# 15

Tin–Nitrogen and Tin–Phosphorus Heterocycles

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In this chapter, rings and cages are described that contain the elements tin and nitrogen, or tin and phosphorus. Ring systems containing elements other than these three are only considered if their chemistry and structure are dominated by stannazane or stannaphosphane units. Polycyclic compounds and cages that are exclusively based upon tin and nitrogen or tin and phosphorus have been known for only a short time and are also dealt with.

15.1 Cyclostannazanes

Alternation of tin and nitrogen atoms leads to formation of four-membered (1) and six-membered (2) ring systems, known as cyclodistannadiazanes and cyclotristannatriazanes respectively:
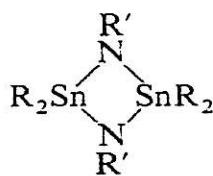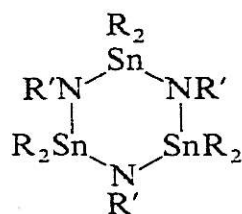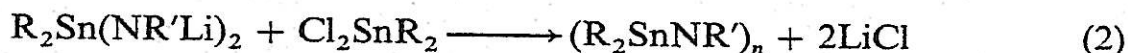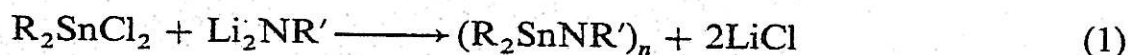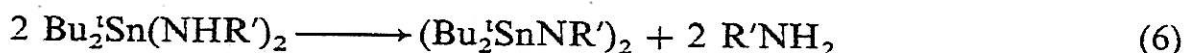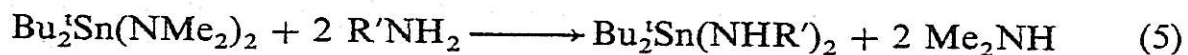

(1)   (2)

15.1.1 Preparation and structure

Several methods have been developed for the synthesis of tin–nitrogen ring systems based upon the formation of tin–nitrogen bonds. This may be achieved by reactions that take place with elimination of a salt (equation

(1), $n = 2$, R = Me, R' = Bu[t];[1] $n = 3$, R_2 = MeCl, R' = Et;[2] and equation (2), $n = 2$, R_2 = MeBu[t], R' = Bu[t];[3,4] R = Me, R' = CMe(CF$_3$)$_2$[5]), elimination of a volatile amine, i.e. transamination (equation (3), $n = 2$, R = Bu[t], R' = Me, CH$_2$Ph;[6] $n = 3$, R = Me, R' = Me, Et[7]) or the elimination of tetramethylstannane (equation (4), $n = 3$, R' = SO$_2$Me, SO$_2$CF$_3$[8,9]):

$$R_2SnCl_2 + Li_2NR' \longrightarrow (R_2SnNR')_n + 2LiCl \qquad (1)$$

$$R_2Sn(NR'Li)_2 + Cl_2SnR_2 \longrightarrow (R_2SnNR')_n + 2LiCl \qquad (2)$$

$$R_2Sn(NR''_2)_2 + H_2NR' \longrightarrow (R_2SnNR')_n + 2HNR''_2 \qquad (3)$$

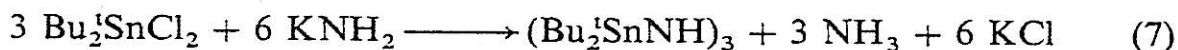$$R'N(SnMe_3)_2 \xrightarrow{\Delta} (Me_2Sn-NR')_n + SnMe_4 \qquad (4)$$

The transamination reaction (3) seems to proceed in two steps, as has been shown for the reaction of bis(dimethylamino)bis(t-butyl)tin with primary aliphatic amines.[6] In the first step the amino groups on the tin atom are interchanged (equation 5), while in the second the primary amine is excluded, probably by hydrogen transfer from one nitrogen atom to the other (equation 6):[6]

$$Bu_2^tSn(NMe_2)_2 + 2\ R'NH_2 \longrightarrow Bu_2^tSn(NHR')_2 + 2\ Me_2NH \qquad (5)$$

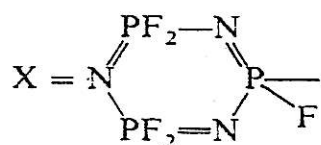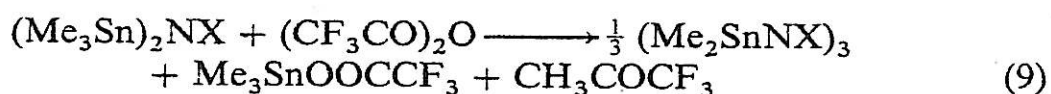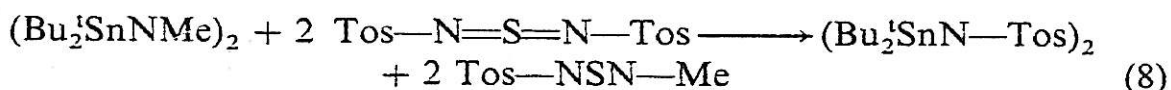$$2\ Bu_2^tSn(NHR')_2 \longrightarrow (Bu_2^tSnNR')_2 + 2\ R'NH_2 \qquad (6)$$

The four-membered ring is favoured against the six-membered when bulky substituents are on either the tin or the nitrogen atoms. No stable eight-membered ring has ever been observed.

Besides the synthetic routes mentioned so far, other special preparations of tin–nitrogen rings have been developed. Elimination of a salt and an amine is observed when bis(t-butyl)dichlorstannane is reacted with potassium amide (equation 7):[3]

$$3\ Bu_2^tSnCl_2 + 6\ KNH_2 \longrightarrow (Bu_2^tSnNH)_3 + 3\ NH_3 + 6\ KCl \qquad (7)$$

Two quite singular procedures are shown in equations (8)[10] and (9):[11]

$$(Bu_2^tSnNMe)_2 + 2\ Tos-N{=}S{=}N-Tos \longrightarrow (Bu_2^tSnN-Tos)_2$$
$$+ 2\ Tos-NSN-Me \qquad (8)$$

$$(Me_3Sn)_2NX + (CF_3CO)_2O \longrightarrow \tfrac{1}{3}\ (Me_2SnNX)_3$$
$$+ Me_3SnOOCCF_3 + CH_3COCF_3 \qquad (9)$$

A peculiar type of ring-compound (**3**) is formed, when amines of low-valent tin(II) are synthesized. As the tin atom in these molecules is not electronically saturated, it behaves as a strong Lewis acid and forms dimers by coordination with the Lewis basic amine ligands:[12]

$$2\ (R_2N)_2Sn: \longrightarrow \quad \begin{array}{c} R_2N-Sn \qquad Sn-NR_2 \end{array} \tag{10}$$

(3)
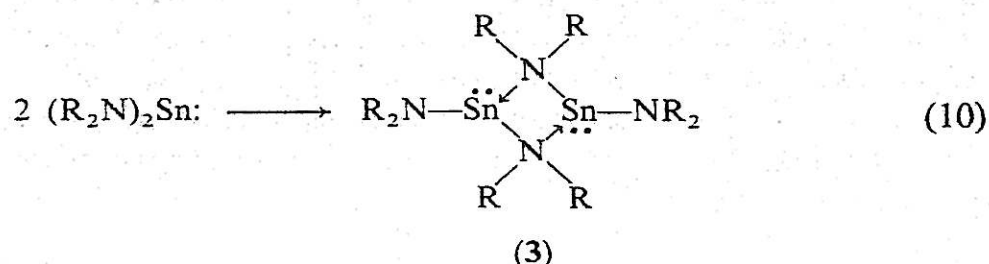
This intermolecular Lewis-acid–base interaction is still important, even when the bis(amino)stannylene is coordinated to transition metals.[13] It can be suppressed if bulky substituents are used on the nitrogen atoms.[B 1]
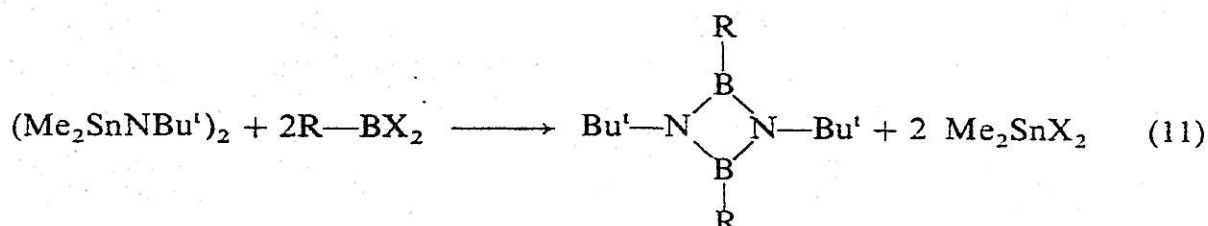
The ring size and composition of cyclostannazanes follow from mass spectra or relative molecular-mass determinations. No direct structural investigations on pure cyclostannazanes by X-ray diffraction have been made.
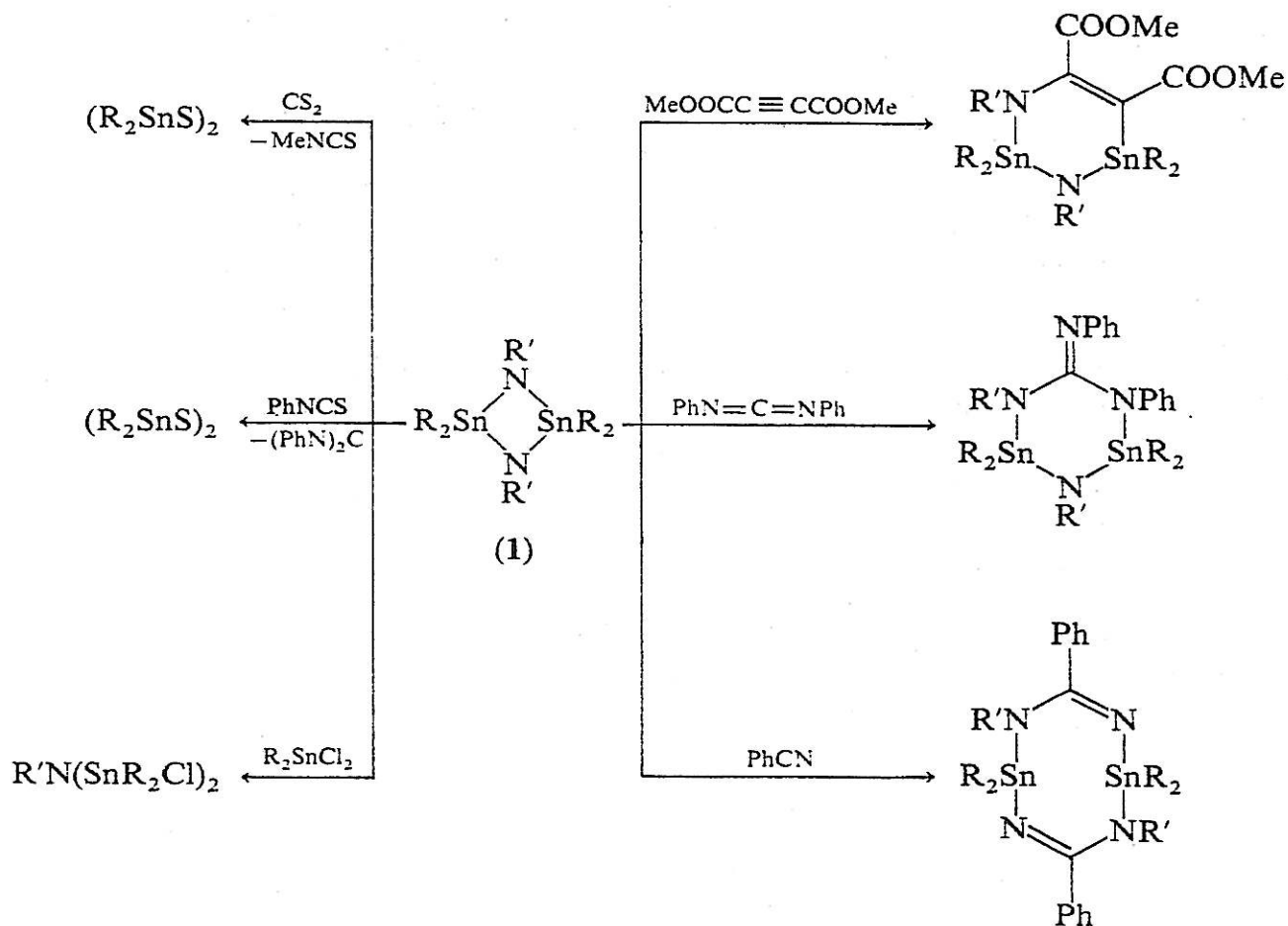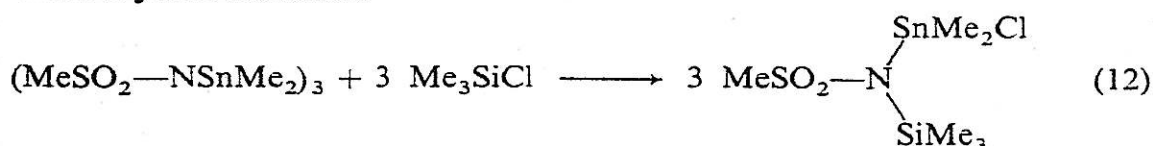
15.1.2   Reactions of cyclostannazanes

All cyclic tin–nitrogen compounds are sensitive to moisture and air, and must therefore be handled under an N_2 or Ar atmosphere. The reactivity of the cyclodistannadiazane $(Bu_2SnN—Me)_2$ has been extensively studied. Besides substitution reactions and ring cleavage, insertions into the Sn—N single bond are observed when this cyclostannazane is allowed to react with C–C or C–N double or triple bonds (R = Bu^t, R′ = Me). In the latter reactions either one or two C–C or C–N components may be inserted, leading to six- or eight-membered cyclic compounds (ring-expansion reactions).[10]

Cyclostannazanes react with various organoelement halides, with complete cleavage of the Sn–N ring. Thus with organoboron dihalides RBX_2 (R = Me, X = Cl, Br) the B_2N_2 ring compound is recovered in 75% yield:[1]

$$(Me_2SnNBu^t)_2 + 2R—BX_2 \longrightarrow Bu^t—N\underset{\underset{R}{|}\underset{B}{}}{\overset{\overset{R}{|}\overset{B}{}}{\diagup\diagdown}}N—Bu^t + 2\ Me_2SnX_2 \qquad (11)$$

A similar ring cleavage has been reported for six-membered rings reacting with trimethylchlorosilane:[8]

$$(MeSO_2—NSnMe_2)_3 + 3\ Me_3SiCl \longrightarrow 3\ MeSO_2—N\begin{smallmatrix} SnMe_2Cl \\ \\ SiMe_3 \end{smallmatrix} \qquad (12)$$

^{119}Sn NMR techniques have been used to confirm that in equimolar solutions of $(Me_2SnNEt)_3$ and $(Me_2SnS)_3$ redistribution of the ring components takes place.[14] Besides the starting compounds, the cycles (4) and (5) are observed:

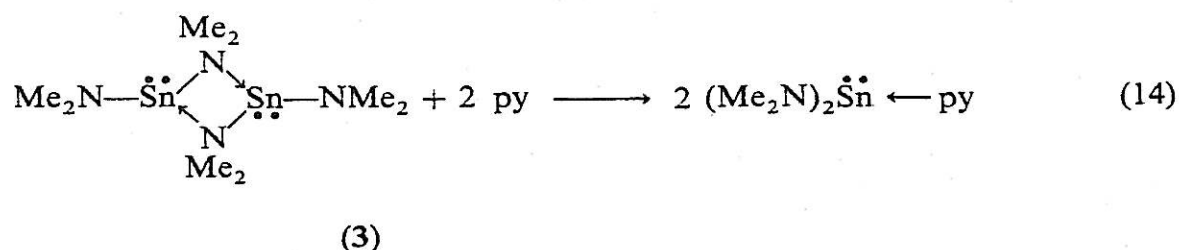(4)   (5)
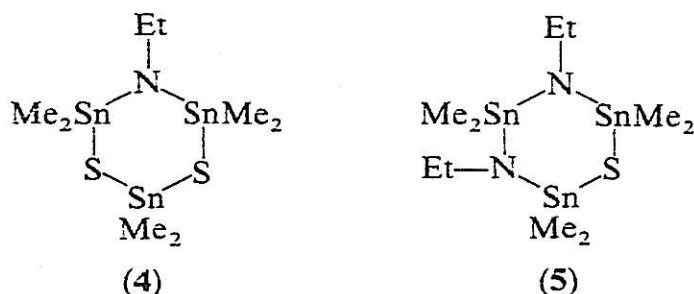
A redistribution of ring components may also be responsible for the formation of (6) in reaction (13).[15] This is a new ring that contains two tin and three nitrogen atoms, and one sulphur atom of oxidation state IV.
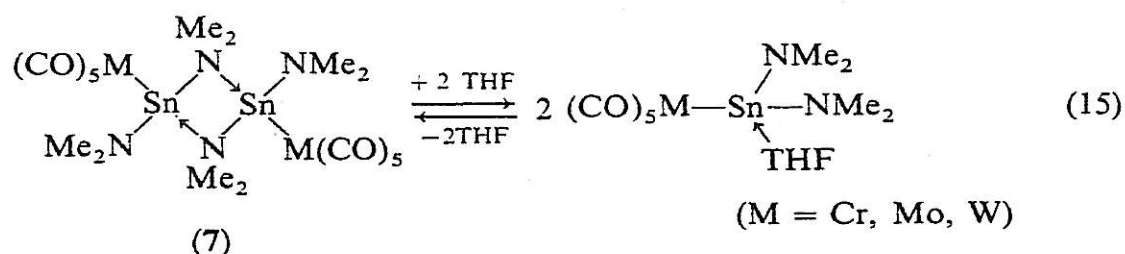
$$2\ (CF_3SO_2\text{---}NSnMe_2)_3 + 6\ CF_3SO_2\text{---}N{=}S{=}O \xrightarrow[-SO_2]{} 3$$

(6)

(13)
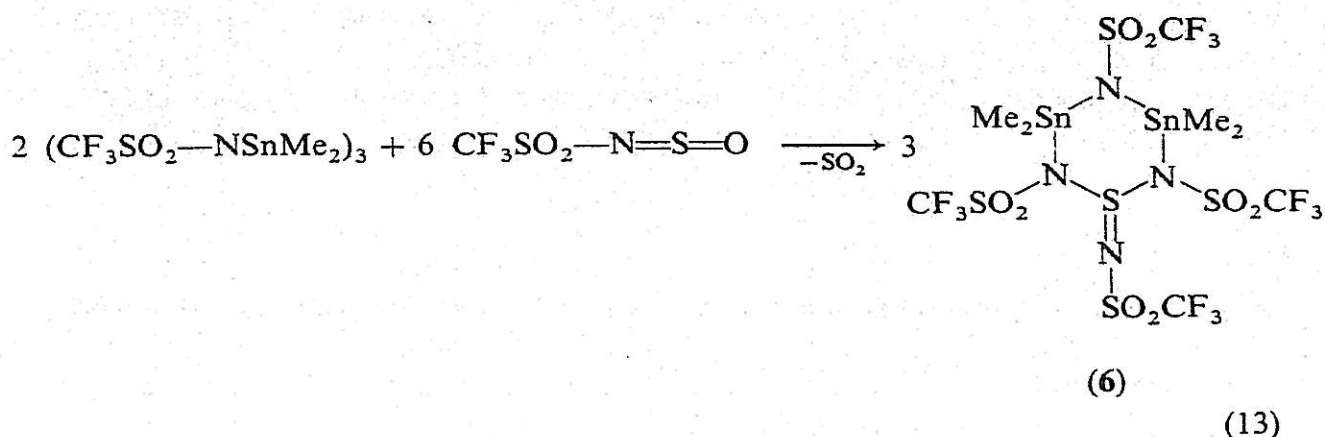
The structure of (6) has been established by X-ray diffraction techniques.[15] The ring is not planar (envelope conformation) with very different Sn–N bond lengths, ranging from 208.4 to 225.1(7) pm.
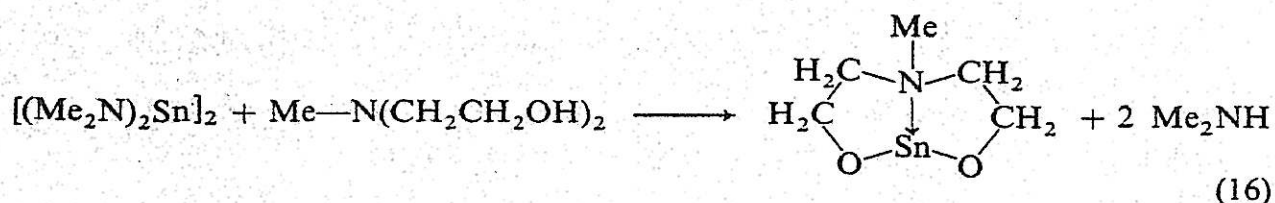
Cyclic compounds arising from Lewis-acid–base interactions of tin(II) with nitrogen ligands as in (3) are always in competition with noncyclic monomeric species when bases are added:[12]

$$Me_2N\text{---}\overset{..}{Sn} \overset{\overset{\displaystyle Me_2}{N}}{\underset{\underset{\displaystyle Me_2}{N}}{\diamond}} \overset{..}{Sn}\text{---}NMe_2 + 2\ py \longrightarrow 2\ (Me_2N)_2\overset{..}{Sn} \longleftarrow py \qquad (14)$$

(3)

The same sort of reaction has been observed for the metal-bonded bis(dimethylamino)stannylene dimer (7):[13]

$$(CO)_5M \overset{\overset{\displaystyle Me_2}{N}}{\underset{\underset{\displaystyle Me_2}{N}}{<}} \overset{NMe_2}{\underset{M(CO)_5}{>}} \underset{-2THF}{\overset{+2\ THF}{\rightleftharpoons}} 2\ (CO)_5M\text{---}\underset{\underset{\displaystyle THF}{\uparrow}}{Sn}\overset{\displaystyle NMe_2}{\text{---}NMe_2} \qquad (15)$$

(7)

(M = Cr, Mo, W)

In this latter reaction there is equilibrium between the THF-free dimeric compound and the base-stabilized monomer. The tin–nitrogen bond in compounds of type (3) is very sensitive to hydrolysis or alcoholysis.[12] An interesting bicyclic compound is formed as follows (for further discussion of these types of compounds see ref. 16):

$$[(Me_2N)_2Sn]_2 + Me\text{—}N(CH_2CH_2OH)_2 \longrightarrow \begin{array}{c} Me \\ H_2C\text{—}N\text{—}CH_2 \\ H_2C \qquad CH_2 \\ O\text{—}Sn\text{—}O \end{array} + 2\ Me_2NH$$

$$(16)$$

15.2 Cyclic silastannazanes and other heterocyclostannazanes
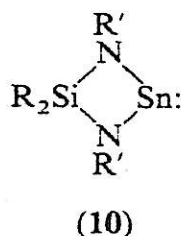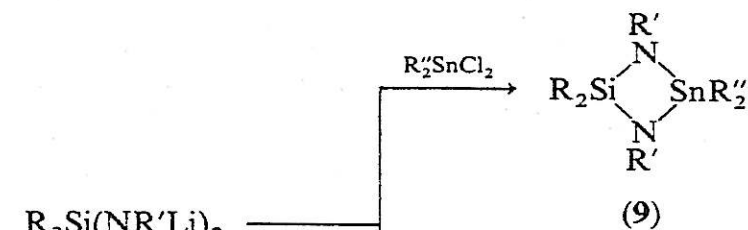
A large number of four-membered cyclic compounds with the element combination SnN_2Si or with other elements in the place of silicon have been reported (see also Section 8.5.2). They are synthesized via salt-elimination reactions:[17-20]

$$R_2Sn(NR'Li)_2 + R_2''MCl_2 \xrightarrow[-LiCl]{} \begin{array}{c} R' \\ N \\ R_2Sn \quad MR_2'' \\ N \\ R' \end{array}$$

$$(8)$$
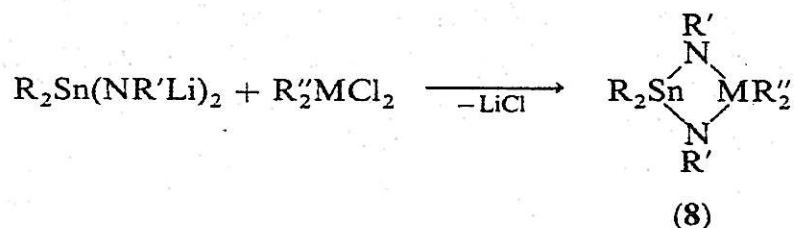
$M = Si, Ge, Pb;\ R = Me,\ R' = CMe(CF_3)_2,\ R'' = Me$[17]

$M = Ge;\ R = Me,\ R' = SiEt_3,\ R'' = Et$[18]

$M = Ti, Zr;\ R = Me,\ R' = CMe(CF_3)_2,\ R'' = Me$[17]

$$R_2Si(NR'Li)_2 \quad\xrightarrow{R_2''SnCl_2}\quad \begin{array}{c} R' \\ N \\ R_2Si \quad SnR_2'' \\ N \\ R' \end{array}$$

$$(9)$$

$R = Me,\ R' = Bu^t$[19,20]

$$\xrightarrow{SnCl_2}\quad \begin{array}{c} R' \\ N \\ R_2Si \quad Sn: \\ N \\ R' \end{array}$$

$$(10)$$

The compounds (10) deserve some comment. In this heterocycle the tin atom is in a formal oxidation state $+$ II, which means that the compound
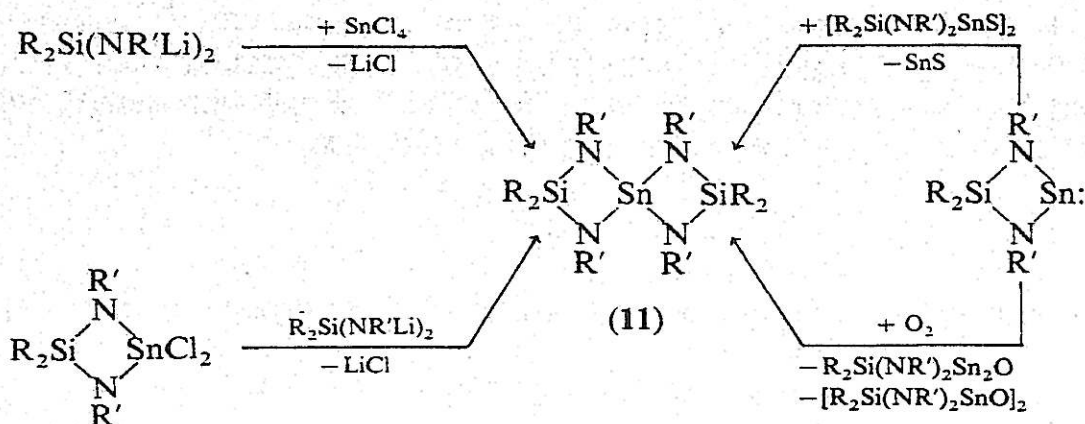
may be considered as a carbene analogue (see also ref 21). This bis-(amino)stannylene is highly reactive: depending on the substituents on the nitrogen atom, it may either be monomeric (R = Bu^t) or dimeric (R = isopropyl) in organic solvents (formulae (10a) and (10b)):[22]

(10a)   (10b)
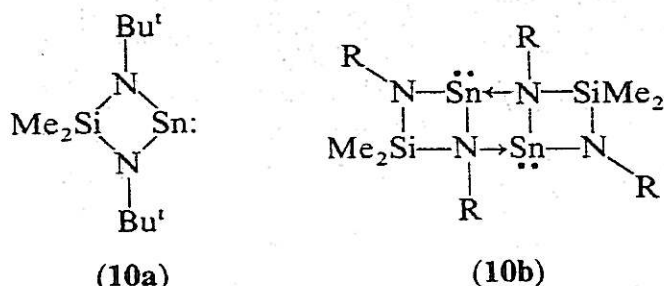
When a hexane solution of (10a) is allowed to crystallize at $-78\,°C$ monoclinic crystals are formed, which contain equal amounts of the monomer (10a) and the dimer (10b).[22] The tin atom in (10a) can be oxidized very easily,[19,23] it can be coordinated by bases (for example pyridine)[22] or can itself coordinate to transition metals[24] with conservation of the four-membered cycle (R = Me, R' = Bu^t, R" = Pr^i):
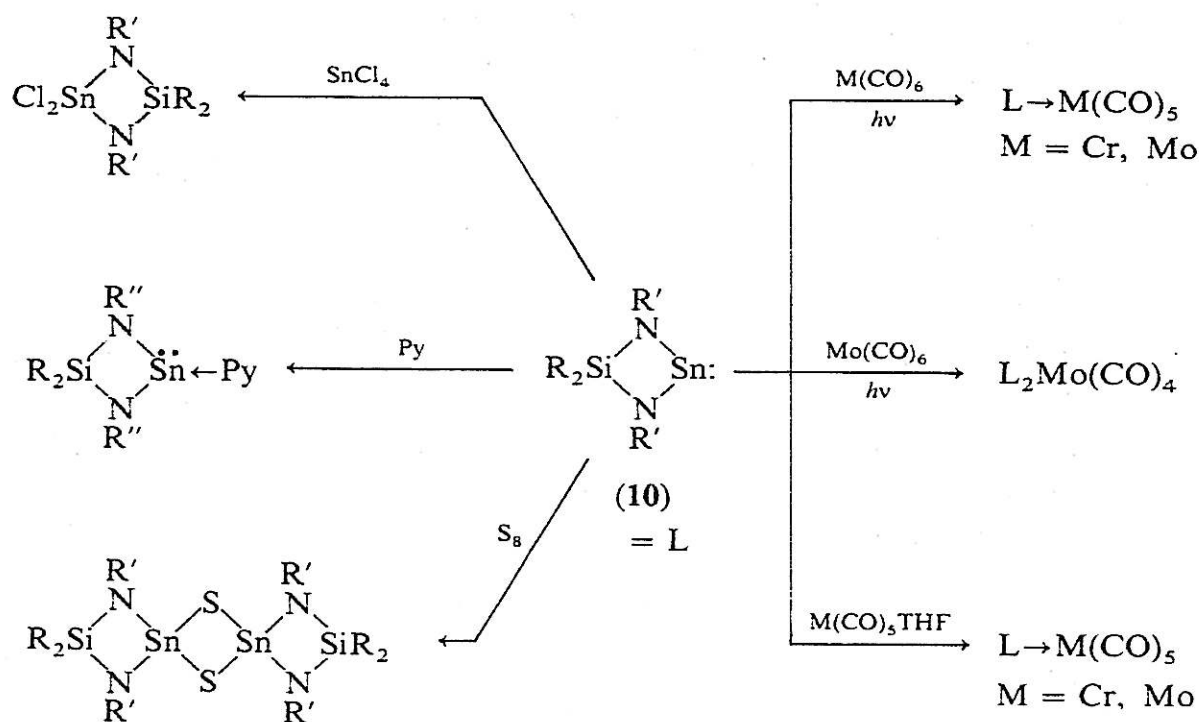

A spirocyclic compound (11) (R = Me, R' = Bu^t)[19,23,25] is obtained in several reactions:

$$R_2Si(NR'Li)_2 \xrightarrow[-LiCl]{+ SnCl_4}$$

$$\xleftarrow[-SnS]{+ [R_2Si(NR')_2SnS]_2}$$

(11)

$$\xrightarrow[-LiCl]{R_2Si(NR'Li)_2}$$

$$\xrightarrow[\substack{-R_2Si(NR')_2Sn_2O \\ -[R_2Si(NR')SnO]_2}]{+ O_2}$$

A spirocyclic compound, analogous to (11) but with selenium as spiro-centre, was prepared by reacting $Me_2Sn(NR'Li)_2$ with $SeCl_4$.[17]

The eight-membered cycle (12) has been synthesized in 80% yield by elimination of both tetramethylstannane and trimethylchlorstannane from a bis(trimethylstannyl)amine (R = Me):[26]

$$4\ CF_3SO_2N(SnR_3)_2 + 2\ R_2SiCl_2 \xrightarrow[\substack{-4R_3SnCl \\ -2\ SnR_4}]{} \quad (17)$$

(12)
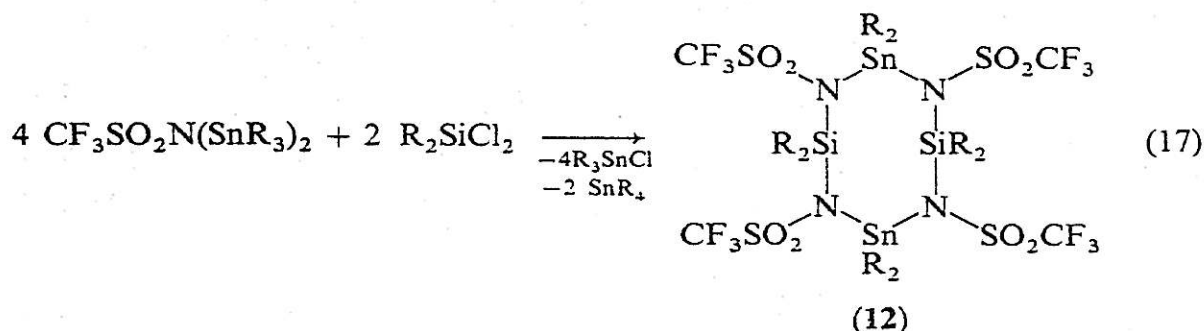
Structural investigations by X-ray diffraction techniques have been performed on several mono-, spiro- and polycyclic compounds described in this section. The tin atom in the monomeric bis(amino)stannylene (10a) maintains its low coordination number of two even in the crystal, and can thus be readily compared with the spirocyclic compound (11) (bond lengths in pm):

(10a)

(11)
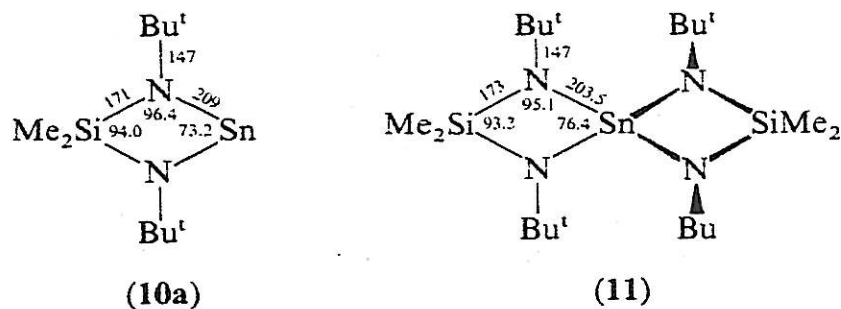
The ring compound (10a) has almost C_{2v} symmetry, while D_{2d}-symmetry must be assumed for the free molecule (11). The four-membered rings in (10a) and (11) are strictly planar with nitrogen atoms in a trigonal planar coordination. The Sn–N bond length in the spirocyclic compound is 5.5 pm less than in the stannylene, which must be explained by a smaller covalent radius for the four-valent tin atom.[B 1] The electron density seems to be shifted into the Si–N bonds (small distances); this effect is more pronounced in (10a) than in (11). As expected, the smallest angle in the rings is connected to the heaviest atom.
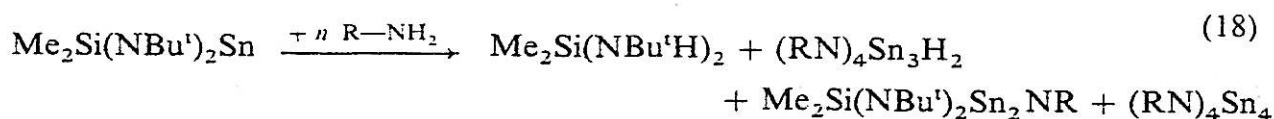
In the dimeric analogue of (10a), depicted in (10b), three four-membered cycles are sharing edges, and are nearly orthogonally aligned with one another (point symmetry: C_i) (bond lengths in pm):[20]


(10b)
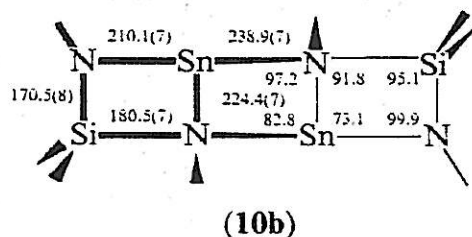
The chemical application of silastannazanes has been studied in the case of compound (10a). The reactions shown on p. 389 give some examples of the reactivity of this cyclic diazasilastannylene. The whole molecule may act as a Lewis acid via the unsaturated tin atom or as a base via the nonbonding electron pairs at the nitrogen and tin atoms. Combining the different electro- and nucleophilic centres, the whole molecule (10a) can act as a mono-, di- or tridentate ligand versus other Lewis-acid–base systems. It is beyond the scope of this book to describe all possibilities, and the reader is referred to some review articles.[B 1 –B 3] However one important use will be described in the following section.

## 15.3 Polycyclic Sn–N compounds and related molecules

When the bis(amino)stannylene (10a) is allowed to react with primary amines, three different polycycles are formed besides the dimethylbis-(t-butylamino)silane, depending on conditions:[27,28]
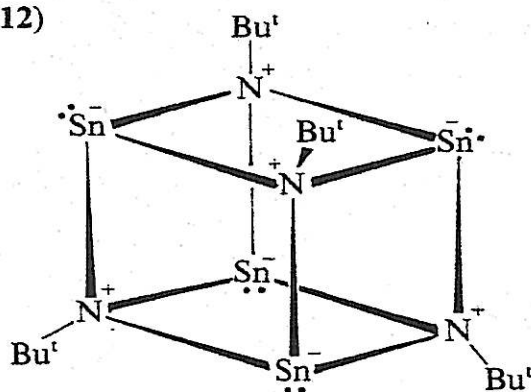
$$Me_2Si(NBu^t)_2Sn \xrightarrow{+ n\ R-NH_2} Me_2Si(NBu^tH)_2 + (RN)_4Sn_3H_2 \tag{18}$$

$$+ Me_2Si(NBu^t)_2Sn_2NR + (RN)_4Sn_4$$

If R is t-butyl then the three compounds can be isolated and identified as (12) (13) and (14):[27]
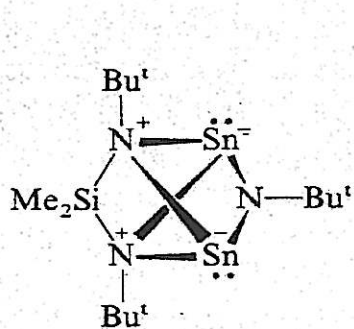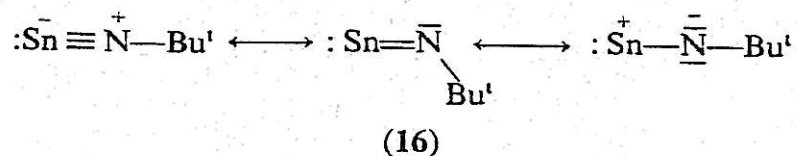
(12)
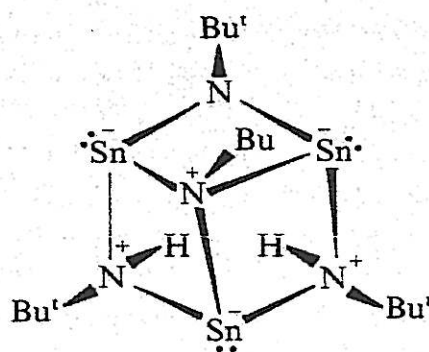
(13)

(14)

In (14) the t-butyl group can be replaced by isopropyl, dimethyl and benzyl amino groups. If the substituent on the nitrogen atoms exhibits more reduced steric requirements then the resulting compound becomes polymeric, as in the case of $(SnN—Me)_n$.[29]

The reaction course of equation (18) has been studied very thoroughly. It has been demonstrated that the educts in equation (18) are in equilibrium with a Lewis-acid–base adduct (15), which can be isolated at $-78\,°C$:[B 3]

$$Me_2Si(NBu^t)_2Sn + H_2N—Bu^t \rightleftharpoons \text{(15)} \tag{19}$$

(15)
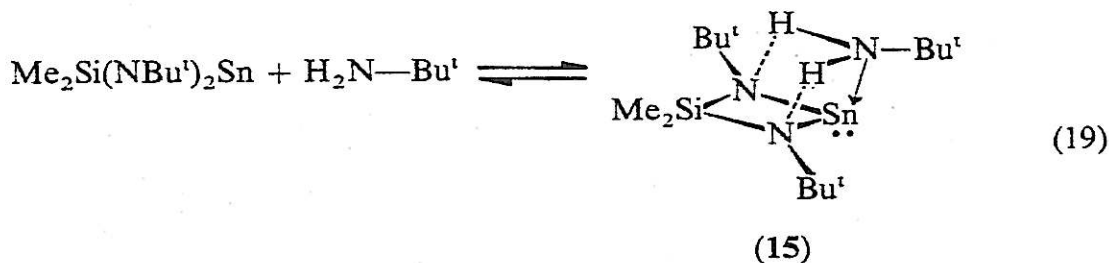
An X-ray structural determination of (15) shows that besides the bond between the tin atom and the nitrogen atom of the t-butylamine, $H \cdots N$ contacts to the nitrogen atoms of the ring have to be considered. It can be assumed that the decomposition of the intermediate (15) proceeds via a hydrogen transfer from the t-butylamine to the diazasilagroup, as indicated

by the structure. Besides bis(t-butylamino)dimethylsilane, the hypothetical intermediate (16) should be formed:

$$:\bar{Sn} \equiv \overset{+}{N}\!\!-\!\!Bu^t \longleftrightarrow \;:Sn\!\!=\!\!\bar{N} \longleftrightarrow \;:\overset{+}{Sn}\!\!-\!\!\overset{\bar{\;\;}}{\underline{N}}\!\!-\!\!Bu^t$$
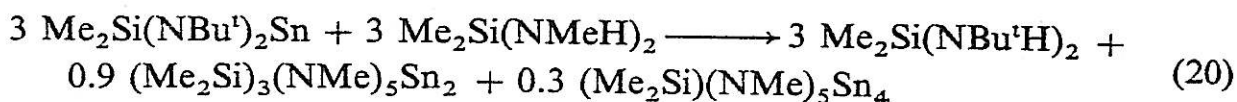$$\backslash$$
$$Bu^t$$

(16)

Compound (16) may then react with the diazasilastannylene to form (12), with itself and t-butylamine to form (13), or may oligomerize to form (14). Compound (13) can be derived from a seco-norcubane by substituting all carbon by nitrogen or tin atoms,[30] while in (14) the polycycle resembles a cube, the corners of which are alternately occupied by nitrogen or tin atoms. In (13) and (14) the tin atoms are in the top of a pyramid with NSnN angles of about 80°. The four-valent nitrogen atoms have SnNSn angles of about 100°. The average Sn–N distance is 220.2 pm and corresponds well with a bond, which should have $\frac{2}{3}$ single- and $\frac{1}{3}$ dative-bond character.[B 1,B 2]

The basic structure of (12) consists of a bisphenoid of two tin and two nitrogen atoms, two opposite edges being bridged by a t-butylamino or a dimethylsilyl group. The three-valent nitrogen atom in (12) can be replaced by an oxygen atom to form (17), which can be isolated as a $SnCl_2$ adduct (X-ray structure[31]):


(17)
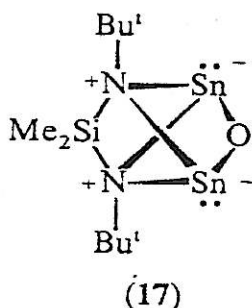
Other types of polycyclic SnNSi compounds are obtained when Me_2Si-$(NBu^t)_2Sn$ is allowed to react with bis(methylamino)dimethylsilane:[29]

$$3\, Me_2Si(NBu^t)_2Sn + 3\, Me_2Si(NMeH)_2 \longrightarrow 3\, Me_2Si(NBu^tH)_2 +$$
$$0.9\, (Me_2Si)_3(NMe)_5Sn_2 + 0.3\, (Me_2Si)(NMe)_5Sn_4 \qquad (20)$$

Bis(t-butylamino)dimethylsilane is recovered quantitatively besides two other products, their structures being established by NMR and X-ray diffraction techniques.[29] The compound $(Me_2Si)_3(NMe)_5Sn_2$ (18) is a tricyclic system with a central Sn_2N_2 ring, while $(Me_2Si)(NMe)_5Sn_4$ (19) resembles a basketane:
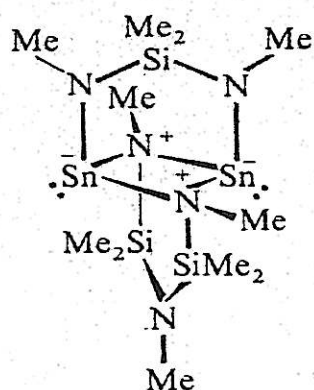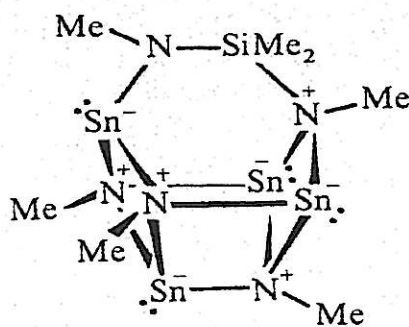
(18)   (19)

Compound (19) shows fluxional properties in solution, as established by NMR techniques.[29] It follows from the product (18) that condensation of two molecules bis(methylamino)dimethylsilane must have occurred during the reaction.

A complicated polycyclic system has been found as a product in the reaction of $Me_2Si(NBu^t)_2Sn$ with oxygen (see p. 389).[32] Two molecules, (17) and the dispiro compound (20), interact via oxygen–tin donor bonds to give a polycyclic compound consisting of thirteen four-membered cycles sharing edges or corners (see Fig. 15.1).
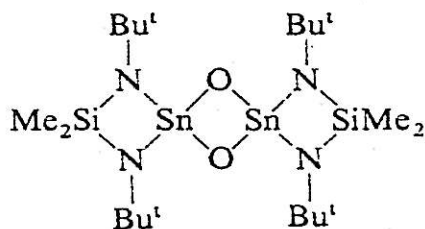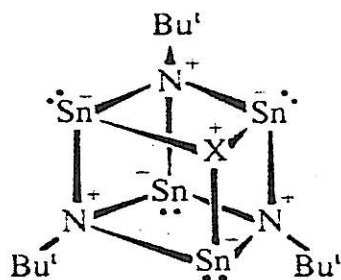

(20)

A derivative of the cage compound (14) with tin(II), nitrogen and oxygen atoms can be synthesized by careful hydrolysis of (13):[33]
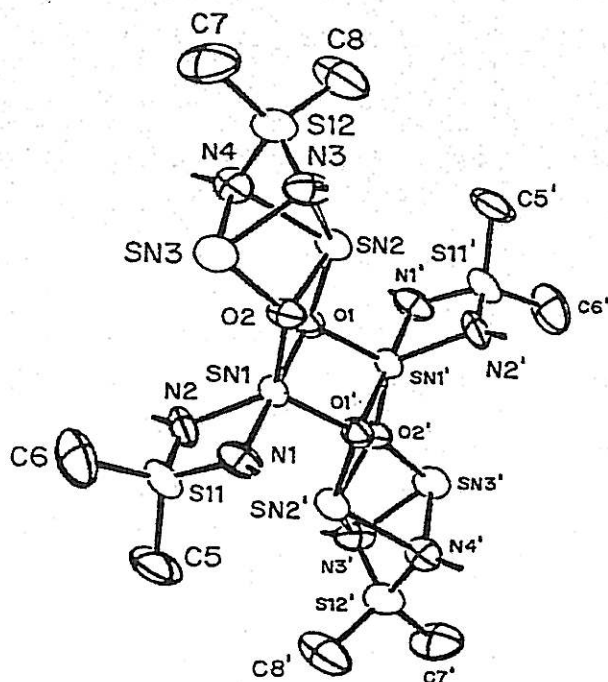
$$4\ Sn_3(NBu^t)_4H_2 + 3\ H_2O \longrightarrow 3\ Sn_4(NBu^t)_3O + 7\ Bu^t{-}NH_2 \quad (21)$$
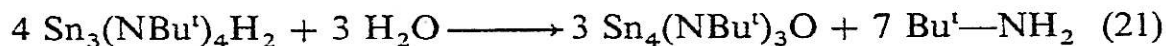
Besides t-butylamine, the cubane-like compound (21a) is obtained in 44% yield:[33]

(21a) X = O
(21b) X = O—AlMe₃

Figure 15.1 The structure of $[Me_2Si(NBu^t)_2]_4Sn_6O_4$ (t-butyl groups have been omitted). (Reproduced with permission from Z. *Anorg. Allg. Chem.* **459** (1979) 208.)

The cubane (**21a**) can be transformed to (**21b**) (X-ray structural character-ization[34]) by a simple addition of trimethylaluminium[33] to the still basic oxygen atom in (**21a**):

$$Sn_4(NBu^t)_3O + \tfrac{1}{2} Al_2Me_6 \longrightarrow Sn_4(NBu^t)_3(O{-}AlMe_3) \qquad (22)$$
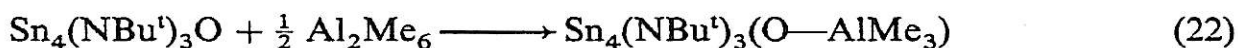
15.4   Cyclostannaphosphanes

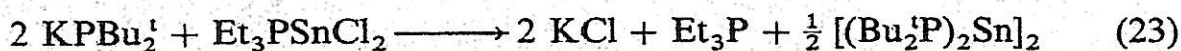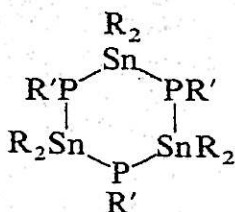### 15.4.1   *Cyclodistannadiphosphanes and cyclotristannatriphosphanes*

In contrast with tin–nitrogen cycles and polycycles, there are only few tin–phosphorus cyclic compounds known at the present time. The only four-membered cycle with tin and phosphorus seems to be present in compound (**22**), which can be rationalized by a Lewis-acid–base interaction of two diphosphinostannylenes:

(**22**)
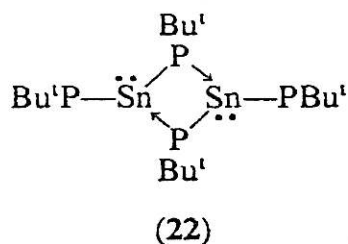
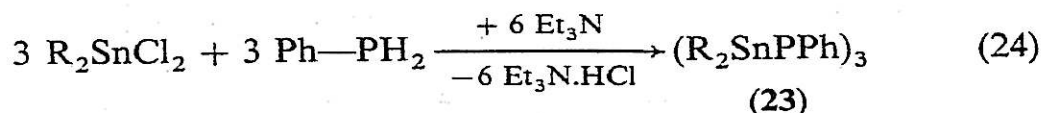Compound (22) can be prepared by reaction (23) in 45% yield.[35]

$$2 \text{ KPBu}_2^t + \text{Et}_3\text{PSnCl}_2 \longrightarrow 2 \text{ KCl} + \text{Et}_3\text{P} + \tfrac{1}{2} [(\text{Bu}_2^t\text{P})_2\text{Sn}]_2 \qquad (23)$$

The structure of (22) follows from molecular-mass determination and NMR spectroscopic data (^{1}H, ^{31}P, ^{119}Sn). No direct structural determination has been performed so far.

$$
\begin{array}{c}
\text{R}_2 \\
\text{Sn} \\
\text{R'P} \quad\quad \text{PR'} \\
| \quad\quad\quad | \\
\text{R}_2\text{Sn} \quad\quad \text{SnR}_2 \\
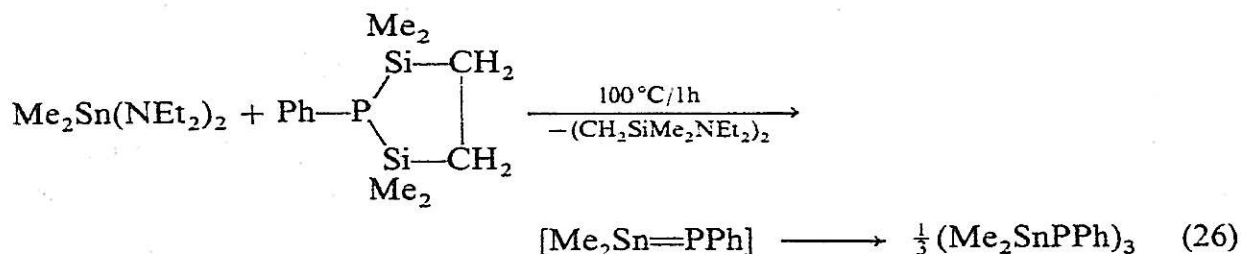\text{P} \\
\text{R'}
\end{array}
$$

(23)

Some cyclic tin–phosphorus compounds with a six-membered ring (23) (R = Me,[36–38] Bu, Ph[36,37]) are obtained by condensation of dichlorodiorgano-stannanes with phenylphosphine (equation 24) or by a salt elimination between trichlorophosphane and lithium triphenylstannane (equation 25)[39] (for other synthetic routes to Sn–P bonds, see ref. 40):

$$3 \text{ R}_2\text{SnCl}_2 + 3 \text{ Ph—PH}_2 \xrightarrow[-6 \text{ Et}_3\text{N.HCl}]{+ 6 \text{ Et}_3\text{N}} (\text{R}_2\text{SnPPh})_3 \qquad (24)$$

(23)

$$\text{PCl}_3 + \text{Ph}_3\text{SnLi} \longrightarrow \tfrac{1}{3}(\text{Ph}_3\text{Sn—PSnPh}_2)_3 + \text{other products} \qquad (25)$$

Very recently an alternative synthetic procedure has been described, which is believed to proceed via a $\text{Me}_2\text{Sn}{=}\text{P—Ph}$ monomeric intermediate:[38]

$$
\text{Me}_2\text{Sn(NEt}_2)_2 + \text{Ph—P}
\begin{array}{c}
\text{Me}_2 \\
\text{Si—CH}_2 \\
\diagup \quad\quad | \\
\diagdown \quad\quad | \\
\text{Si—CH}_2 \\
\text{Me}_2
\end{array}
\xrightarrow[-(\text{CH}_2\text{SiMe}_2\text{NEt}_2)_2]{100\,°\text{C}/1\text{h}}
$$

$$[\text{Me}_2\text{Sn}{=}\text{PPh}] \longrightarrow \tfrac{1}{3}(\text{Me}_2\text{SnPPh})_3 \qquad (26)$$
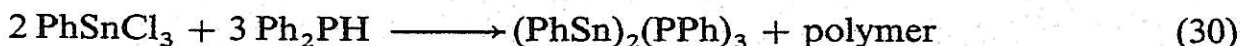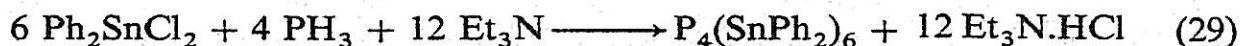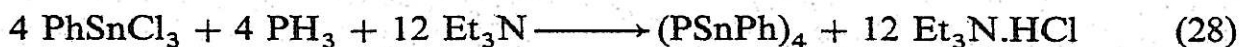
The rings are cleaved by thermolysis, yielding cyclic organophosphanes:[37]

$$(\text{PhPSnMe}_2)_3 \xrightarrow{\Delta} (\text{Me}_3\text{Sn})_2\text{P—Ph} + \tfrac{2}{5}(\text{PhP})_5 + \text{Sn} \qquad (27)$$
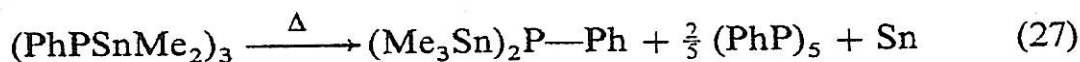
Tin–phosphorus ring compounds are very sensitive to moisture and air.

### 15.4.2. Phosphorus-rich and tin-rich phosphorus-tin cycles and polycycles

A number of polycyclic compounds have been claimed to result when organohalogenostannanes are reacted with phosphine:[41,42]

$$4\,PhSnCl_3 + 4\,PH_3 + 12\,Et_3N \longrightarrow (PSnPh)_4 + 12\,Et_3N.HCl \qquad (28)$$

$$6\,Ph_2SnCl_2 + 4\,PH_3 + 12\,Et_3N \longrightarrow P_4(SnPh_2)_6 + 12\,Et_3N.HCl \qquad (29)$$

$$2\,PhSnCl_3 + 3\,Ph_2PH \longrightarrow (PhSn)_2(PPh)_3 + polymer \qquad (30)$$

The yields of the products in these reactions are very low (5–10%) and the compounds are poorly characterized (for example by IR spectra[42]). The structures (24)–(26) have been proposed; although they are reasonable, they should nevertheless be regarded with some doubt:
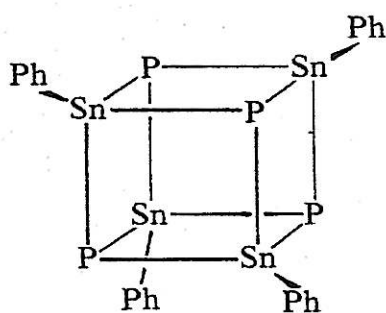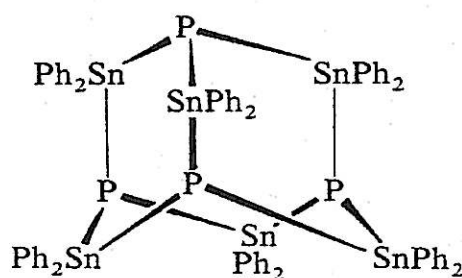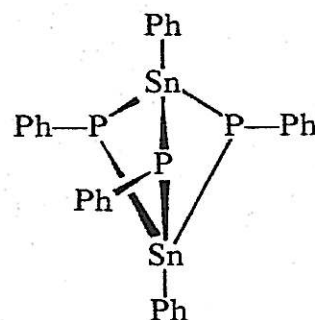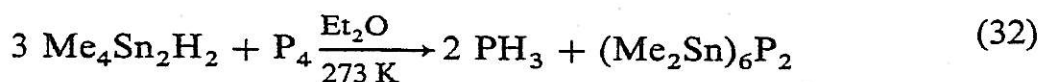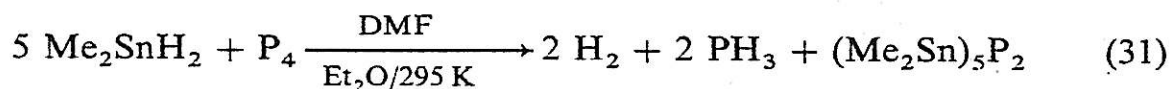

(24) (25) (26)

Tin-rich polycyclic compounds have been synthesized recently by reaction of white phosphorus with tin hydrides:[43–45]

$$5\,Me_2SnH_2 + P_4 \xrightarrow[\text{Et}_2O/295\,K]{\text{DMF}} 2\,H_2 + 2\,PH_3 + (Me_2Sn)_5P_2 \qquad (31)$$

$$3\,Me_4Sn_2H_2 + P_4 \xrightarrow[273\,K]{\text{Et}_2O} 2\,PH_3 + (Me_2Sn)_6P_2 \qquad (32)$$

While $(SnMe_2)_5P_2$ is colourless, decomposing above 400 °C,[43,44] $(Me_2Sn)_6P_2$ is pale yellow with a melting point of 220 °C.[45] Both compounds have been characterized by ^1H and ^{31}P NMR techniques, and their structures have been determined by X-ray diffraction methods. The two molecules are depicted with their structural parameters in Fig. 15.2; the molecular symmetry of $(Me_2Sn)_5P_2$ is C_{2v}, while $(Me_2Sn)_6P_2$ has D_3 symmetry. When irradiated, $(Me_2Sn)_6P_2$ decomposes with elimination of dimethylstannylene, which subsequently polymerizes:[45]

$$(Me_2Sn)_6P_2 \longrightarrow (Me_2Sn)_5P_2 + Me_2Sn: \qquad (33)$$

(a)

(b)
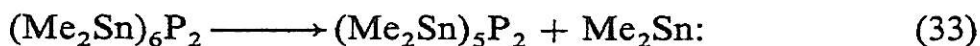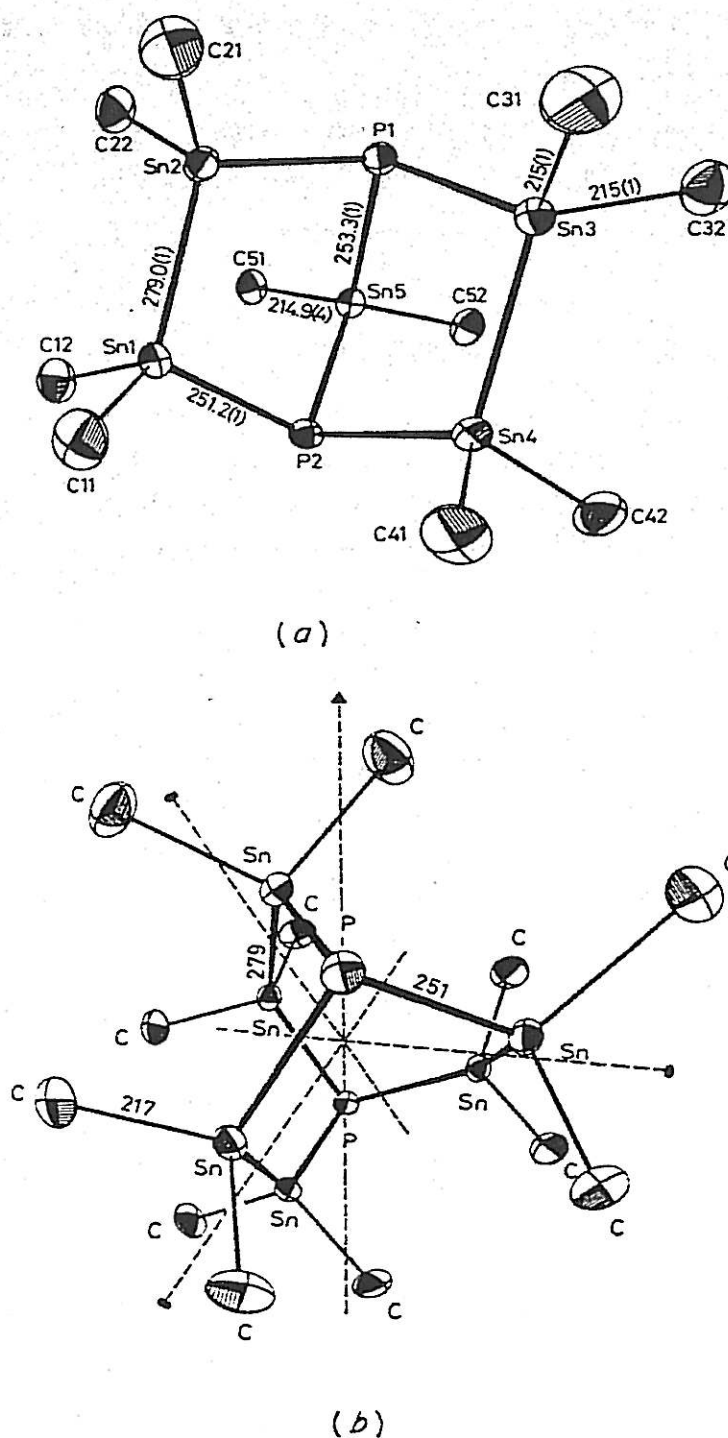
Figure 15.2 (a) The structure of $(Me_2Sn)_5P_2$. (b) The structure of $(Me_2Sn)_6P_2$. Bond lengths in pm. (Reproduced with permission from *Angew. Chem. Int. Ed. Engl.* **17** (1978) 767; **20** (1981) 1029.)

Phosphorus-rich five-membered cycles of the P_4Sn type can be synthesized by the following reactions (R' = Et):[46]

$$Ph_4P_4Na_2 \cdot 6Diox \xrightarrow[-NaCl]{R_2'SnCl_2}$$

$$\xrightarrow[-KCl]{R_2'SnCl_2} R_4P_4K_2$$

$$\begin{array}{c} RP\!\!-\!\!PR \\ RP \diagdown \diagup PR \\ Sn \\ R_2' \end{array}$$

$$Ph_3P_3Na_2 \cdot 2Diox \xrightarrow[-NaCl]{R_2'SnCl_2}$$

(27)

$$\xrightarrow[-Me_3SiCl]{R_2'SnCl_2} Ph_4P_4(SiMe_3)_2$$
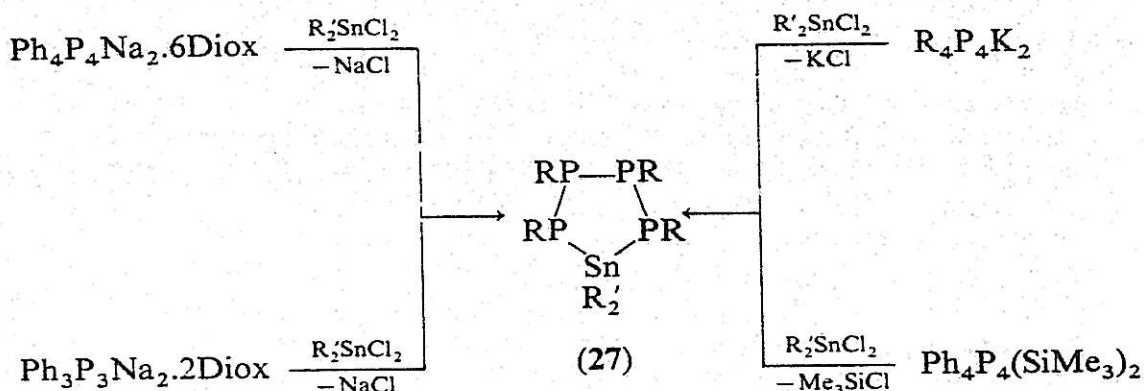
Spectroscopic methods (NMR, mass spectra) have been used to confirm the structure of these five-membered rings (27).[46] The cyclic compounds (27) are decomposed by oxidation with iodine or cleaved by hydrogen chloride:[46]

$$(RP)_4SnR_2' + 9\ I_2 \longrightarrow 4\ RPI_4 + R_2'SnI_2 \tag{34}$$

$$(RP)_4SnR_2' + 2\ HCl \longrightarrow R_2'SnCl_2 + \left\{ \begin{array}{c} R\quad R\quad R\quad R \\ H\!-\!P\!-\!P\!-\!P\!-\!P\!-\!H \end{array} \right\} \tag{35}$$

$$\longrightarrow \tfrac{3}{n}\ (RP)_n + RPH_2$$
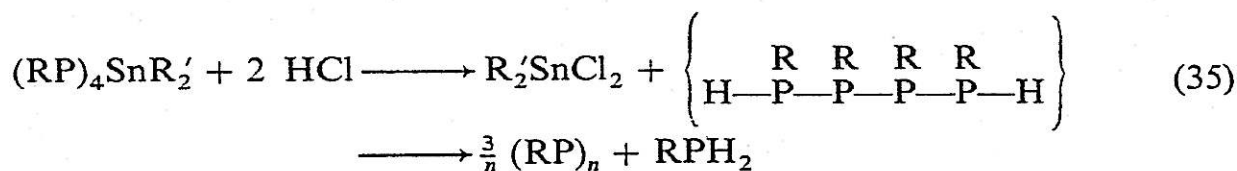
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The Chemistry of Inorganic Homo- and Heterocycles

Volume 1

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1987

L chi 870
FK 2994(1)