn–C(1) and S(3)–Sn–C(1) is 351.3°. The sum of the

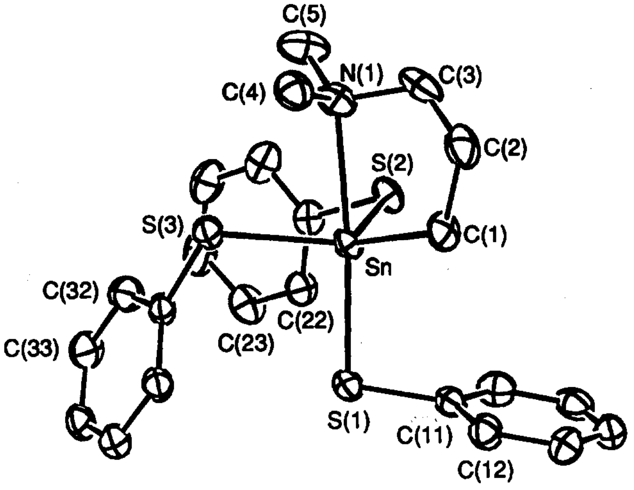


Fig. 1. Molecular structure and crystallographic numbering scheme employed for $[Me_2N(CH_2)_3Sn(SPh)_3]$ (**6**).

axial bond angles S(1)–Sn–S(2), S(1)–Sn–S(3) and S(1)–Sn–C(1) amounts to 300°. The tin atom lies 0.3954(5) Å (*i.e.* in the direction of the S(1) atom) out of the trigonal plane defined by the S(2), S(3) and C(1) atoms. Deviation from the ideal trigonal bipyramidal structure is further demonstrated by the S(1)–Sn–N(1) angle of 168.4(1)°. The intramolecular Sn–N distance of 2.605(6) Å is rather weak and reflects the poor Lewis acidity of the tin centre. In $MeSn(SCH_2CH_2)_3N$, which is comparable with **6** in terms of its substituent pattern $CSnS_3$, the Sn–N distance is much shorter, at only 2.43 Å [17]. Thus the stronger Sn–N interaction in the latter compound is a result of the *atrane* frame rather than of stronger Lewis acidity of the tin atom

As expected for a trigonal bipyramid, the axial Sn–S(1) bond length (2.480(2) Å) is greater than the equatorial Sn–S(2) (2.425(2) Å) and Sn–S(3) (2.419(2) Å) distances. However, this difference is smaller than in $[MeN(CH_2CH_2CH_2)_2SnS]_2$ [3] and $[CH_3OOCCH_2CH_2(Me_2NCS_2)SnS]_2$ [18].

TABLE 3. Selected interatomic parameters (Å,°) for $Me_2N(CH_2)_3Sn(SPH)_3$ (**6**)

Sn–S(1)	2.480(2)	Sn–S(2)	2.425(2)
Sn–S(3)	2.419(2)	Sn–N(1)	2.605(6)
Sn–C(1)	2.150(6)	S(1)–C(11)	1.783(7)
S(2)–C(21)	1.790(7)	S(3)–C(31)	1.775(7)
N(1)–C(3)	1.46(1)	C(1)–C(2)	1.53(1)
C(2)–C(3)	1.51(1)		
S(1)–Sn–S(2)	103.0(1)	S(1)–Sn–S(3)	96.2(1)
S(1)–Sn–N(1)	168.4(1)	S(1)–Sn–C(1)	100.8(2)
S(2)–Sn–S(3)	114.4(1)	S(2)–Sn–N(1)	88.6(1)
S(2)–Sn–C(1)	109.8(2)	S(3)–Sn–N(1)	77.9(1)
S(3)–Sn–C(1)	127.1(2)	N(1)–Sn–C(1)	75.6(2)
Sn–S(1)–C(11)	99.0(2)	Sn–S(2)–C(21)	102.9(2)
Sn–S(3)–C(31)	107.5(2)	Sn–N(1)–C(3)	96.2(4)
Sn–N(1)–C(4)	113.3(4)	Sn–N(1)–C(5)	115.0(4)
C(3)–N(1)–C(4)	111.7(6)	C(3)–N(1)–C(5)	110.6(6)
C(4)–N(1)–C(5)	109.5(6)	Sn–C(1)–C(2)	115.2(5)

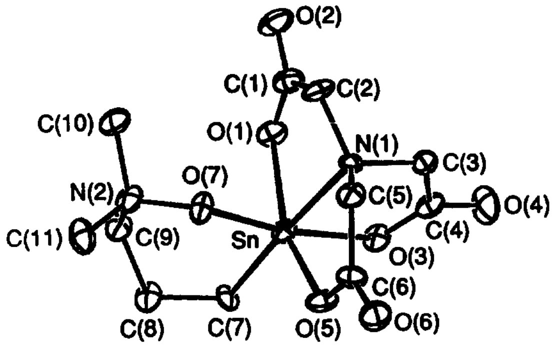


Fig. 2. Molecular structure and crystallographic numbering scheme employed for $[Me_2(O)N(CH_2)_3Sn(OCOCH_2)_3N]$ (**10**).

2.5. Molecular structure of 10

The molecular structure of **10** is shown in Fig. 2, selected bond lengths and bond angles are listed in Table 4. The Sn atom exists in a distorted octahedral geometry with the axial positions being defined by the N(1) and C(7) atoms (*i.e.* N(1)–Sn–C(7) is 176.6(3)°) leaving a basal plane defined by the four O atoms

TABLE 4. Selected interatomic parameters (Å,°) for $Me_2(O)N(CH_2)_3Sn(OCOCH_2)N$ (**10**)

Sn–O(1)	2.103(6)	Sn–O(3)	2.081(6)
Sn–O(5)	2.090(6)	Sn–O(7)	2.101(6)
Sn–N(1)	2.231(7)	Sn–C(7)	2.098(9)
O(1)–C(1)	1.30(1)	O(2)–C(1)	1.21(1)
O(3)–C(4)	1.28(1)	O(4)–C(4)	1.22(1)
O(5)–C(6)	1.30(1)	O(6)–C(6)	1.23(1)
O(7)–N(2)	1.436(9)	N(1)–C(2)	1.49(1)
N(1)–C(3)	1.50(1)	N(1)–C(5)	1.49(1)
N(2)–C(9)	1.51(1)	N(2)–C(10)	1.49(1)
N(2)–C(11)	1.47(1)	C(1)–C(2)	1.54(1)
C(3)–C(4)	1.53(1)	C(5)–C(6)	1.51(1)
C(7)–C(8)	1.53(1)	C(8)–C(9)	1.51(1)
O(1)–Sn–O(3)	88.5(3)	O(1)–Sn–O(5)	154.0(3)
O(1)–Sn–O(7)	89.4(3)	O(1)–Sn–N(1)	76.9(3)
O(1)–Sn–C(7)	106.5(3)	O(3)–Sn–O(5)	89.3(3)
O(3)–Sn–O(7)	166.0(2)	O(3)–Sn–N(1)	80.5(2)
O(3)–Sn–C(7)	99.5(3)	O(5)–Sn–O(7)	86.5(3)
O(5)–Sn–N(1)	77.2(2)	O(5)–Sn–C(7)	99.4(3)
N(1)–Sn–C(7)	176.6(3)	Sn–O(1)–C(1)	118.0(6)
Sn–O(3)–C(4)	118.1(6)	Sn–O(5)–C(6)	117.6(5)
Sn–O(7)–N(2)	122.5(5)	Sn–N(1)–C(2)	106.8(5)
Sn–N(1)–C(3)	107.6(5)	Sn–N(1)–C(5)	105.5(5)
C(2)–N(1)–C(3)	111.3(7)	C(2)–N(1)–C(5)	114.3(7)
C(3)–N(1)–C(5)	111.0(6)	O(7)–N(2)–C(9)	113.2(6)
O(7)–N(2)–C(10)	107.5(8)	O(7)–Sn–C(11)	105.7(7)
C(9)–N(2)–C(10)	109.3(8)	C(9)–N(2)–C(11)	111.2(8)
C(10)–N(2)–C(11)	109.6(9)	Sn–C(7)–C(8)	110.7(6)

which are coplanar to within 0.115(7) Å; the Sn atom lies 0.3597(5) Å out of this plane in the direction of the C(7) atom. The intramolecular Sn–N distance is rather short (2.231(7) Å) and exceeds the sum of the covalent radii of tin and nitrogen (2.15 Å [19]) by only 0.08 Å. In fact, **10** is a mono-organotin tricarboxylate, a class of compounds for which only a few crystal structures have been reported so far [20]. In these structures, the carboxylate ligands are bidentate. In **10**, however, the carboxylate groups are monodentate as a result of the intramolecular Sn–N and Sn–ON coordination, which also prevents the formation of higher oligomers.

3. Experimental details

Solvents were dried by standard methods and distilled prior to use. Elemental analyses were carried out by the Microanalytical Laboratory of the Australian National University, Canberra. Solution NMR spectra were recorded on a JEOL GX 270 FT NMR spectrometer at 200.17 (^{1}H), 67.84 (^{13}C) and 100.75 (^{119}Sn) MHz. Chemical shifts are relative to external Me_4Si (^{1}H, ^{13}C) and Me_4Sn (^{119}Sn). Spectra recorded in D_2O were referenced against internal acetone at 2.0 (^{1}H) and 30.3 (^{13}C) ppm. Mass spectra were recorded on a Hewlett Packard GC/MS 5988A system. Only fragments containing the isotope ^{120}Sn are given.

3.1. *Crystallography*

Intensity data for crystals of [$Me_2N(CH_2)_3Sn(SPh)_3$] (**6**) (0.06 × 0.18 × 0.36 mm³) and [$Me_2(O)N(CH_2)_3$-$Sn(OCOCH_2)_3N$] (**10**) (0.15 × 0.20 × 0.41 mm³) were measured at 293 K on an Enraf-Nonius CAD4F diffractometer fitted with nickel-filtered Cu Kα radiation, $\lambda = 1.5418$ Å. The ω–2θ scan technique was employed to measure data up to a maximum Bragg angle of 75.0° in each case. The data sets were corrected for Lorentz and polarization effects and for absorption using an analytical procedure [21]; max. and min. transmission factors were 0.554 and 0.082, respectively for **6** and 0.287 and 0.082, respectively for **10**. Relevant crystal data are given in Table 5.

The structures were solved from the interpretation of the Patterson synthesis in each case and refined by a full-matrix least-squares procedure based on F [21] using reflections which satisfied the $I \geq 2.5\sigma(I)$ criterion of observability. Non-H atoms were refined with anisotropic thermal parameters and H atoms were included in each model at their calculated positions. After the inclusion of a weighting scheme of the form $w = k/[\sigma^2(F) + |g|F^2]$, the refinements were continued until convergence; final refinement details are listed in Table 5. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied for each model. Fractional atomic coordinates are listed in Tables 6 and 7 and the numbering schemes employed are shown in Figs. 1 and 2 which were drawn with ORTEP [22] at 25% probability ellipsoids. Scattering factors were as incorporated in the SHELX76 program [21] and the refinement was performed on a SUN4/280 computer. Other crystallographic details (available from E.R.T.T.) comprise thermal parameters, H-atom parameters, all bond distances and angles, and tables of observed and calculated structure factors.

TABLE 5. Crystal data and refinement details for $Me_2N(CH_2)_3$-$Sn(SPh)_3$ (**6**) and $Me_2(O)N(CH_2)_3Sn(OCOCH_2)_3N$ (**10**)

	6	10
Formula	$C_{23}H_{27}NS_3Sn$	$C_{11}H_{18}N_2O_7Sn$
Mol. wt.	532.2	409.0
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	9.815(1)	10.115(1)
b (Å)	11.046(1)	11.903(1)
c (Å)	11.939(1)	12.072(1)
α (°)	99.75(1)	90
β (°)	110.25(1)	95.60(1)
γ (°)	90.31(1)	90
V (Å³)	1194.0	1446.5
Z	2	4
D_c (g cm^{-3})	1.481	1.878
$F(000)$	520	816
μ (cm^{-1})	106.98	139.75
No. of data collected	4932	3278
No. of unique data	4916	2978
No. of unique reflections used with $I \geq 2.5\sigma(I)$	3867	2472
R	0.064	0.071
k	1	12.5
g	0.0016	0.0004
R_w	0.068	0.080
Residual$_{\rho max}$ (e Å^{-3})	2.00 (near Sn)	2.31 (near Sn)

3.2. *Synthesis of (3-dimethylaminopropyl)triphenylstannane, $Me_2N(CH_2)_3SnPh_3$ (1)*

A solution of $Me_2N(CH_2)_3MgCl$, prepared from 27 g (0.22 mol) of $Me_2N(CH_2)_3Cl$ and 5.3 g of magnesium in 100 ml of dry THF was added dropwise with magnetic stirring under an atmosphere of argon to 76 g (0.197 mol) of Ph_3SnCl dissolved in 300 ml of THF. The mixture was refluxed for 1 h and most of the THF removed by distillation. Ether (200 ml) was added and the mixture hydrolyzed under ice cooling with saturated ammonium chloride solution. The organic layer was separated and the aqueous layer extracted three times with 50 ml of ether. The combined organic layers were dried over sodium sulphate. The ether was evaporated and the residue dissolved in 50 ml of hexane. The

TABLE 6. Fractional atomic coordinate ($\times 10^5$ for Sn, $\times 10^4$ for remaining atoms) for $Me_2N(CH_2)_3Sn(SPh)_3$ (6)

Atom	x	y	z
Sn	17655(5)	17876(4)	23283(4)
S(1)	582(2)	3733(2)	1976(2)
S(2)	3569(2)	2361(2)	4352(2)
S(3)	−381(2)	629(2)	2234(2)
N(1)	2612(6)	−446(5)	2284(5)
C(1)	2821(7)	1561(6)	1007(6)
C(2)	3700(8)	426(7)	987(7)
C(3)	3954(7)	−185(7)	2073(7)
C(4)	1611(8)	−1348(7)	1280(7)
C(5)	2935(9)	−903(7)	3433(7)
C(11)	1967(6)	4522(6)	1662(5)
C(12)	1842(7)	4548(7)	474(6)
C(13)	2881(8)	5158(7)	205(7)
C(14)	4054(7)	5769(6)	1113(7)
C(15)	4188(7)	5778(6)	2283(7)
C(16)	3177(7)	5172(6)	2582(6)
C(21)	2481(7)	2634(6)	5291(5)
C(22)	1845(7)	3739(6)	5397(6)
C(23)	1123(8)	4026(7)	6204(6)
C(24)	1022(8)	3205(8)	6901(7)
C(25)	1669(8)	2133(7)	6840(7)
C(26)	2418(8)	1811(7)	6007(6)
C(31)	−1530(6)	1694(5)	2675(6)
C(32)	−1591(7)	1810(7)	3839(6)
C(33)	−2562(8)	2552(7)	4166(7)
C(34)	−3473(7)	3204(6)	3353(7)
C(35)	−3428(7)	3107(6)	2208(7)
C(36)	−2441(7)	2360(6)	1871(6)

solution was stored overnight in a fridge and the precipitate formed filtered off. The hexane was removed *in vacuo* leaving 60.5 g (70%) of **1** as a viscous slightly yellow oil. Anal. Found: C, 63.19; H, 6.22; N, 2.98. $C_{23}H_{27}NSn$ (436.18) calcd.: C, 63.33; H, 6.24; N. 3.21%. Mass spectrum (EI). m/e (rel. abundance, %) fragment: 437 (< 5) M^+; 360 (15) $Me_2N(CH_2)_3SnPh_2^+$; 351 (68) Ph_3Sn^+; 197 (68) $Me_2N(CH_2)_3SnPh^+$; 134 (100) $SnCH_2^+$ or SnN^+; 120 (55) Sn^+.

TABLE 7. Fractional atomic coordinate ($\times 10^5$ for Sn, $\times 10^4$ for remaining atoms) for $Me_2(O)N(CH_2)_3Sn(OCOCH_2)_3N$ (10)

Atom	x	y	z
Sn	609(5)	16816(4)	13784(4)
O(1)	−232(7)	157(5)	2200(5)
O(2)	−807(9)	−607(6)	3758(7)
O(3)	−1724(7)	1405(6)	407(5)
O(4)	−3912(8)	1429(9)	364(8)
O(5)	−184(7)	3409(5)	1120(6)
O(6)	−880(7)	5001(5)	1792(7)
O(7)	1556(6)	2105(5)	2641(5)
N(1)	−1359(6)	2150(6)	2604(6)
N(2)	2786(8)	1497(6)	2815(7)
C(1)	−714(10)	198(8)	3156(8)
C(2)	−1117(10)	1361(8)	3560(7)
C(3)	−2735(9)	2021(8)	2039(8)
C(4)	−2810(10)	1584(7)	846(9)
C(5)	−1068(10)	3346(6)	2888(8)
C(6)	−733(9)	3980(7)	1869(7)
C(7)	1393(9)	1339(9)	194(8)
C(8)	2831(11)	1385(11)	726(8)
C(9)	3067(10)	781(9)	1829(7)
C(10)	2710(11)	763(11)	3810(8)
C(11)	3819(10)	2350(10)	3058(10)

3.3. *Synthesis of (3-dimethylaminopropyl)phenoxydiphenylstannane, $Me_2N(CH_2)_3Sn(OPh)Ph_2$ (2)*

A solution of 6.71 g (0.015 mol) of **1** and 1.95 g (0.02 mol) of phenol in toluene was refluxed for 5 h. The solvent was evaporated and the resulting white residue heated to 150° at 4 mmHg to remove any unchanged phenol. The solid was dissolved in dichloromethane/hexane (70/30) and the solution kept in the refrigerator to yield 5.84 g (86%) of **2** as colourless crystals, m.p. 108–111°C. Anal. Found: C, 62.10, H, 6.13, N, 2.87. $C_{23}H_{27}NOSn$ (452.18) calcd.: C, 61.09; H, 6.02; N, 3.10%. Mass spectrum (EI): 360 (33) $Me_2N(CH_2)_3SnPh_2^+$, 274 (< 5) Ph_2Sn^+, 197 (20) $PhSn^+$, 120(11) Sn^+.

3.4. *Synthesis of (3-dimethylaminopropyl)diphenoxyphenylstannane, $Me_2N(CH_2)_3Sn(OPh)_2Ph$ (3)*

A solution of 2 g (4.58 mmol) of **2** and 0.89 g (9.47 mmol) of phenol in toluene (20 ml) was refluxed for 6 h. The solvent was evaporated and the resulting oil kept for 20 min at 150°C and 4 mmHg to remove unchanged phenol. The residue was dissolved in dichloromethane/hexane (70 : 30) and the solution kept in the refrigerator to induce precipitation of an oil. The supernatent layer was decanted off to give 1.76 g (82%) of **3** as an oil. No elemental analysis was carried out. Mass spectrum (EI): 469 (< 5) $Me_2N(CH_2)_3Sn(OPh)_2Ph^+$; 376 (19) $Me_2N(CH_2)_3Sn(OPh)Ph^+$; 283 (< 5) $Me_2N(CH_2)_3SnPh^+$; 197 (13) $PhSn^+$; 120 (9) Sn^+.

3.5. *Reaction of 1 with ethylene glycol to give $[Me_2N(CH_2)_3Sn]_2(OC_2H_4O)_3$ (4)*

A mixture of 1 g (2.29 mmol) of **1** and 1.5 g (24.2 mmol) of glycol was stirred for 5 h at 150°C. The resulting dark brown viscous liquid was washed with 5 ml of dichloromethane. The residue was heated *in vacuo* (4 mmHg) for 1 h at 150°C to remove all volatile material and leave **4** as a dark brown glassy highly hygroscopic solid. No elemental analysis was performed. Mass spectrum (EI): 532 (< 5) $[Me_2N(CH_2)_3Sn]_2(OC_2H_4O)_2^+$, 446 (< 5) $Me_2N(CH_2)_3Sn_2(OC_2H_4O)_2^+$, 266 (< 5) $Me_2N(CH_2)_3Sn(OC_2H_4O)^+$, 120 (< 5) Sn^+.

3.6. *Reaction of 1 with pinacol to give $[Me_2N(CH_2)_3Sn]_2(OC_2Me_4O)_2$ (5)*

A mixture of 1.5 g (3.43 mmol) of **1** and 1 g (9 mmol) of pinacol was stirred for 22 h at 150°C. All volatile material was then removed *in vacuo* (4 mmHg) at 150°C to leave 0.97 g (75%) of **5** as a hygroscopic solid, m.p. 140–145°C. Anal. Found: C, 44.54; H, 7.62; N, 3.12. $C_{28}H_{60}N_2O_6Sn_2$ (758.21) calcd.: C, 44.36; H, 7.98; N, 3.69%. Mass spectrum (NCl): 674 (35) $Me_2N(CH_2)_3Sn_2(OC_2Me_4O)_3^+$.

3.7. Synthesis of 3-dimethylaminopropyltin trithiophenolate $Me_2N(CH_2)_3Sn(SPh)_3$ (6)

A mixture of 2.04 (4.68 mmol) of **1** and 1.47 g (12.46 mmol) of pinacol was heated at 150°C for 30 h. The volatile material was removed *in vacuo* and the residue dissolved in dichloromethane. The ^{119}Sn NMR spectrum of this solution confirmed the complete converson of **1** into **5**. Subsequently, 1.54 g (14 mmol) of phenylmercaptan were added and the mixture was stirred for 10 min. The solvent was removed *in vacuo* and the residue recrystallized from methanol to give 2 g (80%) of **6** as colourless crystals, m.p. 105–106°C. Anal. Found: C, 52.43; H, 5.19; N, 2.66. $C_{23}H_{27}NS_3Sn$ (532.38) calcd.: C, 51.89; H, 5.12; N, 2.63%.

3.8. Synthesis of 3-dimethylaminopropyltrichlorostannane hydrochloride $[Me_2N(CH_2)_3SnCl_4]^- H^+$ (7)

A mixture of 6 g (13.8 mmol) of **1** and 6 g (96.8 mmol) of glycol was stirred at 150°C for 6 h. All volatile material was removed *in vacuo* and the residue dissolved in 50 ml of dry toluene. Then 10.5 ml (82.6 mmol) of trimethylchlorosilane were added from a syringe with stirring. After 6 h stirring the precipitate was filtered off, and suspended in a mixture of 50 ml of dry dichloromethane and 5 ml of trimethylchlorosilane. The mixture was stirred for a further 18 h and the then colourless precipitate was filtered off, washed with ether, and dried *in vacuo* to give 4.1 g (95%) of **7**, m.p. 175–180°C. Anal. Found C, 16.94; H, 3.76; N, 3.88; Cl, 40.66. $C_5H_{13}Cl_4NSn$ (347.69) calcd.: C, 17.27; H, 3.77; N, 4.03; Cl, 40.79%.

3.9. Synthesis of 3-dimethylaminopropylstannatrane $Me_2N(CH_2)_3Sn(OCH_2CH_2)_3N$ (8)

A solution of 0.923 g (2 mmol) of **2** and 0.298 g (2 mmol) of triethanolamine in 10 ml of xylene was refluxed for 24 h with stirring. The solvent was removed *in vacuo* and the residue kept for 1 h at 100°C and 0.1 mmHg to remove the phenol formed in the reaction yielding 0.65 g (93%) of **8** as a colourless viscous oil. No elemental analysis was performed.

3.10. Synthesis of 5-(3-dimethylaminopropyl)triptychloxazastannolidone $Me_2N(CH_2)_3Sn(OCOCH_2)_3N$ (9)

A mixture of 1.06 g (2.34 mmol) of **2** and 0.448 g (2.34 mmol) of nitrilotriacetic acid in 15 ml of DMF was stirred magnetically and heated to 140°C. After 1 h precipitation of **9** occurred. The colourless precipitate was filtered off, washed twice with dichloromethane, and dried, to give 0.8 g of **9** (90%), m.p. 240–260°C (decomposition). Anal. Found: C, 32.93; H, 4.87; N, 7.31. $C_{11}H_{18}N_2O_6Sn$ (392.98) calcd.: C, 33.62; H, 4.62; N, 7.13%.

3.11. Synthesis of 5-(3-dimethylaminopropyl-N-oxide)-triptychoxazastannolidone $Me_2(O)N(CH_2)_3Sn(OCOCH_2)_3N$ (10)

A solution of 1.056 g (2.4 mmol) of **1** and 0.463 g (2.4 mmol) of nitrilotriacetic acid in 30 ml of DMF was kept for 22 h at 120°C. The solvent was then removed *in vacuo* to yield a brown viscous residue. Methanol was added to give a deep red solution and some precipitate (0.2 g, m.p. > 360°C). The mixture was filtered and the filtrate kept in the fridge to give 0.2 g (20.4%) of **10** as colourless crystals, m.p. 280°C (decomposition). Anal. Found: C, 32.34; H, 4.31; N, 6.80. $C_{11}H_{18}N_2O_7Sn$ (408.98) calcd.: C, 32.30; H, 4.40; N, 6.85%.

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