Pentacoordinated tetraorganotin and silicon compounds—synthesis and structures

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Abstract - Starting from di- and trifunctional Grignard reagents of the general types $E(CH_2CH_2CH_2MgCl)_2$ (E= NMe, O, S) and $N(CH_2CH_2CH_2MgCl)_3$ the cyclic organotin and organosilicon compounds $R_2M(CH_2CH_2CH_2)_2E$ and $RM(CH_2CH_2CH_2)_3N$ (M= Si, Sn; R= Cl, Br, I, CH_3) are described. X-ray studies confirm these compounds to exhibit pentacoordinated structures with intramolecular donor-acceptor interactions. The strength of these interactions depends from the nature of the substituents bonded to the metal center. The dynamic processes which are observed by nmr investigations are interpreted in terms of a dissociation-inversion mechanism and an "in-out" equilibrium. First results are reported concerning the preparation of a two nitrogen containing difunctional Grignard reagent and its reaction with tin tetrachloride providing hexacoordinated tin compounds.

INTRODUCTION

Very often classical structural formulas give the idea that only those relations between atoms are of importance being symbolized by conventional two-electron bonds. However, many details of the interactions between atoms and atom groups being important for the reactivity as well as the conformation and the ground state energies of molecules are not obvious by structural formulas commonly used by chemists. Most of these intramolecular effects are caused by orbital interactions. In the area between coordination chemistry and intramolecular interactions the 1-element-5-stanna(sila)bicyclo [3.3.0] octanes and the 1-aza-5-stanna(sila)tricyclo [3.3.3.0] undecanes should be of considerable interest. Furthermore, the preparation of these compounds should answer the question after the extension of the coordination sphere in tetraorganotin and tetraorganosilicon compounds.

In the last years it has been shown by a lot of investigations that bi- and tricyclic derivatives of tin (ref.1) and silicon (ref.2) of the types (A), (B) and (C) exhibit trigonal bipyramidal structures with strong intramolecular 1,5-interactions. Usually, these compounds are designated as diptych and triptych derivatives, respectively, as well as metallatranes.


M = Si , Sn
E = NR, S, O, PR
Y = O, S, NR

(A)   (B)   (C)
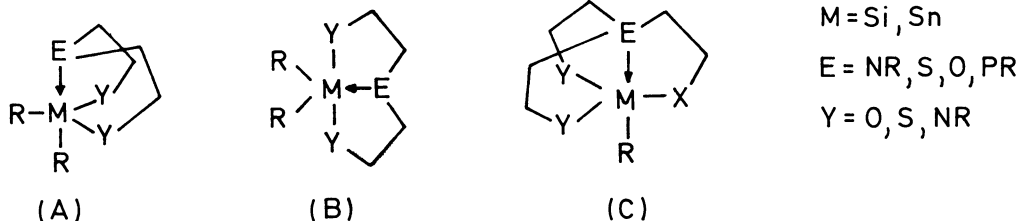
In the following paper we will use the diptych and triptych nomenclature. Therefore, a compound of the type (A) with M=Sn, E=N, Y=S and R=Me is designated as dimethyldiptychoxazstannolidine.
The hitherto known investigations carried out on compounds of the types (A) and (B) lead to the following general conclusions. (i) The M-E coordination depends from the electronegativity of the atoms attached to the tin atom (ref.3). (ii) The polarity role is valid (isomers A and B)(ref.4). (iii) The dynamic stereochemistry of these compounds is interpreted in terms of a dissociation-inversion mechanism (ref.1).
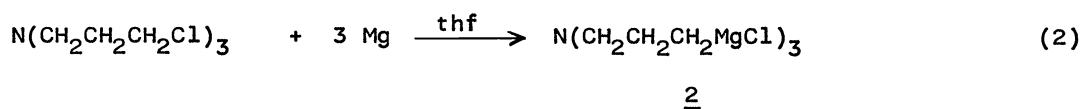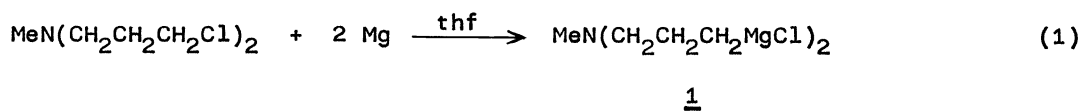
(iiii) There is no correlation between the structure of the compounds and
their biological activity.

In connection with these results the structure of the corresponding tetra-
organotin and tetraorganosilicon compounds (type D and E) should be inter-
esting because these derivatives can also be interpreted in terms of ex-
perimental accessible intermediates along the SN2 reaction pathways of
these elements. Furthermore, a comparison with the stereochemical behaviour
of manxine (F)(ref.5) becomes possible and last not least results can be
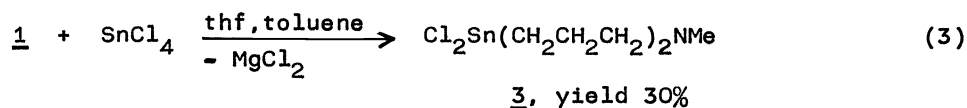expected being of general importance for the organometallic chemistry.

$$
\begin{array}{ccc}
\text{(D)} & \text{(E)} & \text{(F)}
\end{array}
$$
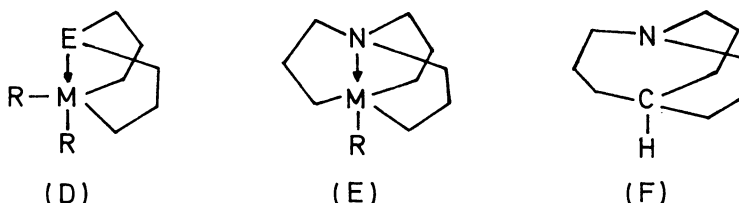
RESULTS

The nitrogen containing di- and trifunctional Grignard reagents **1** and **2** are
available in quantitative yields by the reaction of bis or tris(γ-chloro-
propyl)amines with magnesium in thf (equ.1,2).

$$MeN(CH_2CH_2CH_2Cl)_2 \ + \ 2\ Mg \ \xrightarrow{\text{thf}} \ MeN(CH_2CH_2CH_2MgCl)_2 \qquad (1)$$

$$\underline{\mathbf{1}}$$

$$N(CH_2CH_2CH_2Cl)_3 \ + \ 3\ Mg \ \xrightarrow{\text{thf}} \ N(CH_2CH_2CH_2MgCl)_3 \qquad (2)$$

$$\underline{\mathbf{2}}$$

They are stable in solution over a long time and can be handled without
problems under inert conditions. Structural investigations on these com-
pounds have not been carried out to date but they should adopt a similar
structure like the corresponding oxygen derivatives of F.BICKELHAUPT and
co-workers being intramolecular stabilized cyclic organomagnesium deriva-
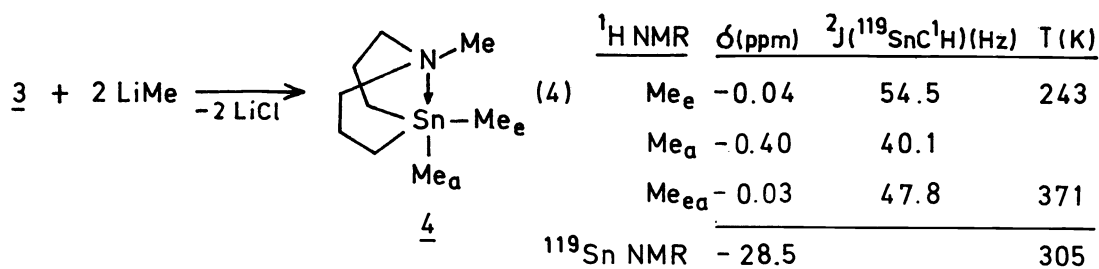tives (ref.6).

Diptych structures

Under dilution conditions the reaction of compound **1** with tin tetrachloride
leads in good yields to the dichlorodiptychstannolidine **3** (equ.3)(ref.7).

$$\underline{\mathbf{1}} \ + \ SnCl_4 \ \xrightarrow[-\ MgCl_2]{\text{thf,toluene}} \ Cl_2Sn(CH_2CH_2CH_2)_2NMe \qquad (3)$$

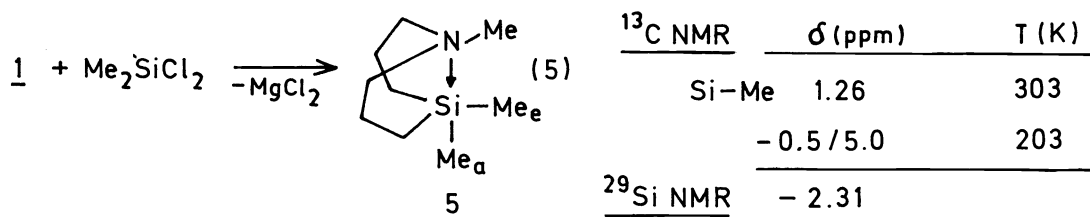$$\underline{\mathbf{3}}, \text{ yield } 30\%$$

Both nmr and X-ray studies reveal the trigonal bipyramidal structure of
compound **3** in solution and in the solid state, respectively. The Sn-N
distance amounts to 244 pm.

The treatment of the dichloro derivative **3** with lithium methyl yields quan-
titatively the tetraorganotin compound **4** (equ.4). Its pentacoordinated
structure is confirmed especially by the nonequivalence of the methyl
groups bonded at the tin atom. The very different $^2J(^{119}Sn-C-^1H)$ coupling
constants prove unambigously the apical-equatorial positions of these
organo groups.

$$\underline{3} + 2\ LiMe \xrightarrow[-2\ LiCl]{} \underline{4} \quad (4)$$

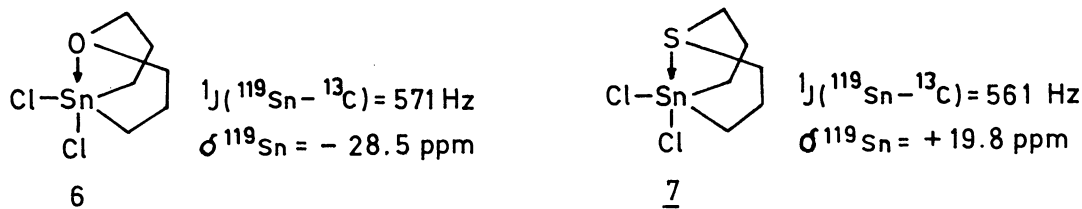| ^{1}H NMR	δ(ppm)	$^2J(^{119}SnC^1H)$(Hz)	T(K)
Me$_e$	-0.04	54.5	243
Me$_a$	-0.40	40.1	
Me$_{ea}$	-0.03	47.8	371
^{119}Sn NMR	-28.5		305

Raising the temperature coalescence takes place. From line shape analysis a free activation enthalpy has been calculated of about 60 kJ/mol. The mechanism being responsible for the coalescence is interpreted in terms of a dissociation-inversion process (ref.1). Similar results have been obtained in the case of the diptychsilanolidine $\underline{5}$ being available as a distillable liquid according to equ.(5)(ref.8). Also in this case the pentacoordinated structure is confirmed by nmr measurements.

$$\underline{1} + Me_2SiCl_2 \xrightarrow[-MgCl_2]{} \underline{5} \quad (5)$$

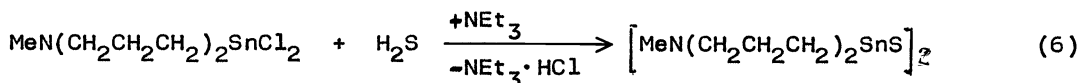| ^{13}C NMR	δ(ppm)	T(K)
Si-Me	1.26	303
	$-0.5/5.0$	203
^{29}Si NMR	-2.31	

The lower free activation enthalpy of about 45 kJ/mol is in agreement with the lower Lewis acidity of organosilicon compounds compared with organotin compounds (ref.9)(compare also t-Bu$_2$Sn(OCH$_2$CH$_2$)$_2$NMe, $\Delta G^* = 63.3$ kJ/mol (ref.3); (C$_4$H$_8$O)$_2$Si(OCH$_2$CH$_2$)$_2$NMe, $\Delta G^* = 45.0$ kJ/mol (ref.10)).

The corresponding pentacoordinated diptych derivatives $\underline{6}$ and $\underline{7}$ are available from difunctional Grignard reagents as those of bis(μ-chloropropyl)ether or bis(μ-chloropropyl)sulphide.

$^1J(^{119}Sn-^{13}C) = 571$ Hz
$\delta^{119}Sn = -28.5$ ppm

$\underline{6}$

$^1J(^{119}Sn-^{13}C) = 561$ Hz
$\delta^{119}Sn = +19.8$ ppm

$\underline{7}$

Both the nmr data and the X-ray investigations confirm a trigonal bipyramidal arrangement for these compounds also. The reaction with lithium methyl leads to the formation of the corresponding tetraorganotin derivatives which have been isolated as volatile liquids. In these derivatives the Sn-O and Sn-S interaction, respectively, are considerable weaker in comparison with the nitrogen substituted derivative discussed above. A splitting of the methyl signals in the 500 MHz ^{1}H nmr spectra could not be observed even at -80°C. These results are in agreement with earlier observations showing the lower donor capacity of oxygen and sulphur compared to nitrogen (ref.3).

The apical-equatorial bonded chlorine atoms include an angle of about 90° due to the trigonal bipyramidal geometry of the diptych derivatives. Thus, these compounds should be appropiate precursors for the preparation of fourmembered ring structures. This is illustrated by the reaction of compound $\underline{3}$ with H$_2$S (equ.6). In the presence of triethylamine the spiro compound $\underline{8}$ is obtained in high yield.

$$MeN(CH_2CH_2CH_2)_2SnCl_2 + H_2S \xrightarrow[-NEt_3\cdot HCl]{+NEt_3} \left[MeN(CH_2CH_2CH_2)_2SnS \right]_2 \quad (6)$$

$$\underline{8}$$

The X-ray investigation show compound 8 to contain a nearly planar Sn_2S_2-four-membered ring with different Sn-S distances for the apical and equatorial sulphur atoms, respectively (Fig.1)(ref.11).
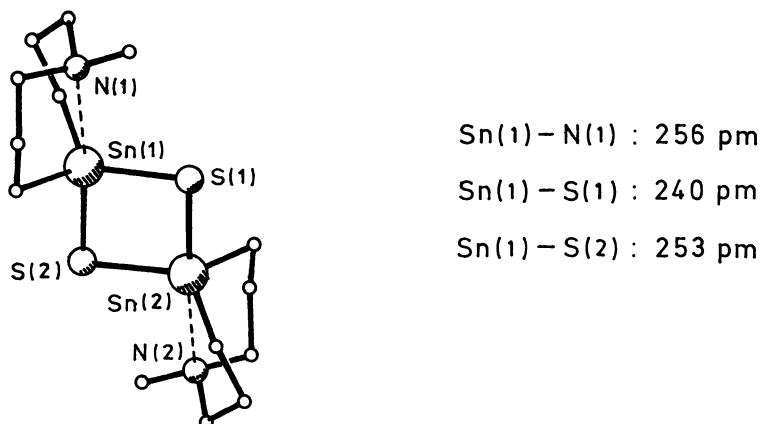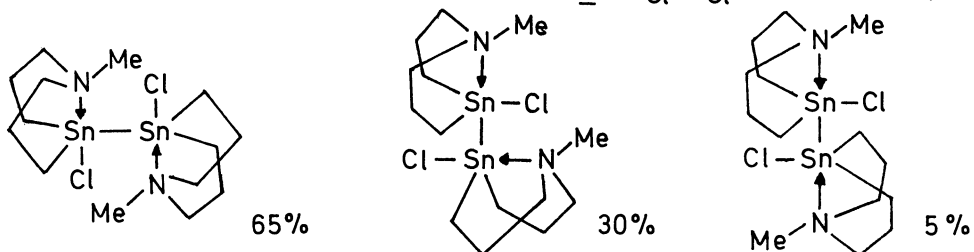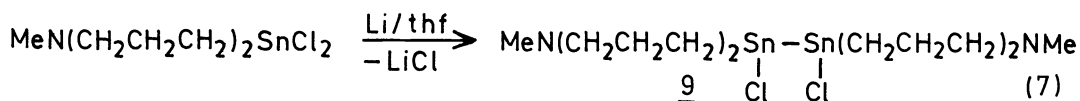

Sn(1)—N(1) : 256 pm

Sn(1)—S(1) : 240 pm

Sn(1)—S(2) : 253 pm

Fig.1. Molecular structure of $\left[MeN(CH_2CH_2CH_2)_2SnS\right]_2$.

First investigations show the possibility to vary the heteroatoms within the four-membered ring.

The reaction of compound 3 with lithium yields the distannane 9 showing a remarkable thermal stability (m.p. 235°C) (equ.7) in comparison with $Me_2ClSnSnClMe_2$.

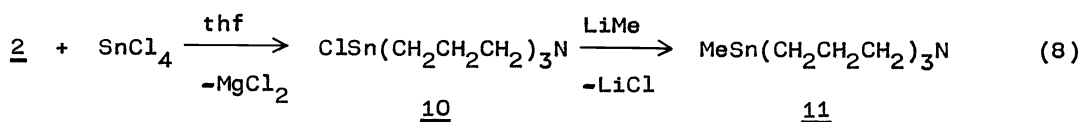$$MeN(CH_2CH_2CH_2)_2SnCl_2 \xrightarrow[-LiCl]{Li/thf} MeN(CH_2CH_2CH_2)_2\underset{\underset{Cl}{|}}{Sn}-\underset{\underset{Cl}{|}}{Sn}(CH_2CH_2CH_2)_2NMe \quad (7)$$

                                                                    9

| | 65% | 30% | 5% |

$\delta^{119}Sn[ppm]$ − 31.30   − 41.39 /−42.75   − 53.39

$^1J(^{119}Sn-^{117}Sn)[Hz]$ 6816   6551   6297

The reason should be the high electron density within the tin-tin bond. Furthermore, compound 9 exhibit a particular stereochemical behaviour (ref.12). In solution at least three diastereomeres are observed represented by four ^{119}Sn nmr signals. Due to the equatorial positions of the tin atoms bound to each other connected with a high s-electron density within this bond the greatest $^1J(^{119}Sn-^{117}Sn)$ coupling constant has been observed for the deminating isomer. In addition a hindered rotation about the tin-tin bond has been found for the first time.

Triptych structures

From the stereochemical point of view stronger intramolecular 1,5-interactions should be observed in the case of the tricyclic derivatives (E). The reaction of the trifunctional Grignard compound 2 with tin tetrachloride yields compound 10 in about 15 % (equ.8). By the reaction with methyl lithium compound 10 is easily transformed into the tetraorganotin compound 11 (ref.7).

$$\underline{2} \ + \ SnCl_4 \ \xrightarrow[-MgCl_2]{thf} \ \underset{\underline{10}}{ClSn(CH_2CH_2CH_2)_3N} \ \xrightarrow[-LiCl]{LiMe} \ \underset{\underline{11}}{MeSn(CH_2CH_2CH_2)_3N} \tag{8}$$

The X-ray structure shows for compound $\underline{10}$ a Sn-N interaction of 237.2 pm (ref.13). The great Sn-Cl distance of 261.3 pm is remarkable being 22 pm longer than the sum of the covalent radii of tin and chlorine. The temperature dependent nmr spectra are interpreted in terms of an "in-out" equilibrium with a free activation enthalpy of about 70 kJ/mol (Fig.2).
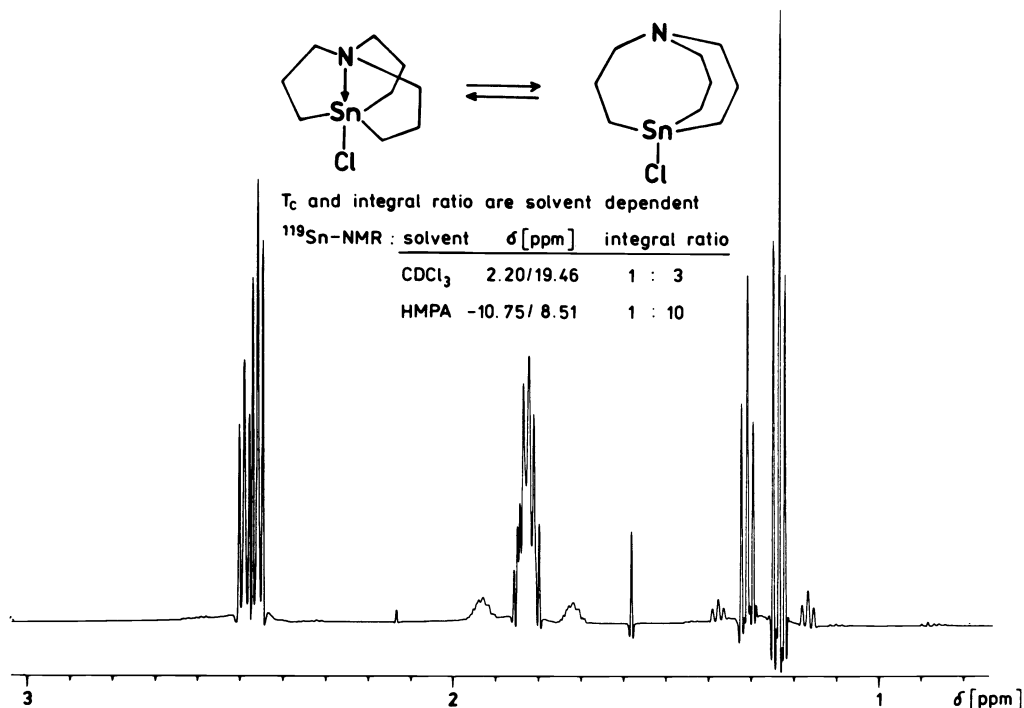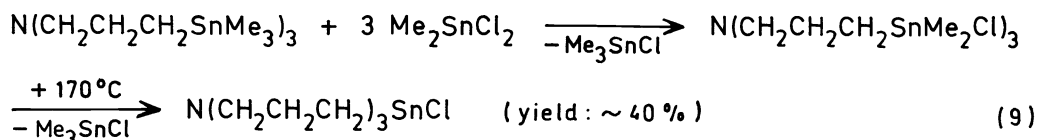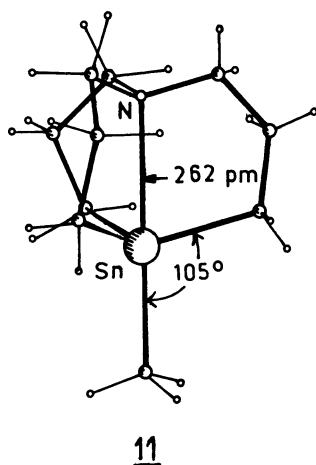

Tc and integral ratio are solvent dependent

^{119}Sn-NMR :

solvent	δ[ppm]	integral ratio
CDCl$_3$	2.20/19.46	1 : 3
HMPA	-10.75/ 8.51	1 : 10

Fig.2. ^{1}H NMR spectrum (500 MHz) of ClSn(CH$_2$CH$_2$CH$_2$)$_3$N in CDCl$_3$ at 25°C.

Also in compound $\underline{11}$ the intramolecular Sn-N interaction has found to be unambigously smaller than the sum of the van der Waals radii of tin and nitrogen (ref.14). Therefore, this compound can be regarded as the first pentacoordinated tetraorganotin compound found for the solid state. However, a distortion is observed towards a tetrahedron due to the lower Lewis acidity compared with compound $\underline{10}$. In solution the apical position of the methyl group becomes clear by the very small ^{1}J(^{119}Sn-13C) coupling constant in the ^{13}C nmr spectrum.
The low yield obtained by the Grignard reaction caused us to look for another approach to get the interesting cage structure $\underline{10}$. Starting from tris(γ-trimethylstannylpropyl)amine the triptych compound $\underline{10}$ has been obtained in good yield by the reaction with Me$_2$SnCl$_2$ and stepwise cleavage of Me$_3$SnCl (equ.9).

$$N(CH_2CH_2CH_2SnMe_3)_3 \ + \ 3 \ Me_2SnCl_2 \ \xrightarrow[-Me_3SnCl]{} \ N(CH_2CH_2CH_2SnMe_2Cl)_3$$

$$\xrightarrow[-Me_3SnCl]{+ 170\,°C} \ N(CH_2CH_2CH_2)_3SnCl \quad (yield : \sim 40\,\%) \tag{9}$$

^{13}C NMR: δ Sn–$\underline{C}H_3 = -4.09$ ppm

$^{1}J(^{119}Sn–^{13}C) = 171$ Hz

δ Sn–$\underline{C}H_2 = 8.25$ ppm

$^{1}J(^{119}Sn–^{13}C) = 405$ Hz

^{119}Sn NMR: $\delta = -14.41$ ppm

11

Fig.3. Molecular structure of $MeSn(CH_2CH_2CH_2)_3N$

The already mentioned great Sn–Cl distance in compound 10 favours the transition to an ionic structure. The reaction with silver tetrafluoroborate yields the ionic triptych derivative 12(equ.10).

$$18 + AgBF_4 \xrightarrow[-AgCl]{} \left[\text{(structure)} \right]^{\oplus} BF_4^{\ominus} \qquad (10)$$

12 δ^{119}Sn : + 103.0 ppm (thf)
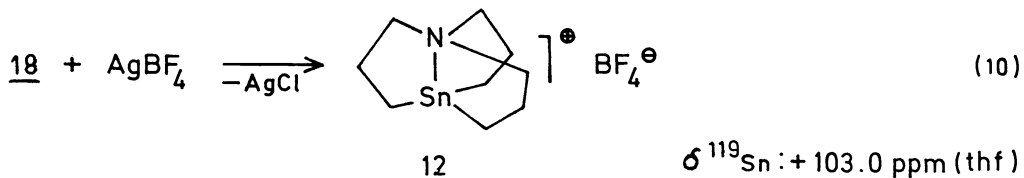
Its ^{119}Sn nmr chemical shift is in agreement with a tetracoordinated tin atom. Further studies to elucidate the nature of this ion are currently under work.
Like the tin containing triptych structures the silicon derivative 13 is available in 15 % yield by the reaction of compound 2 with methyltrichlorosilane (equ.11)(ref.8).
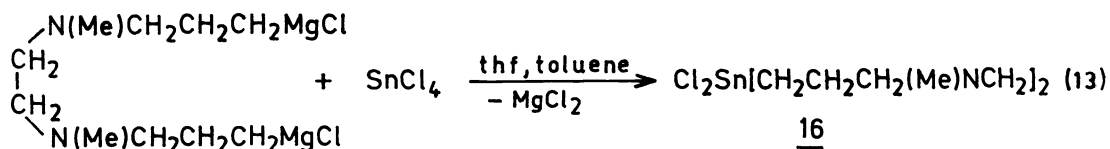
$$2 + MeSiCl_3 \xrightarrow[-MgCl_2]{} \text{(structure)} \quad 13 \qquad (11)$$
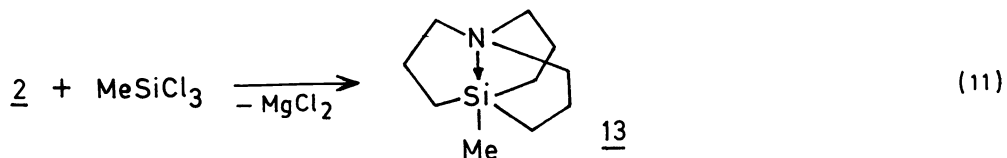
Here again the transannular Sn–N interaction and the trigonal bipyramidal structure is especially confirmed by the different $^{1}J(^{29}Si–^{13}CH_3)$ and $^{1}J(^{29}Si–^{13}CH_2)$ coupling constants (ref.8).
The methyl group of compound 13 shows an increased reactivity as it is shown by the reaction with Me_2SnCl_2. According to equation (12) the chloro triptych derivative 14 can be obtained in nearly quantitative yield. Compound 14 also exhibit an "in-out" equilibrium.

$$13 + Me_2SnCl_2 \longrightarrow Me_3SnCl + \text{(structure)} \quad 14 \qquad (12)$$
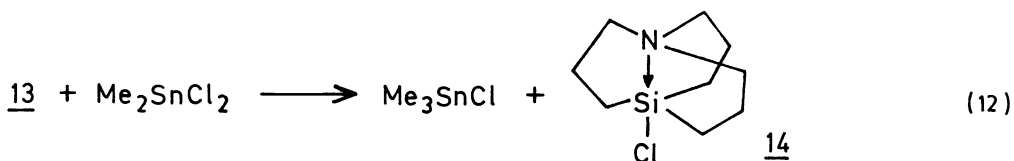
However, the activation parameters have found to be considerable smaller in comparison with compound 10.
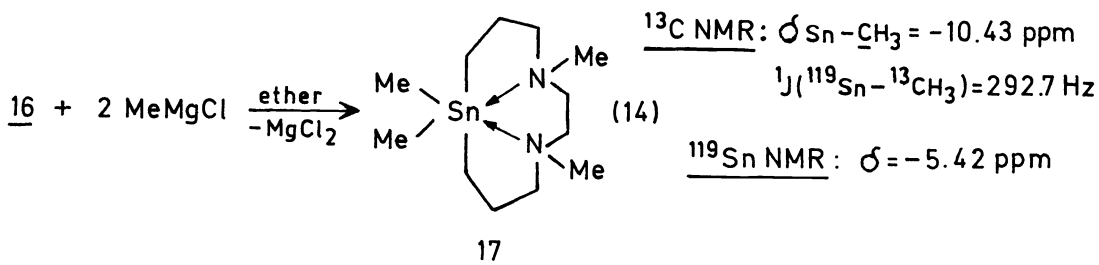
At present we are concerned with the extension of the concept in order
to obtain also six- and seven coordinated tetraorganotin and tetraorgano-
silicon compounds. First investigations show that also the two nitrogen
containing Grignard reagent 15 can be prepared in acceptable yields.

$$\begin{array}{c} \diagup N(Me)CH_2CH_2CH_2MgCl \\ CH_2 \\ | \\ CH_2 \\ \diagdown N(Me)CH_2CH_2CH_2MgCl \end{array} + SnCl_4 \xrightarrow[-MgCl_2]{thf,toluene} Cl_2Sn[CH_2CH_2CH_2(Me)NCH_2]_2 \quad (13)$$

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By the reaction of compound 15 with tin tetrachloride the eleven-membered
ring 16 has been obtained containing a hexacoordinated tin atom (equ.13).
The observation of two ^{119}Sn nmr signals of different intensity reveal
this compound to exist in terms of a cis-trans equilibrium in solution
with the trans-isomer dominating.

	trans	cis
^{119}Sn NMR (186.5 MHz)	− 177.3 ppm	− 173.8 ppm
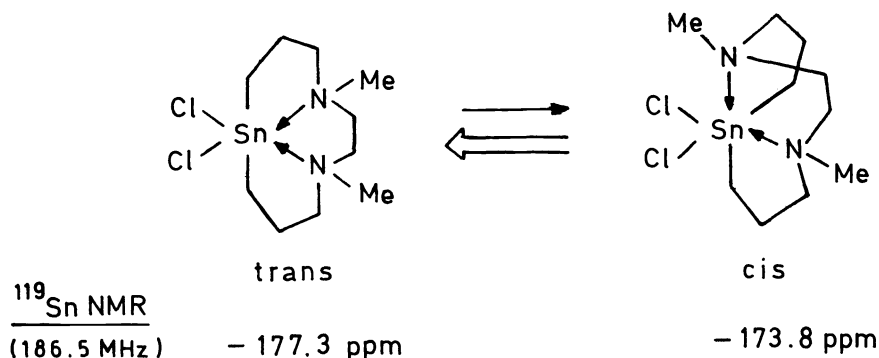
Compound 16 reacts with MeMgCl to yield the methylated derivative 17 being
a distillable colourless liquid (equ.14).

$$16 + 2 \text{ MeMgCl} \xrightarrow[-MgCl_2]{ether}$$ (14)

^{13}C NMR: δ Sn$-\underline{C}H_3$ = −10.43 ppm

$^1J(^{119}Sn-^{13}CH_3)$ = 292.7 Hz

^{119}Sn NMR: δ = −5.42 ppm

17

At present we are concerned with the extension of our preparativ material
in order to get more information concerning the intramolecular Sn-N inter-
actions in this type of compounds.
Further interesting results can be expected from the stereochemical point
of view as well as for the reactivity of metal to carbon bonds and the
homogeneous catalysis by the development of Grignard reagents containing
three or more nitrogen or phosphorus atoms.

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