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# TIN(II) IN NOVEL RINGS AND CAGES

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(Received

## INTRODUCTION: MOLECULAR $Sn^{II}$ -COMPOUNDS

As it is well known, there is a marked tendency for group-IV-elements with increasing periodic number to use only 2 of the 4 outershell electrons for bonding in their compounds ("inert s-pair effect"[1]). The element has the formal oxydation state + II. While these compounds may be stabilized without difficulty as ionic salts or in complexes, molecular derivatives of this bonding type are harder to synthesize. One reason for this is assumed to be the low coordination number 2 of the element which implies an electron sextette in contrast to the energetically more stable octette. With reference to the lightest congener the "carbene", this class of compounds has been designated as "carbene-analogues"[2], of which the "stannylenes", derivatives of the divalent tin, are considered in more detail.

In figure 1 the electron deficient monomer $SnX_2$ is compared with two associated species. On synthesizing molecules of the first type, one should try to overcome the electron lack at the central atom by choosing substituents X with electron donor properties or by restricting the aggregation. Principally there are mainly three possibilities:

1) stabilization of small molecules $SnX_2$ at high temperatures and low pressure or by dilution in matrix at low temperatures;

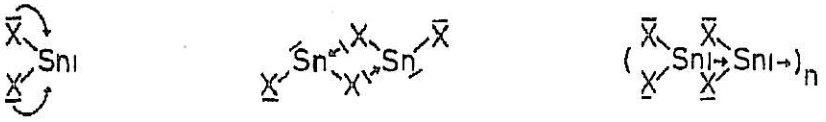


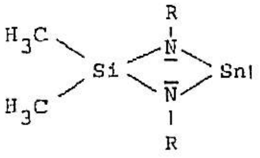
Figure 1: $SnX_2$ and possible "associated" products.

2) stabilisation of the monomer by introducing strong inductive + I-ligands or ligands with a lone electron pair at the $\alpha$-atom;

3) hindrance of the polymerisation of $SnX_2$ by introducing bulky substituents X.

All three possibilities have been tested in the past. In the early 1940s the halides $SnX_2$ (X = Cl, Br, I) were shown by electron diffraction to represent monomer angular molecules in the gas phase$^{3)}$. Bis-(cyclopentadienyl)-tin(II) may be regarded as an example of stabilization via method 2$^{4)}$, as it is monomer in solution for a short time showing tendencies to associate. Depending on the point of view, the coordination number 2 in this compound may be regarded as a borderline-case, considering the special electronic properties of the ligands. In the early 1970s, method 2 and 3 were used successfully by M.F. Lappert$^{6,7)}$ and J.J. Zuckerman and coworkers$^{8)}$ and it was the former who succeeded for the first time in stabilizing a derivative of a divalent tin at normal conditions. They used, on one side, the bulkiness of ligands like $(CH(Si(CH_3)_3)_2)$ or $(N(Si(CH_3)_3)_2)$ preventing polymerisation (see figure 1) and, on the other side, their strong + I effect. Ligands with a free electron pair at the $\alpha$-atom, but without steric hindrance like $(N(CH_3)_2)$, do not give monomers$^{9)}$.

When we started our own experiments in the field of molecular divalent tin compounds we tried to take into account structural aspects besides the already mentioned possibilities. It has been known for a long time that Sn(II) tends to have angles of about 90° between the ligands in complexes or ionic solids, the lone electron pair occupying predominantly the s-orbital$^{10)}$. This caused us to include the tin atom into a strained four membered ring$^{11)}$:



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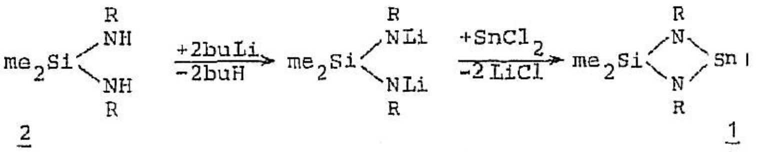
The resulting cyclic diazastannylene 1 with R = $C(CH_3)_3$ is monomer in nonpolar solvents up to high concentrations and crystallizes - in the monoclinic phase - in a mixture of monomers and dimers[12] ($(Sn(CH(Si(CH_3)_3)_2)_2)$ has been found to exist only as a dimer in the solid[13]).

The following report deals with the synthesis, the properties, and the reactions of the cyclic stannylene 1. As we knew the molecular and structural data of the reactive molecule 1 from the very beginning, we were curious to see whether this fact would be of great help in choosing adequate reactants or in mechanistical studies. It is for this reason that we have been interested - besides preparation - in a thorough and careful analysis of the products and the reaction path way. Apart from physical and chemical standard methods, such as mass-, NMR-, IR-, UV-spectroscopy, and the quantitative analysis, we used X-ray structure determination at low and ambient temperatures, kinetical experiments and low-temperature NMR-spectroscopy.

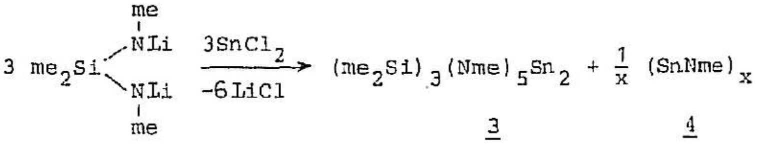
## SYNTHESIS OF CYCLIC DIAZASILASTANNYLENES

According to reaction scheme I, cyclic diazastannylenes 1



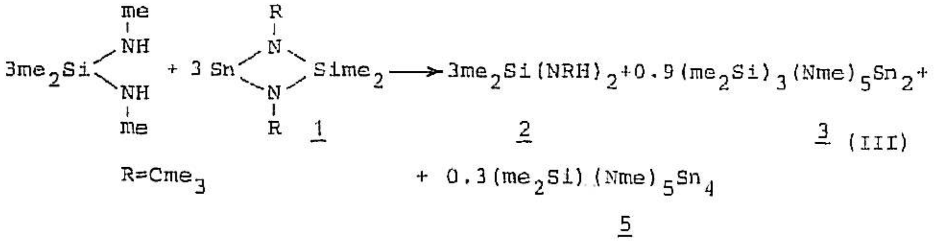
2 1 (I)

(me = $CH_3$, bu = $CH_2$-$CH_2$-$CH_2$-$CH_3$) are prepared in high yields from the easily obtainable diazasilanes 2[14] by lithilation and a successive reaction with tin(II)chloride[11,15]. This simple synthesis works well, if the organic ligands R correspond to isopropyl or tert-butyl. On substituting these bulky rests (see below) by the smaller methyl-group, no corresponding methyl-derivative of 1 can be prepared[16]. According to reaction II,



(II)

polymers like $(SnNme)_x$ precipitate out of the solution, whereas compound 3 remains dissolved and can be crystallized from benzene solution. The polycycle 3 has a great tendency to form, as can also be seen from reaction III. This aminolysis reaction does not lead to a cyclo-diazasilastannylene with methyl substituents



$$3me_2Si(NHme)_2 + 3\,Sn\begin{matrix}\diagup N(R) \diagdown\\ \diagdown N(R) \diagup\end{matrix}Sime_2 \longrightarrow 3me_2Si(NRH)_2 + 0.9(me_2Si)_3(Nme)_5Sn_2 + 0.3(me_2Si)(Nme)_5Sn_4 \quad \text{(III)}$$

R=Cme$_3$; 1; 2; 3; 5

at nitrogen either. In contrast to reaction II, the formation of 4 is suppressed in favour of compound 5, which is formed besides 2 and 3. 5 crystallizes out of a benzene solution, its structure as well as the structure of 3 have been solved (see

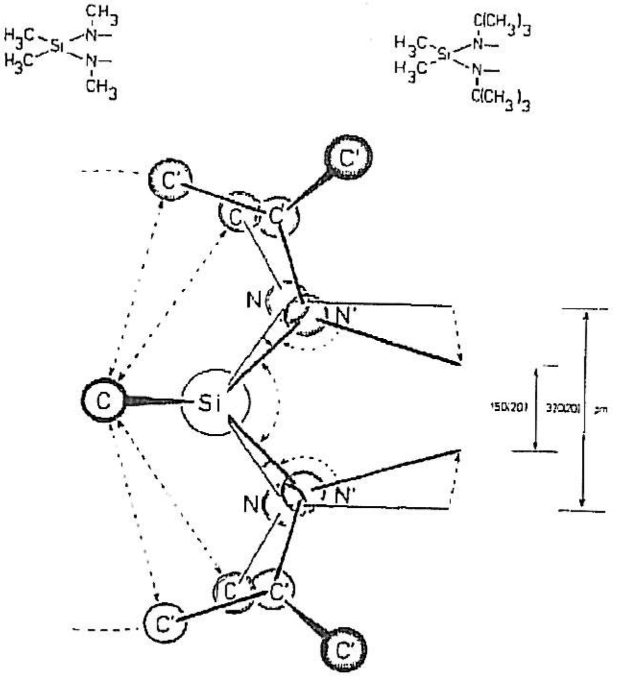


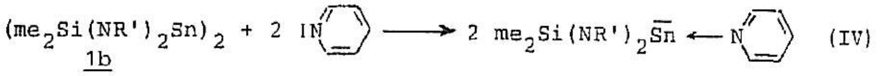
Figure 2: The different space occupied by organic substituents in N,N'-dimethyl- and N,N'-di-tert-butyl-dimethyl silanes. For the sake of simplicity a planar configuration has been assumed.

following chapter). The different reactivity of the diazasilane 2 compared with the corresponding methyl-substituted compound can be understood by the different space occupied by the methyl-group versus the tert-butyl-group. While in the latter case a mono-substitution by $SnX_2$ is enforced by the bulkiness of the ligands, a second substitution may also take place in the methyl-derivative linking two tin atoms to one diazasilagroup (figure 2). Nevertheless, the formation of the ligand $-\overset{|}{N}-\overset{|}{Si}-\overset{|}{N}-\overset{|}{Si}-\overset{|}{N}-$ as presented in 3 (see below) is astonishing and seems to stem from a redistribution reaction.

## THE PROPERTIES OF CYCLIC DIAZASILASTANNYLENES

In table 1, some of the properties of the compounds 1, 3, and 5 have been summarized. As expected, the dimeric 1b has a higher melting point than the monomeric 1a, the different structures being shown in figure 3[15].

By reaction of the strong base pyridine with the dimer 1b, a monomeric 1:1 pyridine-adduct can be prepared according to equation IV[15]:



1b

(IV)

The stronger base pyridine displaces the weaker base of the intermolecular ligand in 1b.

| | $SnSiN_2C_{10}H_{24}$<br>1a | $SnSiN_2C_8H_{20}$<br>1b | $Sn_2Si_3N_5C_{11}H_{33}$<br>3 | $Sn_4SiN_5C_7H_{21}$<br>5 |
|---|---|---|---|---|
| solid | a) orange crystals (monoclinic)<br>b) yellow crystals (triclinic) | colourless crystals (monoclinic) | colourless crystals (triclinic) | red crystals (monoclinic) |
| liquid | red | colourless | colourless | - |
| melting point (°C) | 5 | 64.5 | 162 | dec. |
| mol.mass calc.: | 319.1 | 291.0 | 557.1 | 678.1 |
| found : | 324 | 585=2x292.5 | 544 | - |
| density (g/cm³) | a) 1.45<br>b) 1.43 | 1.53 | 1.39 | 2.52 |

Table 1: Properties of some azasilastannanes[15,16].

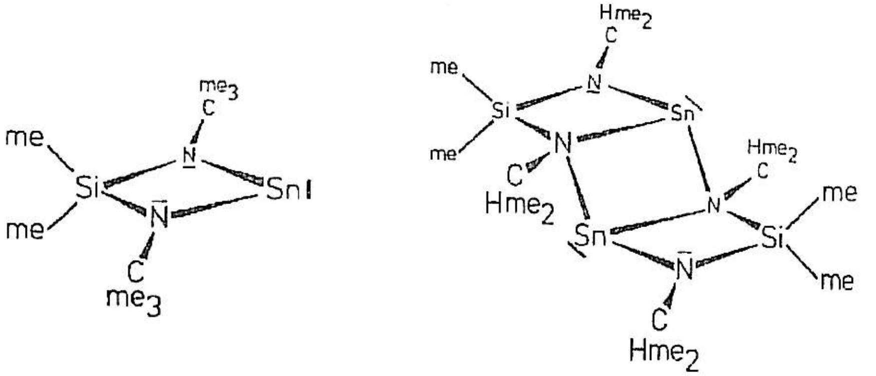
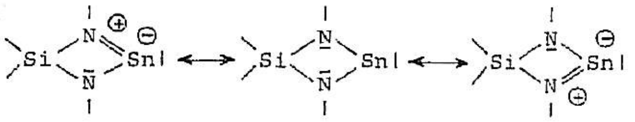


Figure 3: The different structures of the N,N'-bis-tert-butyl- and N,N'-bis-isopropyl-derivative of 1 in the liquid phase and in solution.

While the monomeric 1a is coloured in solution and weakly coloured in the solid, the dimer 1b is always colourless. The different structures of the monoclinic phase of 1a, which consists of a 1:1 mixture of monomers and dimers, and the triclinic phase of 1a, where only dimers are present, are also reflected by different colours. Obviously the coordination number of tin is important in that respect: while the compounds with c.n. 2 at the tin atom are coloured, they are not with c.n. 3. Corvan and Zuckerman studied this effect with a variety of compounds and confirmed our findings17). The electronic reason for the colour of the monomeric stannylenes, nevertheless, still has to be found and understood.

The low-temperature X-ray investigation on the structure of 1a reveals molecular data which are compiled in figure 4. The most remarkable of these is the coplanarity of the four ring-atoms with the central C-atoms of the tert-butyl-groups (symmetry: $C_2$). A possible pπ → pπ bond from the filled p-orbitals at the nitrogen atoms into empty p-orbitals at the tin atom cannot be ruled out on this basis. On the other hand, the Sn-N-bond is rather long (expected value for a Sn(II)-N bond distance according to Pauling : 215 pm19)) and of the mesomeric structures the one without any formal charges



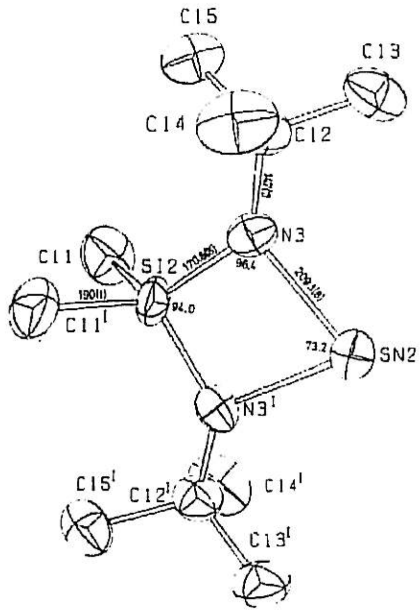


Figure 4: The molecular data (in pm and °) of the monomeric stannylene 1a[12].

should be of the greatest importance. The strong tendency of the cyclic diazastannylenes to achieve an 8-electron-configuration at tin by addition of a base gives a chemical proof of the rather weak interaction between the nitrogens and tin within the ring.

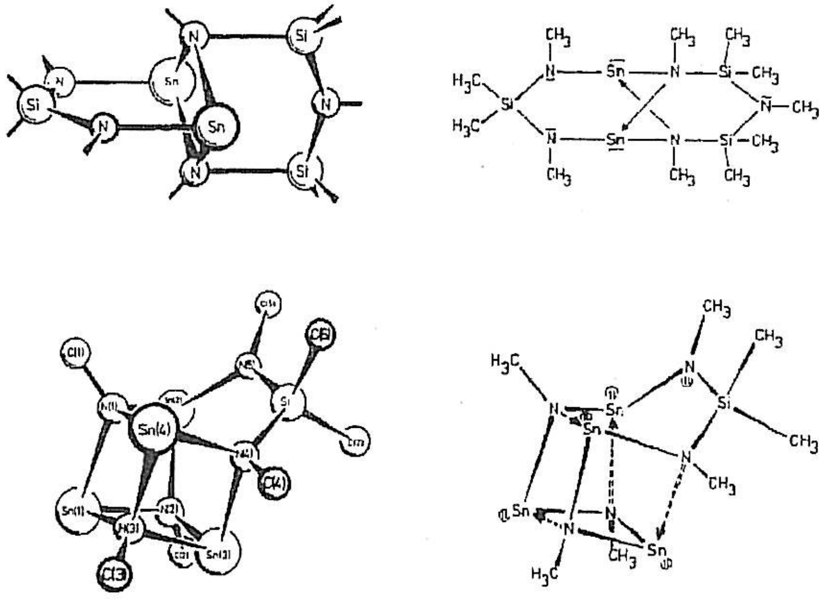


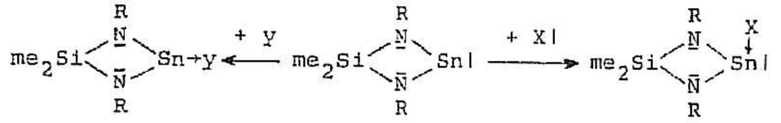
Figure 5: The structures of the polycycles 3 and 5.

Both products 3 and 5 have been characterized by high-resolution $^1$H-NMR-spectroscopy and in the case of 5 by X-ray-structure analysis$^{16)}$. In figure 5, the resulting molecular structures are illustrated. In both molecules, the tin atoms always display a trigonal pyramidal coordination, the electron gain at tin being realized by bonding to nitrogen atoms within the ring. From a formal point of view, the two polycycles can be understood as ten-membered rings which fold up by Lewis-acid-base interactions between the divalent tin and the trivalent nitrogen atoms. In the case of 3 a $Sn_2N_2$-ring results bridged over in the 1,3- and 2,4-position by three-membered chains, whereas molecule 5 may be described as a $Sn_4N_4$-cubane-structure being enlarged by "$me_2Si$-Nme" at one edge. Parts of these structures will be found to occur more frequently in Sn(II)-chemistry as will be shown later. 5 shows valence fluctuation at ambient temperature and will be described together with another example of this kind in a separate chapter.

## THE REACTIONS OF THE CYCLIC STANNYLENE 1,3-BIS(TERT-BUTYL)-2,2-DIMETHYL-1,3,2,4$\lambda^2$-DIAZASILASTANNETIDINE

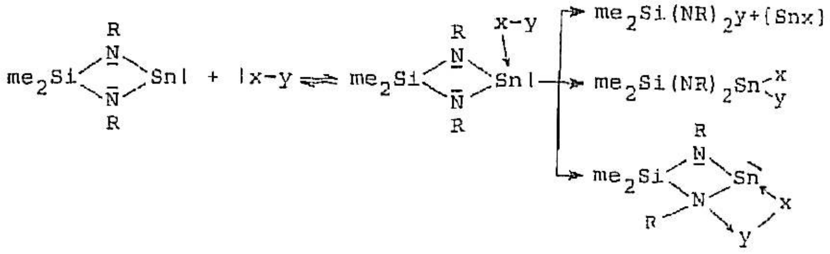
According to the special electronic configuration at the tin atom, the reactions of the cyclic diazasilastannylene 1 may be divided into those where the tin is acting as a Lewis-acid (Va) and those, where it is acting as a Lewis-base (Vb).

(Vb)



(Va)

Besides the group-IV-element, the two nitrogen atoms in the ring may participate in the reaction. The adducts are often not stable with respect to further reactions, especially the one shown in equation Va. We can generally differentiate between a homolytic cleavage, an insertion, or a double or triple adduct formation following reaction scheme VI.



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THE REACTION OF THE DIAZASTANNYLENE 1 AS A LEWIS-ACID

*THE FORMATION OF LEWIS-ACID-BASE ADDUCTS*

The diazastannylene 1 forms 1:1 adducts with bases like pyridine, tetrahydrofurane or diethylether, the tin atom thus attaining an eight-electron configuration. These adducts can be crystallized at lower temperatures in the case of pyridine but are generally not stable with respect to separation into the components at ambient temperature or reduced pressure. The adduct formation of 1 with tert-butylamine has been studied more carefully[19)]. On the basis of $^1$H-NMR- and U.V.-spectroscopic data VII is an equilibrium reaction with a very fast exchange of

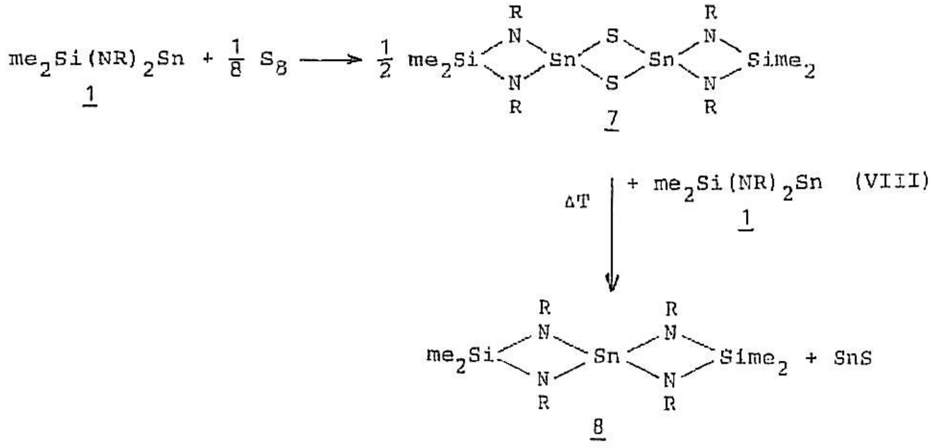
$$\underset{\underline{1}}{me_2Si(NR)_2Sn|} + H_2\bar{N}R \rightleftharpoons \underset{\underline{6}}{me_2Si(NR)_2\bar{S}n \leftarrow NH_2R} \qquad (VII)$$

ligands in the adduct 6. The equilibrium constant k at 25°C for reaction VII has been found to have a value of 2.5 (l/mol). Despite the difficulty of preparing 6, the adduct can be isolated at −80°C by crystallisation from a pentane solution as a colourless solid which is extremely sensitive to moisture and decomposes at temperatures near −40°C (see also below!)[20)].

The formation of double Lewis-acid-base adducts, as in the dimer of 1, has already been mentioned and illustrates again the lack of electrons at the tin atom in the ring. As there is a second nitrogen atom in ring 1, we may conclude that the whole diazasilastannylene can also react as a tridentate ligand. This is the case for certain substrates, as will be explained below.

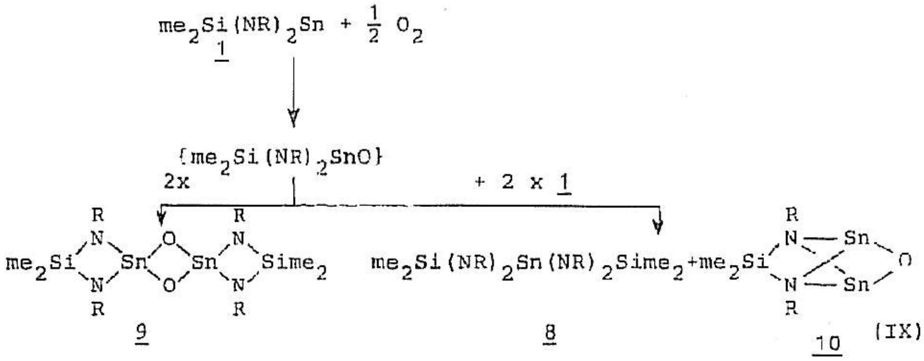
### *THE INSERTION REACTION OF THE DIAZASTANNYLENE 1*

Oxygen and sulfur react very rapidly with 1 in nonpolar solvents. Following scheme VIII, a dispiro-compound 7 is formed, when 1 is treated with elemental sulfur, tin attaining coordination and oxydation number 4[21]. This process can be regarded as the insertion of a carbene-analogue into a S–S-single bond[2]. At elevated temperatures, 7 can be converted with excess stannylene 1 to the simple mono-spiro-compound 8 and grey SnS precipitates from the solution. The rate-determinating step of this reaction is a bimolecular one, as



can be concluded from kinetical experiments[21]. The complete structure determination[22] reveals 8 to possess the high $D_{2d}$-symmetry with the Sn-IV-atom coordinated by 4 nitrogen atoms at a fairly short distance (Sn-N: 203 pm). The mechanism of the second reaction in VIII seems to be the addition of 1 to the sulfur atoms in 7 followed by a redistribution of the ligands.

In some respects oxygen reacts similar to its heavier congener sulfur, but in contrast to VIII the corresponding SnO is not precipitated out of the mixture and reacts further with the stannylene 1. On the basis of the structure determination of product 11[23] and the characterization of 8 the reaction course IX can be formulated. The dispiro-compound 9 and 2 molecules of 10 interact yielding the "macromolecule" 11, the structure of which is shown in figure 6. In this highly



(IX)

$2\times\underline{10} + \underline{9} \longrightarrow \underline{11}$

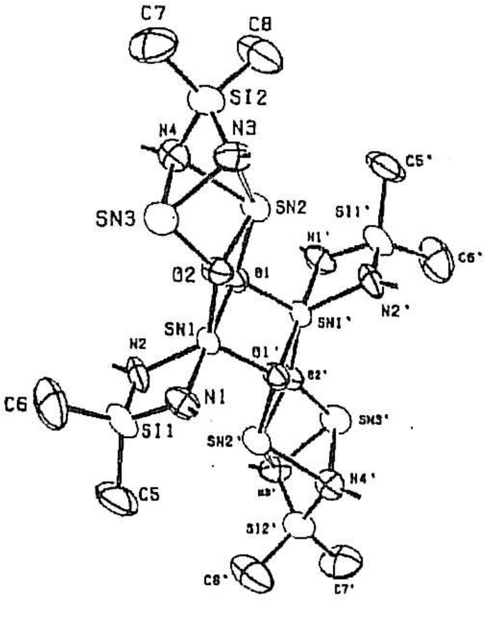
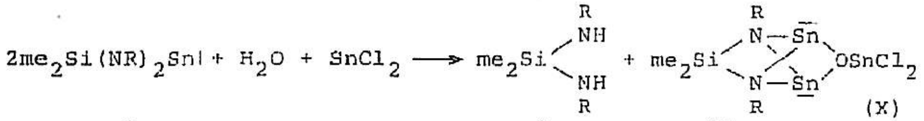


Figure 6: The structure of the polycycle $\underline{11}^{23)}$; the tert-butyl groups are not drawn.

connected polycycle, which has a centre of symmetry, tin atoms in oxydation state IV with fivefold coordination are present besides tin(II)-atoms which have 3 or 4 nearest neighbours. The frequent occurence of four membered rings is quite remarkable. The whole molecule may also be characterized as a three-dimensional solid structure wrapped up by organic groups.

### *HYDROLYSIS AND AMINOLYSIS OF THE CYCLIC STANNYLENE 1*

The cage compound 10, which has been shown to be a component of molecule 11, is also formed in the hydrolysis of 1[24] (X). In the presence of tin(II)-chloride the adduct 12 crystallizes out of the reaction mixture. This cage is quite unique in structural chemistry and may be described in terms of the structural formula given in figure 7. From this description every tin atom attains the noble gas electron configuration. The Sn-N-bond lengths are all equal within standard deviations with a mean value of 232 pm, the six membered cage approaching mm ($C_{2v}$)-symmetry. The oxygen atom is in the centre of a trigonal planar coordination. From the rather short Sn-Sn distance of 310 pm it cannot be ruled out that the cage in compound 12 may also be described as a cluster.



1 2 12 (X)

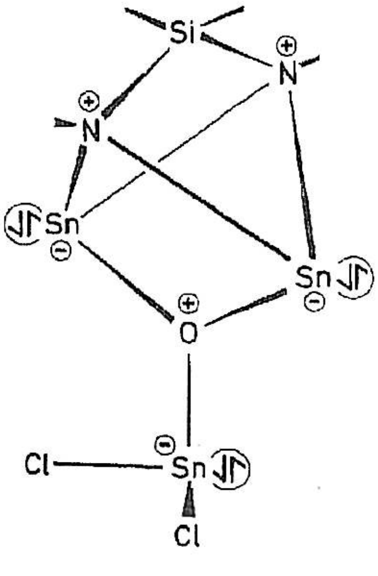
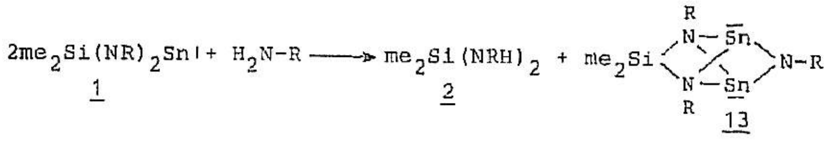


Figure 7: A description of the cage molecule 12 in terms of two-electron-bonds.

The O-$SnCl_2$-group in cage 12 can be formally replaced by an amino-group without great change in the structure, when stannylene 1 is allowed to react with organic amines as tert-butyl-amine (scheme XI). From $^1H$-NMR- and other analytical



(XI)

data the structural relationship of 12 and 13 can be proved. As in reaction X, the diazasilane 2 turns out to be an excellent leaving group. This aminolysis, which is a general reaction of 1, has been studied by us in detail with tert-butyl-amine, our findings being displayed in figure 8. In the first step, the adduct of $|XH_2$ and 1 is formed, as we already described in a former chapter. This compound is thermolabile and decomposes yielding the stable diazasilane 2. Substracting this molecule from the adduct 6 leaves the hypothetical intermediate $(SnX)^{26)}$. In the presence of further stannylene (molar ratio 1 : amine = 2:1) (SnX) is trapped forming the cage 13. If, however, there is an excess of tert-butyl-amine (SnX) reacts with the amine forming the compound $(SnX)_3XH_2$ (14).

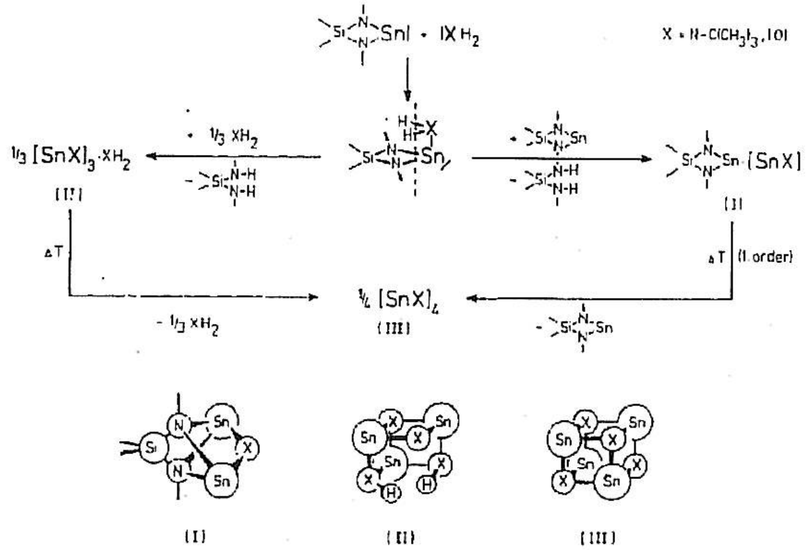


Figure 8: The reaction of 1 with tert-butyl-amine; the numbers I, II, and III correspond to 13, 14, and 15 respectively.

Accordingly the ratio of the products 13:14 can be controlled by the molarity of the reactants. 14 has been established to possess norcubane-like structure by X-ray structure determination[27] (see lower part of figure 8). It has fluctuating properties, as described in a separate chapter. Following figure 8, the two products 13 and 14 can be transformed to the highly symmetric cubane-like molecule $(SnX)_4$ (15) at temperatures >200°C. If starting from the norcubane-like cage, tert-butyl-amine is split off, whereas in the other case stannylene 1 acts as a leaving group. This second fact is very interesting, as it illustrates quite nicely that the cage 13 can be understood as a triple coordination of (SnX) by the tridentate ligand diazasilastannylene.

The thermolysis of 13 is of first order, as established by NMR-experiments[28], and this makes the short-lived occurrence of (SnX) very plausible. $|SnN\text{-}Cme_3$ may be regarded as a heavier congener of the isonitrile $|C{\equiv}N\text{-}Cme_3$. While the carbon derivative is stabilized by a triple bond between carbon and nitrogen, the iminostannylene polymerizes to give the tetramer with a cubane-like structure. We encounter here a well-known principle in inorganic chemistry which states that higher row elements usually stabilize by using only single bonds, whereas first row elements may use double bonds[29]. The cage 15 can best be compared with tetrameric iminoalanes[30], the aluminium organyl group being substituted by tin with an electron pair occupying the fourth coordination site. The very high Td($\bar{4}3m$)-symmetry of 15 (see also figure 8) is reflected in the spectroscopic[25] as well as in the structural data, for example only one signal can be detected in the $^1$H-NMR-($\delta$ = 1.52 ppm) and in the $^{119}$Sn-NMR-spectrum ($\delta$(vs $Snme_4$) = 710.8 ppm downfield)[31].

As already mentioned, amines other than tert-butyl-amine can be utilized in the aminolysis of 1. Recently we have also tried hydrazine-derivatives and found them to react similarly as shown in equation XII for N,N-dimethylhydrazine[32].

$$4\ \underset{\underline{1}}{me_2Si(NR)_2Sn} + 4\ H_2N\text{-}Nme_2 \longrightarrow 4\ \underset{\underline{2}}{me_2Si(NRH)_2} + \underset{\underline{16}}{(SnN_2me_2)_4} \quad \text{(XII)}$$

In contrast to the reaction of 1 with tert-butyl-amine, the tetramer 16 forms directly without any heating, and the diaminosilane 2 is obtained again in nearly quantitative yield.

16 differs from 15 in its deep red colour and its crystal structure. The molecular $N_4Sn_4$-cubane-like cage is still present in solution, but aggregates in the solid state to one-dimensional chains as shown in figure 9.

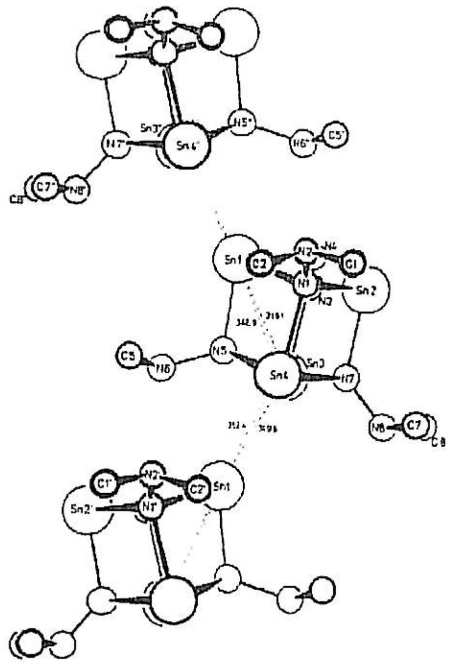


Figure 9: Part of the crystal structure of 16[32].

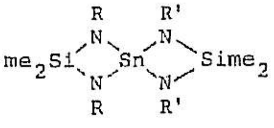
Some peculiar properties of the crystals of 16, due to this very astonishing arrangement, are being investigated.

### *THE REACTION OF THE DIAZASTANNYLENE 1 WITH TIN TETRACHLORIDE*

According to equation XIII, 1 reacts with tin tetrachloride in a benzene solution to form the diazadichlorostannane 17

$$\underset{\underline{1}}{me_2Si(NR)_2Sn} + SnCl_4 \xrightarrow[-SnCl_2]{} \underset{\underline{17}}{me_2Si(NR)_2SnCl_2} \qquad (XIII)$$

$$\underset{\underline{17}}{me_2Si(NR)_2SnCl_2} + me_2Si(NR'Li)_2 \xrightarrow[-2LiCl]{}$$



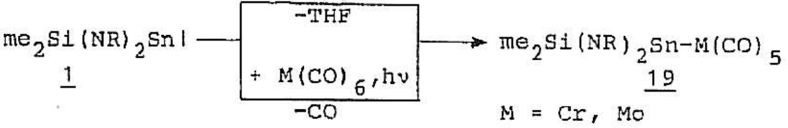
18

with precipitation of tin(II)chloride[21]. The first reaction may be regarded as a substitution or a redox-type reaction. The unsymmetrically substituted tin(IV)-compound 17 is an excellent starting material for further bonding of tin to electronegative ligands. As an example, XIII illustrates the preparation of the unsymmetrical spiro-compound 18[21].

## THE REACTION OF THE DIAZASILASTANNYLENE 1 AS A LEWIS-BASE

From the examples given so far, it seems unlikely that 1 may also react as a Lewis-base as the main property of the tin-(II)-atom seems to be that of an electrophile. Nevertheless, as the tin atom in 1 possesses an electron pair, it should also act as a base with very strong acids or with elements which are able to compensate the electron lack at tin by back-donation such as the transition metals.

Following the ideas of Lappert and coworkers[33], who succeeded in the synthesis of the first stannylene-metal complex, we converted the diazastannylene 1 to a penta-carbonyl-chromium or -molybdenum complex as shown in scheme XIV[34]. In the metal coordination sphere ligands, such as tetrahydrofurane (THF) and carbonmonoxide, can be displaced by 1. In contrast to the reaction of $(Sn(Nme_2)_2)_2$ with $Fe(CO)_5$, no addition of the Sn-N-bond to the carbonyl-ligand has been observed[35]. The structures



$$\underset{1}{me_2Si(NR)_2Sn|} \xrightarrow[\substack{+\ M(CO)_6,h\nu \\ -CO}]{\substack{+\ (CO)_5M(THF) \\ -THF}} \underset{\substack{19 \\ M\ =\ Cr,\ Mo}}{me_2Si(NR)_2Sn{-}M(CO)_5} \qquad (XIV)$$

of 19 have been established by spectroscopic methods and can be ascribed to the mm ($C_{2v}$)-symmetry. The two metals Cr and Mo differ quite strongly in their reactivity: With $Mo(CO)_6$, a lot of other interesting compounds result besides 19, their properties and structures being studied at the moment[36].

## REACTIONS OF THE Sn-N- AND Sn-O-CAGE-COMPOUNDS

As we have already shown in a previous chapter (figure 8) the cages 13 and 14 can be transformed by controlled thermolysis to the cubane-like molecule $(|SnNR)_4$ (15). Another typical reaction for the norcubane-like molecule 14 is the transaminolysis with 1 at elevated temperatures as shown in scheme XV.

$$\underset{\underline{1}}{me_2Si(NR)_2Sn|} + \underset{\underline{14}}{(RN)_4Sn_3H_2} \xrightarrow{\Delta T} \underset{\underline{2}}{me_2Si(NRH)_2} + \underset{\underline{15}}{(RNSn|)_4} \qquad (XV)$$

The marked tendency of tin to form a Sn-O-bond rather than a Sn-N-bond can be used for introducing oxygen besides tin and nitrogen into the cage 15. Following equation XVI, this can best be done by mild hydrolysis of the cage 14, whereas the closed cage 15 does not react in the same way[37]. In the most remarkable red-coloured cage 20 three different main-group elements are bonded together, again forming a $Sn_4N_3O$-cube of $C_{3v}$ - symmetry, as established by spectroscopic methods. Thus the oxygen atom has a trigonal pyramidal coordination, which implies that four electron lone-pairs are in close contact (one at the oxygen and three at the tin atoms). It is not astonishing that cage 20 reacts as a base towards acids like aluminiumtrimethyl (XVII) to form the adduct 21. 21 is isoelectronic to cage 15 which means that in the latter one $N\text{-}Cme_3$ group has been substituted by $O\text{-}Alme_3$ (a corresponding $Bme_3$-adduct to 21 cannot be synthezised). The crystals of 15 and 21 are isotypic, the crystal structure determination of 21 revealing the very high symmetry of the molecule (see figure 10)[38]. 21 can be transformed into 15 by thermolysis following equation XVIII.

$$4\ \underset{\underline{14}}{(RN)_4Sn_3H_2} + 3\ H_2O \xrightarrow[RNH_2]{} 3\ \underset{\underline{20}}{(RN)_3Sn_4O} + 7\ RNH_2 \qquad (XVI)$$

$$\underset{\underline{20}}{(RN)_3Sn_4O|} + \frac{1}{2}\,(Alme_3)_2 \longrightarrow \underset{\underline{21}}{(RN)_3Sn_4O + Alme_3} \qquad (XVII)$$

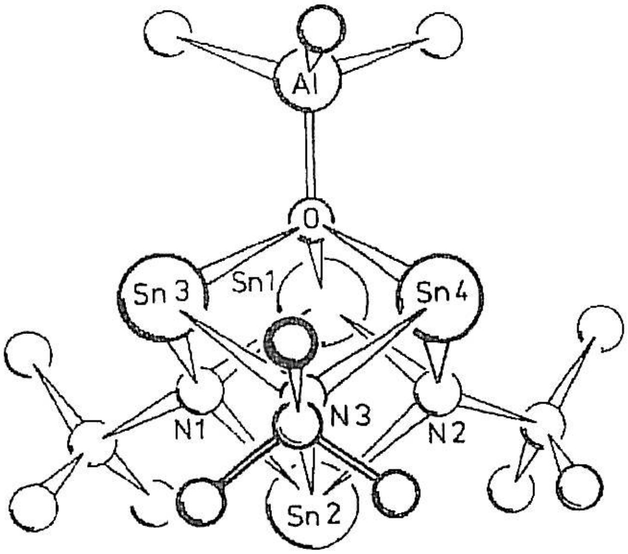


Figure 10: The molecular structure of cage 21 as established by X-ray-structure determination[38].

Until now we did not succeed in detecting the "leaving group" $\{SnOAlme_3\}$ even in the mass spectrum, so further experiments have to be carried out.

$$4\ \underset{\underline{21}}{(RN)_3Sn_4OAlme_3} \xrightarrow{\Delta T} 3\ \underset{\underline{15}}{(RN)_4Sn_4} + 4\{SnOAlme_3\} \qquad (XVIII)$$

VALENCE FLUCTUATION IN Sn-N-CAGES

From the cages considered so far in this review (3, 5, 10, 12, 13, 14, 15, 16, 20, 21;) two compounds show a peculiarity which will be discussed here in more detail: the valences between the atoms are not fixed but fluctuate at ordinary temperatures. Experimentally this property can be derived from NMR-spectra, which show a signal-distribution due to molecules of higher symmetry than the one established by X-ray structure determination. When the samples are allowed to cool down, the expected pattern in the NMR-spectrum occurs. The two substances which show this fluctuation effect, the cages 5 and 14, have one common property: besides the trivalent tin atoms and the tetravalent nitrogen atoms they include trivalent nitrogen atoms, still having a free electron pair. The latter can displace tetravalent N-atoms by a sort of a "reversible substitution" creating fluctuating bonds.

The consequence of this for cage 5 is shown in figure 11:

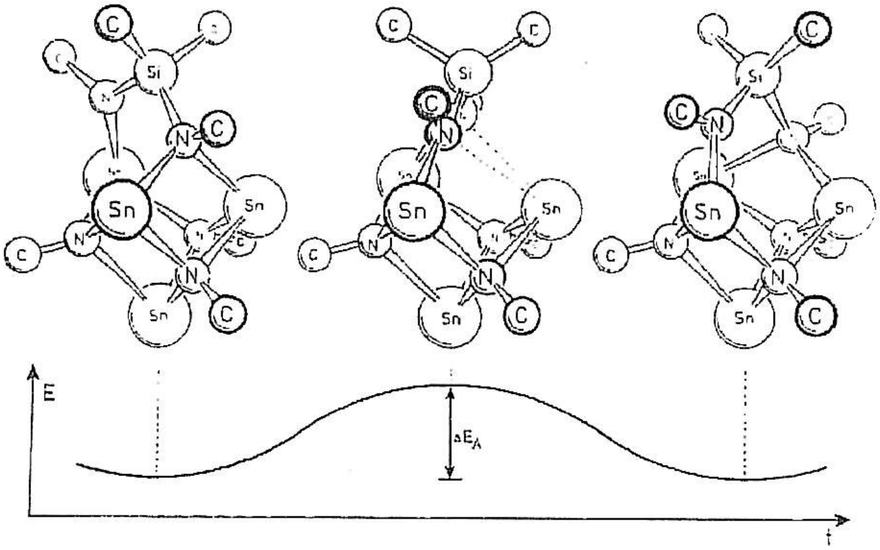


Figure 11: Valence fluctuation in cage compound 5. One of three different transition states is shown[16].

one of the two nitrogen atoms of the diazasila-group has three bonds, the other one has four. After having passed through the transition state, the coordination numbers of the two atoms are inversed, the resulting molecule being congruent to its initial. The movement can be described as a "rotation" of the diazasila-group over the $Sn_4(Nme)_3$-part of the cage. It can be frozen on the $^1$H-NMR-time-scale at about - 50 °C[16].

The fluctuation in cage 14 is even more complicated. From the $^1$H-NMR-spectra two different movements can be recognized: one is due to the migration of two hydrogen atoms attached to the nitrogen atoms, the other one is due to a fluctuation of bonds within the Sn-N-cage. In figure 12 the possible mechanisms are demonstrated. In the $^1$H-NMR-time-scale all movements in the molecule 14 cease at - 50 °C. When the sample is allowed to warm up, the 3 different signals of the tert-butyl-groups (integration: 2:1:1) - according to the mirror symmetry of 14 - vanish in favour of 2 signals of a ratio 3:1.

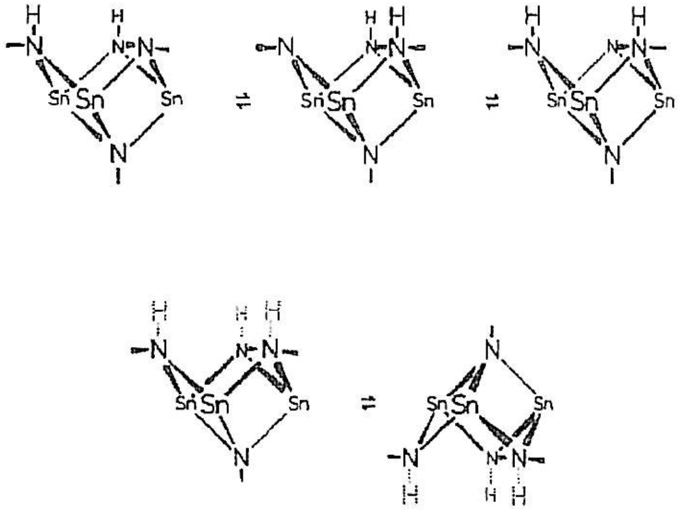


Figure 12: Valence fluctuation in $Sn_3(NCme_3)_4H_2$ (<u>14</u>) according to $^1H$-NMR-spectroscopic results[31].

The molecule <u>14</u> has subsequently adopted $C_{3v}$ ( 3 m)-symmetry, which means that three nitrogen atoms are equal (migration of the H-atoms as shown in figure 12). The 3:1-signal ratio is again altered when the temperature is raised to 60°C, where only 1 signal is present for the tert-butyl-groups. The molecule has now adopted Td($\bar{4}$ 3 m)-symmetry, which can most reasonably be explained by a fluctuation of bonds within the cage. One of the possible mechanisms, shown in the lower part of figure 12, is in some respect similar to the change of chair- to boat-conformation of six-membered rings.

## <u>STRUCTURAL ASPECTS OF MOLECULAR TIN(II)-COMPOUNDS</u>

To sum up our results in structural investigations, we can note the following general points in the structural chemistry of molecular tin(II)-compounds:

(a) Monomeric stannylenes are hard to synthesize and even more difficult to stabilize in a crystal structure. In general, the divalent tin atom tends to achieve a higher coordination number by addition of a nucleophile. The preferred bond arrangement is the trigonal pyramidal one, the tin atom attaining an 8-electron configuration. Besides the rarely encountered tetra-coordination, the trigonal planar bond arrangement as in the pentacarbonyl-chromium-complex should be mentioned.

(b) A higher coordination number at the tin atom is reflected in longer mean Sn-N-distances: c.n. 2 :209, c.n. 3 :222-224 and c.n. 4 :240 pm.

(c) The mean value of the bond angles at the 3-coordinated tin atoms varies for different structures from 75°-86°, whereas the mean Sn-N-distance remains nearly constant.

(d) The cubane-like molecules as 15, 16 and 21 deviate strongly from a cube, the bond angles at the heavier Sn-atom approaching 80° and at the lighter N atom 100°.

(e) On the whole, the diazasilastannylene 1 can be considered as a 0-, 1-, 2- and 3-dentate ligand with several donor- or acceptor-functions, as summarized in figure 13.

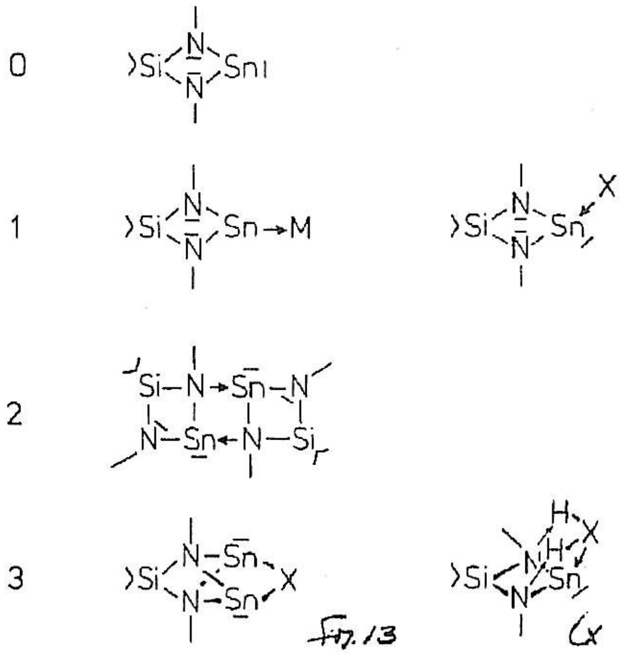


Figure 13: The different possibilities of coordination for the diazastannylene 1.

This may, of course, be considered as merely formal, but it is very helpful in elucidating some of the reaction principles.

## CLOSING REMARKS

The chemistry and structural aspects of the cyclic diazastannylene 1 in many respects seem to rely on straightforward principles which to some extent can be deduced from the chemistry of ionic and complexed tin(II)-compounds$^{10,39)}$, from open-chain diazastannylenes$^{40,41)}$, and to a minor extent from organic stannylenes mostly prepared as intermediates$^{42,43)}$. Some aspects are nevertheless new and lead to novel rings and cages which can easily be prepared. The reason for this outstanding property of 1 seems to be the structurally fixed multi-functionality of the molecule.

We thank the following organisations for supporting our work: Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie and Hoechst AG, Germany.

## REFERENCES

1) J.E. Huheey, Inorganic Chemistry: Principles of Structure and Reactivity, Harper & Row, New York, 1972, p.620-22.

2) W. Kirmse, Carbene Chemistry, Academic Press, New York 1971.

3) M.W. Lister and L.E. Sutton, Trans. Faraday Soc. 37, 406 (1941).

4) E.O. Fischer and H. Grubert, Z. Naturforsch. 11b, 423 (1956).

5) A. Almenningen, A. Haaland and T. Motzfeld, J. Organmetal. Chem. 7, 97 (1967).

6) P.J. Davidson and M.F. Lappert, J. Chem. Soc., Chem. Comm. 1973, 317.

7) D.H. Harris and M.F. Lappert, J. Chem. Soc., Chem. Comm. 1974, 895.

8) C.D. Schaeffer and J.J. Zuckerman, J. Am. Chem. Soc. 96, 7160 (1974).

9) P. Foley and M.Zeldin, Inorg. Chem. 14, 2264 (1975).

10) J.D. Donaldson, Progress in Inorganic Chemistry, J. Wiley, New York, Vol. 8, 287-356 (1967).

11) M. Veith, Angew. Chem. 87, 287 (1975); Angew. Chem. Int. Ed. 14, 263 (1975).

12) M. Veith, Z. Naturforsch. 33b, 7 (1978).

13) D.E. Goldberg, D.H. Harris, M.F. Lappert and K.M. Thomas, J. Chem. Soc., Chem. Comm. 1976, 261.

14) W. Fink, Helv. Chim. Acta 47, 498 (1964).

15) M. Veith, Z. Naturforsch. 33b, 1 (1978).

16) M. Veith and M. Grosser, results to be published.

17) P.J. Corvan and J.J. Zuckerman, Inorg. Chim. Acta 34, L 255 (1979).

18) L. Pauling, The nature of the chemical bond, Verlag Chemie, Weinheim, 1968.

19) M. Veith and M.L. Sommer, unpublished results.

20) M. Veith and G. Schlemmer; an X-ray structure determination of 6 at −100°C has just been performed.

21) M. Veith, O. Recktenwald and H. Humpfer, Z. Naturforsch. 33b, 14 (1978).

22) M. Veith, Z. anorg. allg. Chem. 446, 227 (1978).

23) M. Veith and O. Recktenwald, Z. anorg. allg. Chem. 459, 208 (1979).

24) M. Veith, Chem. Ber. 111, 2536 (1978).

25) M. Veith, M.L. Sommer and D. Jäger, Chem. Ber. 112, 2581 (1979).

26) The decomposition of 6 seems to be a first order reaction but may of course be more complex.

27) M. Veith, Z. Naturforsch. 35b, 20 (1980).

28) M. Veith and R. Bachmann, unpublished results.

29) L.D. Petit, Q. Rev., Chem. Soc. 25, 1 (1975).

30) H. Nöth and P. Wolfgardt, Z. Naturforsch. 31b, 697 (1976).

31) M. Veith and H. Lange, to be published.

32) M. Veith and G. Schlemmer, results to be published.

33) J.D. Cotton, P.J. Davison, D.E. Goldberg, M.F. Lappert and K.M. Thomas, J. Chem. Soc., Chem. Comm. 1974, 893.

34) M. Veith, H. Lange, M.-L. Sommer and R. Bachmann, 9. Int. Conf. on Organomet. Chem., Dijon 1979, Abstr. A45.

35) W. Petz and A. Jonas, J. Organomet. Chem. 120, 423 (1976); see also: W. Petz, J. Organomet. Chem. 165, 199 (1979).

36) M. Veith, H. Lange and K. Bräuer, to be published.

37) M. Veith and H. Lange, Angew. Chem. 92, 408 (1980); Angew. Chem. Int. Ed. 19, 401 (1980).

38) M. Veith and O. Recktenwald, results to be published.

39) R. Nesper and H.G. von Schnering, Acta Crystallogr. A34, 158 (1978).

40) M.J. Gynane, M.F. Lappert, S.J. Miles and P.P. Power, J. Chem. Soc., Chem. Comm. 1976, 256.

41) D.H. Harris and M.F. Lappert, J. Organomet. Chem. Libr. 2, 13 (1976).

42) C. Grugel, W.P. Neumann and P. Seifert, Tetrahedron Letters 25, 2205 (1977).

43) W.P. Neumann, "The Stannylenes $R_2Sn$", in M. Gielen, P.G. Harrison: The Organometallic and Coordination Chemistry of Germanium, Tin and Lead, Freund Publ., Tel-Aviv 1978.

Journal of Organometallic Chemistry Library 12

# Organometallic Chemistry Reviews

Including Plenary Lectures from the Third International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin and Lead, held in Dortmund, July 21st–25th, 1980

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ELSEVIER SCIENTIFIC PUBLISHING COMPANY
Amsterdam – Oxford – New York 1981

ELSEVIER SCIENTIFIC PUBLISHING COMPANY
Molenwerf 1, 1014 AG Amsterdam
P.O.Box 211, 1000 AE Amsterdam, The Netherlands

*Distributors for the United States and Canada:*

ELSEVIER/NORTH-HOLLAND INC.
52 Vanderbilt Avenue
New York, N.Y. 10017

ISBN 0-444-42025-8 (Vol. 12)
ISBN 0-444-41446-2 (Series)

Printed in The Netherlands