

# ANGEWANDTE CHEMIE

Volume 26 · Number 1

January 1987

Pages 1-92

International Edition in English

## Unsaturated Molecules Containing Main Group Metals

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Molecules in which there are neighboring electrophilic and nucleophilic centers are unusually reactive. Oligomerization can be prevented only by bulky groups attached to the main group metal atom that would act as electron pair acceptor, or to the basic non-metal atom. The basic and the acid centers behave as a single unit in chemical reactions; the system is similar to a "double bond" whose  $\pi$ -electron density is largely concentrated at one atom. The unsaturated nature of these molecules can be seen in (for example) their addition reactions with hydrogen compounds of non-metals, or in reactions that are distantly related to cycloadditions at homopolar double bonds. The selection of suitable reaction partners leads to polycyclic, cage-like molecules containing metal atoms. If these atoms possess lone pairs (as is usual in the lower oxidation states of the third and fourth main groups), these can be utilized to form bonds to further (Lewis acid) metal centers. In some cases large assemblies can be built up from polycyclic systems in this way; a characteristic of these assemblies is a one-dimensional array of metal atoms. Commonly occurring structural features of the polycyclic species are tetrahedra, trigonal bipyramids and cubes.

### 1. Introduction

Two properties of metallic elements are particularly conspicuous on their incorporation into molecules: their low electronegativity (compared with the ligands) and their marked tendency to maximize their coordination number. The resulting electrophilicity at the metal atom causes nucleophiles to attack this part of the molecule preferentially and the first reaction step is thus coordination. Such an intermolecular reaction can lead to a stable compound that is generally described as a Lewis acid/Lewis base complex.<sup>(1)</sup>

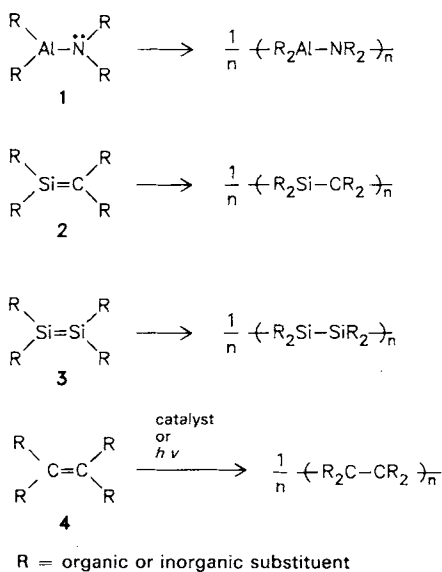
Here we wish to consider only those Lewis acids in which one or more non-metal atoms bearing lone pairs are bound to the electrophilic main group metal. Such com-

pounds thus formally contain neighboring Lewis acid and Lewis base centers, which can lead to intra- or intermolecular interactions. The compounds are generally unstable with respect to oligomerization because of the marked heteropolar contribution to the metal/non-metal bond. An expansion of the coordination at the metal atom results, which can be interpreted as filling an electron vacancy.<sup>(1)</sup> Although this model may seem very primitive and superficial (it is concerned largely with "counting electrons") it should nevertheless be noted that parallels between the oligomerization of such special Lewis acid/Lewis base systems and of element-element double bonds do exist. This can be illustrated by a comparison of the reactivity of the aluminum compound **1** with that of the isosteric or (in the broader sense) isoelectronic molecules **2**, **3** and **4** (Scheme 1).

A common property of compounds **1-4** is that they oligomerize or polymerize under suitable (generally different)

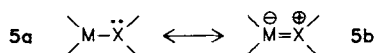
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conditions. Compound **1** reacts instantaneously to form four- or six-membered rings (depending on the substituent R) that do not decompose to the monomers even at high temperatures.<sup>[2,3]</sup> Compound **2** is also converted spontaneously into the corresponding oligomer; it can be obtained as a monomer only by the use of sterically demanding substituents R (kinetic stabilization).<sup>[4-6]</sup> Compound **3** possesses a completely non-polar double bond (in contrast to **1** and **2**), but here again the monomer is only stable when such kinetic effects are exploited.<sup>[7]</sup> Monomers of **2** and **3** are obtained as extremely short-lived intermediates when suitable precursors are photolyzed or thermolyzed; they can be chemically identified by trapping reactions.<sup>[8,9]</sup> The ethene derivatives **4**, on the other hand, are kinetically especially stable with respect to their oligomers and polymers and can only be converted into these photochemically or catalytically.<sup>[10,11]</sup>



Scheme 1.

It is apparent from this comparison of the compounds **1-4** that the tendency to oligomerize is correlated with the polarity of the relevant bond and that heavy elements (because of their reluctance to form  $\pi$ -bonds<sup>[12]</sup>) amplify this effect. Compounds such as **1**, which contain a Lewis acid and a Lewis base, can be classified on the basis of a simple model as "unsaturated" and represent, at least formally, a limiting case of the double bond. Irrespective of the contributions of the individual mesomeric forms **5a** and **5b**, this can be represented as follows for a main group metal M and a non-metal X:



In this review we have not considered it important to present evidence for the existence of one or the other mesomeric form (there are incidentally other possible formulations, e.g. as an ion pair); we prefer to show how this model can be exploited synthetically. The reactivity of the compounds is best represented, not by treating M and X in

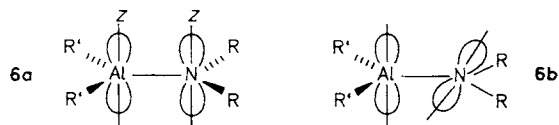
**5** separately as acid and base but by considering the cooperation of both centers—*similarly* to the behavior of double bonds. We concern ourselves with compounds of type **5** that either exist as monomers under normal conditions or can be assumed as intermediates. After considering the general principles we present examples that are mostly drawn from our own work.

## 2. The Synthesis of Metallacycles with Lewis Acid and Lewis Base Centers

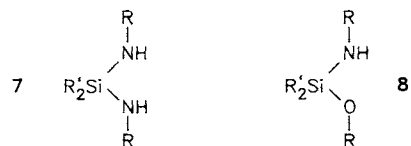
### 2.1. The Choice of Ligand at the Metal Atom

As already explained, compounds that, like **1**, contain a Lewis acid and a Lewis base center are unstable with respect to oligomerization. Apart from the use of sterically demanding groups (to reduce the tendency to intermolecular reactions), one further important point should be considered; this will be discussed with respect to **1** as an example. An intramolecular stabilization of the aluminum atom (by a contribution from limiting structure **5b**) is only possible if the occupied orbital on the N atom possesses the same symmetry as the acceptor orbital ( $p_z$  on the Al atom); this would require an  $sp^2$  hybridization of the nitrogen. An additional requirement, however, is that both p orbitals are parallel (**6a**). It can be shown, for an open chain system with free rotation about the bond joining the Lewis acid to the Lewis base, that both conditions presented here (steric requirements, electronic effects) tend to compete with, rather than reinforce, each other.

In tris(bis(trimethylsilyl)amino)aluminum (R = SiMe<sub>3</sub>, R' = N(SiMe<sub>3</sub>)<sub>2</sub> in **6**), which indeed contains three-coordinate aluminum,<sup>[13,14]</sup> the R<sub>2</sub>N-moiety is however rotated by 50° from the (R')<sub>2</sub>Al moiety (as depicted in **6b**). Because of this large dihedral angle between the  $p_z$  orbitals, there can only be a weak donor-acceptor interaction between the two atoms.



If the aluminum and nitrogen atoms are incorporated in a small ring system, however, such a rotation is no longer possible. This consideration prompted us to incorporate electrophilic metal atoms in ligand systems derived from the donor-substituted silanes **7**<sup>[15]</sup> and **8**,<sup>[16]</sup> which should lead to high stabilization. Starting from **7** and **8**, we can in



principle construct compounds containing any metallic element (see formulas **9-15**; the Roman subscripts refer to the main group number. For examples see also Table 1). All the molecules **9-15** share the common feature that the

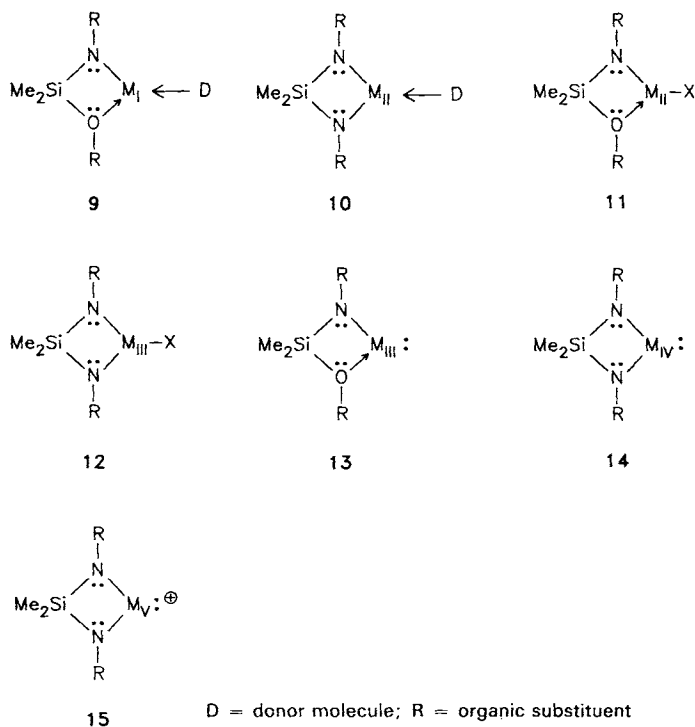


Table 1. Metallacycles **9–15** synthesized so far [19–24]. R = *t*Bu; high yields with the exception of **10a**.

Cpd.	M	D/X	Cpd.	M	Cpd. [a]	M
<b>9a</b>	Li	$\frac{1}{2}$ THF [b]	<b>13a</b>	Tl <sup>I</sup>	<b>15a</b>	P
<b>9b</b>	Li	$\frac{1}{2}$ dioxane	<b>14a</b>	Ge <sup>II</sup>	<b>15b</b>	As
<b>9c</b>	Li	$\frac{1}{2}$ C <sub>3</sub> H <sub>5</sub> N	<b>14b</b>	Sn <sup>II</sup>	<b>15c</b>	Sb
<b>10a</b>	Mg	THF [b]	<b>14c</b>	Pb <sup>II</sup>	<b>15d</b>	Bi
<b>12a</b>	Al	Me				
<b>12b</b>	Al	Ph				
<b>12c</b>	In	Me				

[a] AlCl<sub>3</sub> as counterion. [b] THF = tetrahydrofuran.

metal atom (Lewis acid) formally possesses six outer electrons and is adjacent to two non-metal atoms with “non-bonding” electron pairs.

The ring structure and the stabilizing effect of silicon on the sp<sup>2</sup> hybridization at the nitrogen or oxygen atom should ensure the coplanarity of the generally trigonal planar ligand spheres at the metal and the non-metal atom (assuming monomeric structures). The metal atoms can display either their maximum oxidation state or an oxidation state two units lower (**13**, **14**); they may be present as metal cations (**15**). Any organic group R may be chosen, but the principle of “kinetic stabilization” should be borne in mind; *tert*-butyl groups have proved especially useful. The completion of the outer electron complement and the coordinative saturation of the metal atom in **9** and **10** are achieved by bonds from donor molecules.

## 2.2. Synthesis of the Metallacycles

The metallacycles **9–15** can be synthesized by a variety of methods,<sup>[18]</sup> some of which are presented as examples in Eqs. (a)–(f). Corresponding syntheses can be carried out with compound **8**. The most important and generally applicable syntheses are (a), which proceeds with

“salt formation”, and the redox or metal exchange reactions (d) and (e), respectively. The amine transfer reaction (b), the direct hydrogen–metal exchange (c) and the thermolysis (f) are of more specialized interest.<sup>[19,24]</sup> We have so far succeeded in preparing the compounds listed in Table 1. Attempts to prepare a compound corresponding to formula **11** led (for magnesium) only to [Me<sub>2</sub>Si(*Nt*Bu)(*Ot*Bu)]<sub>2</sub>Mg.<sup>[22]</sup>

## 3. Properties and Structures of the Metallacycles 9–15

Mass spectrometry in the gas phase, molecular weight determinations in solution and X-ray structure analyses in the solid state all show that the compounds **9–15** are

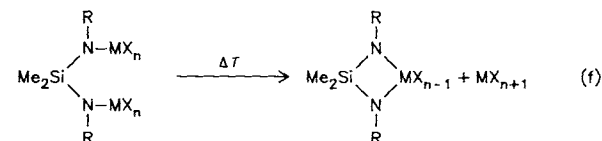
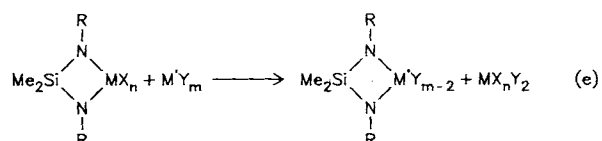
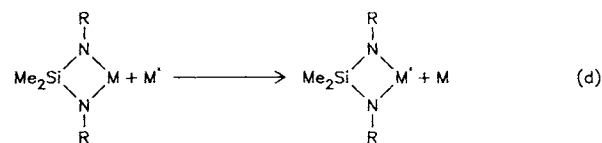
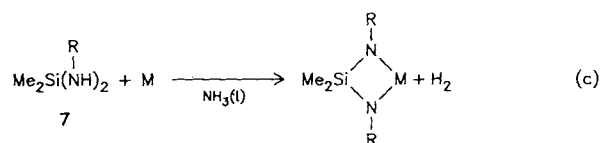
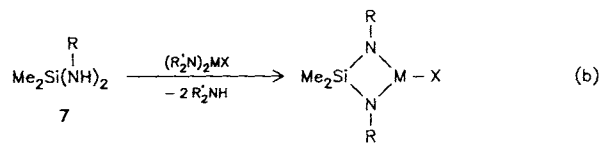
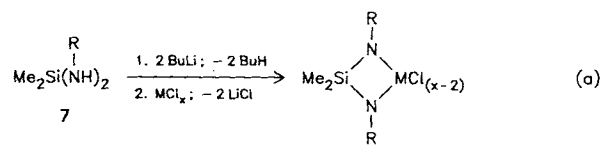


Table 2. Structures of some metal-containing cyclic molecules in different states of matter. E.N. = electronegativity.

Compound	M	E.N. [25] of the metal atom	Degree of association		
			Gas phase	Benzene soln.	Crystal
<b>9a</b> , <b>9b</b>	Li	0.98	—	dimeric	dimeric
<b>10a</b>	Mg	1.31	—	dimeric	dimeric
<b>12a</b>	Al	1.61	dimeric	dimeric	dimeric
<b>12c</b>	In	1.78	monomeric	dimeric	dimeric
<b>13a</b>	Tl <sup>I</sup>	1.62	monomeric	monomeric	—
<b>14a</b>	Ge <sup>II</sup>	1.85	monomeric	monomeric	—
<b>14b</b>	Sn <sup>II</sup>	1.80	monomeric	monomeric	monomeric/dimeric
<b>14c</b>	Pb <sup>II</sup>	1.87	monomeric	monomeric	—

either monomeric or dimeric; none of them forms a "coordination polymer". Table 2 shows that physical conditions (e.g. the state of matter) and the electronegativity of the metal atom both have a direct influence on the tendency to dimerize; as expected, the tendency to coordinative saturation at the metal is greater for more electropositive metals and for more closely neighboring molecules. The indium derivative **12c**, for example, is monomeric in the gas phase but dimeric in benzene solution and in the solid state. Interesting results have been obtained for the tin derivative **14b**; crystallization from hexane yields a monoclinic modification in which monomers and dimers are both present in the lattice,<sup>[26]</sup> but crystallization from molten material gives a second, triclinic, modification that only contains dimers.<sup>[27]</sup>

All the compounds that contain lower valent metals and are monomeric are also colored; the heavier the metal atom, the further the light absorption is shifted to the red (**14a** is yellow, **14b** red, **14c** dark red). Dimerization is accompanied by a marked change in color; molten **14b** (containing only monomers) is red, the monoclinic modification (1 : 1 monomer : dimer) orange, the triclinic modification (only dimers) pale yellow.<sup>[27]</sup> The differing coordination numbers at the metal are obviously reflected in the color of the compounds, as is also the case for tin(II) amides.<sup>[28]</sup> The cations containing elements of the fifth main group (**15a-d**), like the corresponding isoelectronic compounds **14**, are also colored.<sup>[24]</sup>

Figures 1-3 show the results of X-ray structure analyses of the compounds **14b** and **15c** (as examples of monomeric units) and of **12c** and **9a** (as examples of different types of dimers). In **14b** and **15c** the four-membered ring is almost planar and the N-atoms trigonal planar coordinated. As discussed in Section 2, this causes the empty p orbitals on the metal atoms<sup>[30]</sup> and the filled p orbitals on the nitrogen atoms to be parallel. A resonance formula corresponding to **5b** is possible from strictly geometric considerations but does not appear to lead to a noticeable shortening of the M-X bond. The molecule  $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$  is, like **14b**, monomeric in the gas phase; electron diffraction studies show that the  $\text{Si}_2\text{N}$  planes are not coplanar with, but are instead orthogonal to, the  $\text{SnN}_2$  plane; however, the Sn-N bond length is identical to that in **14b**.<sup>[31]</sup>

The dimeric **12c** (Fig. 2) can be considered as a cycloadduct of two monomeric units. The dimer of **14b**<sup>[27]</sup> and the magnesium compound **10a**<sup>[20]</sup> display a similar structural type. Common to all three molecules is a polycyclic structural element consisting of three edge-bridged perpendicular four-membered rings ("step structure"). The electron transfer from the  $\lambda^4$ -N atom to the In atom is reflected in the drastically lengthened bonds to this atom, compared with the  $\lambda^3$ -N atom.<sup>[29]</sup> As in [2+2]-cycloaddition reactions of ethene derivatives,<sup>[32]</sup> the bond lengths in the addition product are all increased with respect to those in the starting materials. The structural data for **10a**, **12c** and **14b** can be transcribed as the chemical formulas **16a-c** ( $\text{R} = t\text{Bu}$ ;  $\text{M} = \text{Mg}, \text{In}, \text{Sn}$ ;  $\text{X} = \text{THF}, \text{Me}$  or lone pair).

There is however a danger of reading too much into the formulas **16a-c** as regards the real electronic states; the formal charges in **16a** might be taken to indicate a high electron density at the metal atom, which would be incon-

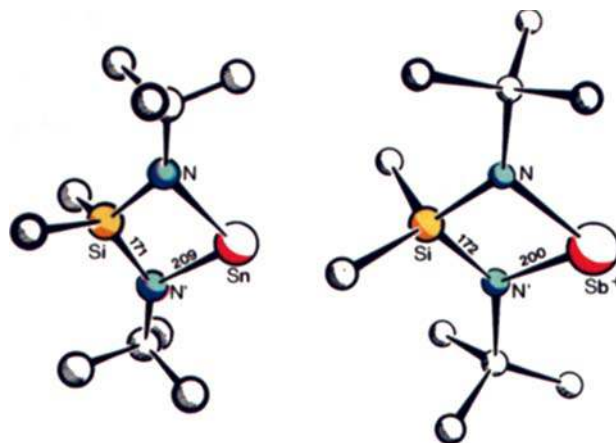


Fig. 1. Molecular structures of **14b** [27] (left) and **15c** (without counterion) [28] (right). Here and in the following figures, the metal atoms (acceptors) are colored red or orange, the donor atoms blue or green; C-bonded H-atoms omitted (distances in pm).

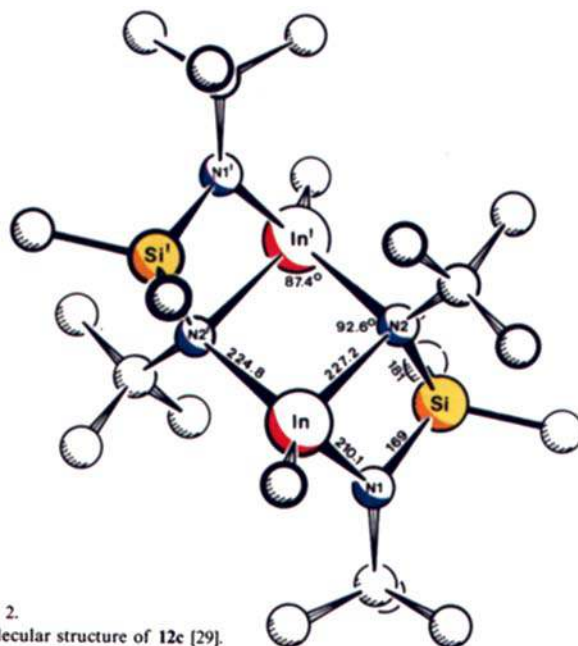


Fig. 2. Molecular structure of **12c** [29].

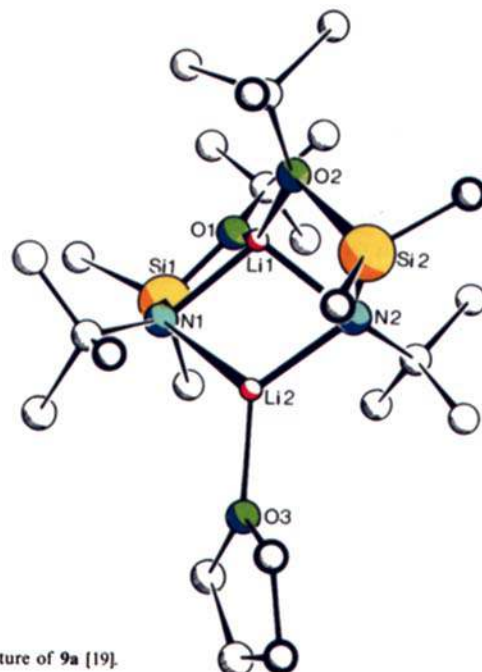
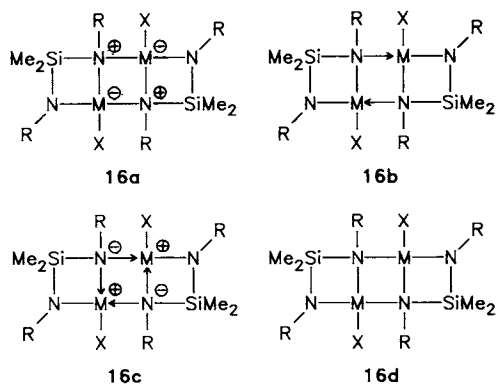
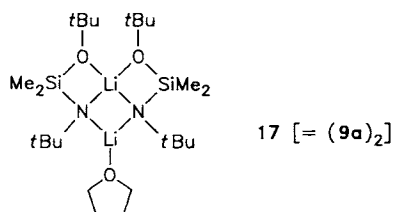


Fig. 3. Molecular structure of **9a** [19].



sistent with the electronegativities of the elements M and N.<sup>[25]</sup> The donor-acceptor bond shown by an arrow in **16b** should differ appreciably in length from the N-M single bond; this is indeed the case for dimeric **14b**,<sup>[27]</sup> but not for dimeric **12c**.<sup>[29]</sup> Finally, there are formulations such as **16c** with ionic charges, which are structurally difficult to distinguish from **16a**. Although the formulas **16a-c** are fairly readily comprehensible for the molecules discussed here, more complicated systems are more difficult to formulate in a similar manner and are thus more liable to misinterpretation. To avoid this problem, it is often more sensible to dispense with the formulas with formal charges and arrows, as in **16d**; each line represents an electron pair, irrespective of the nature of the bond (2-center 2-electron or donor-acceptor). The reader will be able to interpret the particular bonding implied by, for instance, the four-coordinate nitrogen atom.

In contrast to the compounds **10a**, **12c** and **14b** (dimer), in which all metal atoms are coordinatively saturated (which usually implies a noble gas configuration), dimeric **9a** (Fig. 3) contains two lithium atoms, only one of which is four-coordinate; the other is bonded to two nitrogen atoms and the oxygen of a donor tetrahydrofuran molecule, resulting in the unusual coordination number three.<sup>[33]</sup> The point symmetry of **9a** is close to  $C_2$  symmetry, the twofold axis passing through both lithium atoms and the donor oxygen. This oxygen displays trigonal planar coordination, and is thus, like the  $\lambda^3$ -lithium atom,  $sp^2$  hybridized. It can be shown that the dihedral angle between the p orbitals of both atoms (ca.  $45^\circ$  in **9a**) results from steric effects that make a parallel arrangement impossible. It is not clear why the structure of the lithium derivative **9a**<sup>[19]</sup> is so different from that of the isoelectronic magnesium derivative **10a**; **9a** does not react with excess tetrahydrofuran. As for **16**, different representations of the formula are possible; we prefer **17**, corresponding to **16d** (cf. lithium compounds in Ref. [34]). The structural type **9a**



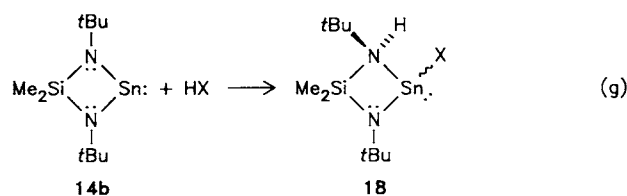
(Fig. 3) is preserved in exchange reactions of the donor THF (as shown by X-ray structure determinations of **9b** and **9c**); this feature is however restricted to lithium compounds.<sup>[19]</sup>

#### 4. Reactions of Monomeric Metallacycles

The concept advanced in Sections 1 and 2, of regarding the Lewis acid/Lewis base systems defined at the outset as limiting cases of molecules with a  $\pi$  double bond, can be tested by methods other than structural analysis. Unsaturated molecules are expected, in particular, to undergo addition reactions. We shall here analyze selected reactions of the monomeric metallacycles to see if this expectation is borne out in practice. We restrict ourselves to the addition of hydrogen compounds of non-metals and their derivatives to the molecules **14** and to reactions that may by extended analogy be regarded as cycloadditions (for further examples see, e.g., Refs. [35, 36]).

##### 4.1. Addition of Hydrogen Compounds of Non-Metals to **14**

The tin(II) compound **14b** (monomeric in solution) reacts with hydrogen compounds H-X (X = halogen,  $C_5H_5$ ) according to the general equation (g).<sup>[37,38]</sup> The germanium compound **14a** also reacts in this way.<sup>[39]</sup> The ad-



**18a-d**: X =  $C_5H_5$ , Cl, Br, I

dition products **18a-d** can be isolated and characterized; Figure 4 shows the result of an X-ray structure determination of **18b**.<sup>[38]</sup> As expected, the  $\lambda^4$ -N-Sn bond is appreciably longer than  $\lambda^3$ -N-Sn ( $\Delta = 40$  pm). The *cis* position of the hydrogen and chlorine atoms (with respect to the ring plane) is caused by steric effects. Molecules of the type **18**

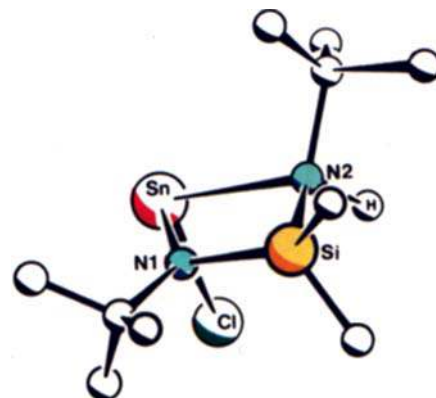
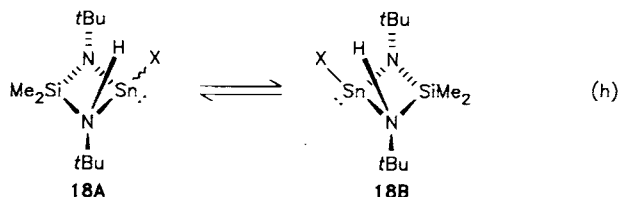
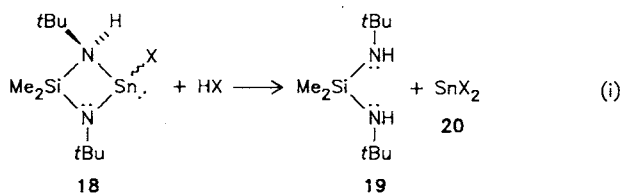


Fig. 4. Molecular structure of **18b** [37].

are conformationally unstable in solution (as shown by temperature-dependent NMR studies); equation (h) shows the equilibrium involved<sup>[37-39]</sup> (only two of the four possible isomers are represented (cf. Ref. [37])). **18A** and **18B** are mirror images; each contains two chiral centers ( $\lambda^4$ -N and Sn). The formal replacement of the SnX group in **18** by  $\text{ElX}_2$  (El = Al, Ga, In, Tl; X = Me or halogen) leads to compounds that are similar to **18** in many respects, especially with regard to temperature-dependent "ligand redistribution" within the molecule.<sup>[21,29]</sup>

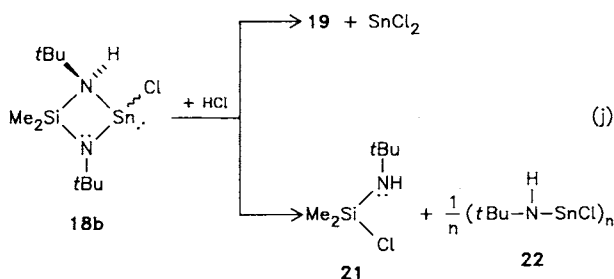


Apart from the explicitly mentioned hydrogen compounds in Eq. (g), alcohols, thiols and secondary amines can also react in a similar manner with **14b**; the difference is that the intermediate **18** cannot be isolated. The reaction continues by further addition of HX and breaking of both Sn-N bonds, leading to the bis(amino)silane **19** and derivatives **20** of divalent tin [Eq. (i)].<sup>[37-39]</sup> Dihalides of tin are

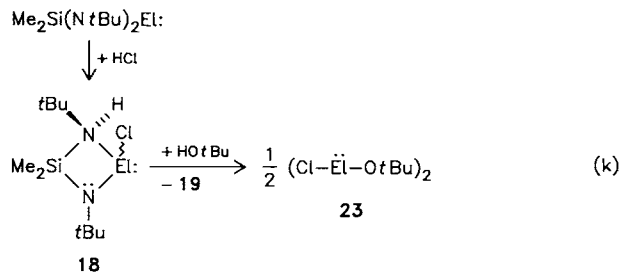


**20a-d**: X = C<sub>6</sub>H<sub>5</sub>, NMe<sub>2</sub>, OtBu, StBu

also obtained when compounds **18** are allowed to react with a further mole equivalent of hydrogen halide, but interesting side reactions also take place [Eq. (j)] for compound **18b**.<sup>[37]</sup> The ratio of products SnCl<sub>2</sub> and **22** can be influenced by temperature and concentration.

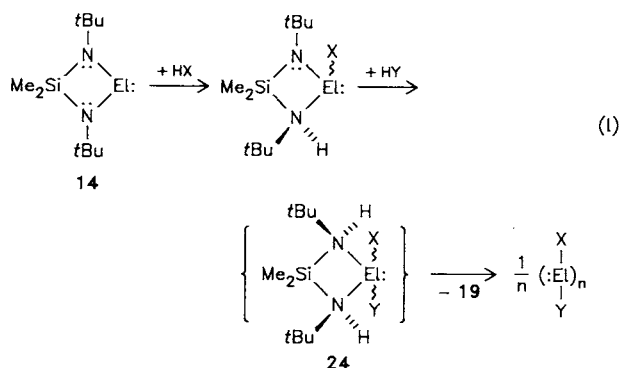


Whereas alternative methods of preparing **20a-d**<sup>[40]</sup> are available, the addition reaction (g) is particularly suitable for preparing asymmetrically substituted germanium(II) or tin(II) compounds<sup>[41]</sup> such as **23** [Eq. (k)], which are otherwise obtainable only with difficulty or not at all.<sup>[39]</sup> The cyclic species **14a, b** function in Eq. (k) in two separate reaction steps as formally unsaturated systems; the Lewis acid/base adduct **24** is obviously unstable [Eq. (l)]. The



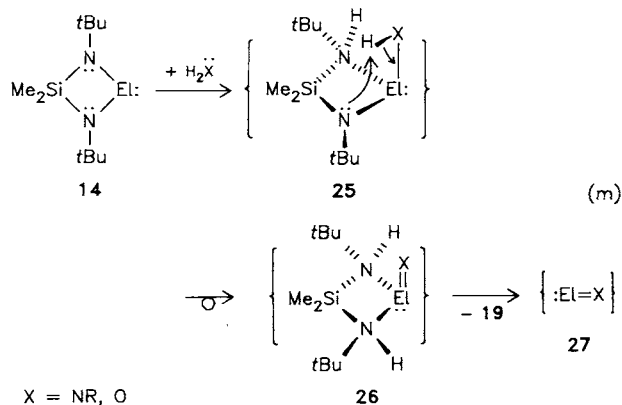
El = Ge, Sn

bis(amino)silane **19** is, for a coordinating molecule, extremely bulky (because of the *tert*-butyl groups on the nitrogen atoms) and thus dissociates readily from the metal



atom. A detailed consideration of the reaction sequence (l) raises the question whether two hydrogen atoms can be simultaneously transferred to **14**, rather than in two separate steps. Such a reaction could be expected with hydrogen compounds that contain two element-hydrogen bonds, such as primary amines or water. Since the basic group X is only available for reaction once (in contrast to the successive reactions (l)), double bonds should be formed in the product after addition of the hydrogen, as shown in Eq. (m). The intermediates **25** and **26** are hypothetical and serve only to demonstrate the analogy to reaction (l).

The experimental test of this idea indeed shows that the reaction of compound **14** with primary amines (and in principle also with water) leads, apart from the quantitatively generated bis(amino)silane **19**, to a compound whose empirical composition corresponds to formula **27**<sup>[23a,42]</sup> or that contains **27** as a constituent of a larger molecule.<sup>[43]</sup> The product should however not be repre-



X = NR, O

sented as a monomer containing a double bond, but rather as a tetramer. Figure 5 shows the molecular structure of  $(\text{SnNtBu})_4$ , which contains a central  $\text{Sn}_4\text{N}_4$  cube.<sup>[44]</sup> All the "bond lines" between tin and nitrogen atoms can be interpreted as  $\sigma$  bonds. A more detailed discussion of this and related bonding systems is presented in Section 4.2.

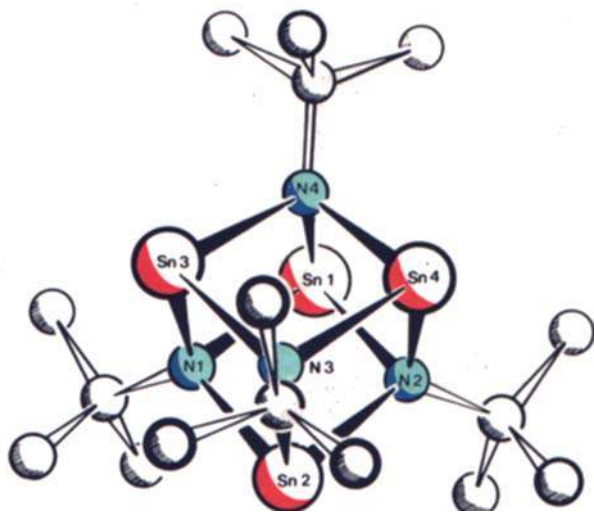
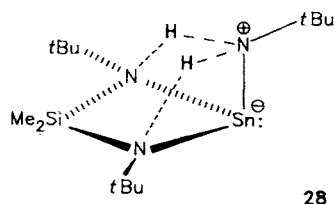


Fig. 5. Molecular structure of  $(\text{SnNtBu})_4$  [44].

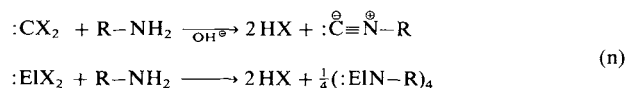
Equation (m) could be formally classified as a simple substitution reaction, where the element El in **14** is replaced by two hydrogen atoms. A thorough analysis of the reaction of *tert*-butylamine with the bis(amino)stannylenes **14b** shows that the first step should be formulated as an addition reaction.<sup>[45]</sup> The unstable intermediate **28** was successfully characterized by a low temperature X-ray structure determination. The nitrogen of the *tert*-butylamine in **28** interacts not only with the tin atom, but also via hydrogen bonds with the nitrogen atoms of the diazasilastannetane ring. The  $\text{N}_2\text{Sn}$  group of **14b** thus functions as a "trihapto" ligand with respect to the  $\text{NH}_2$  group of the primary amine; this is an attractive confirmation of the concept that both Lewis bases and the Lewis acid act together as one unit. In this connection the formal similarity between the  $\text{N}_2\text{Sn}$  system and an allyl anion should be noted,<sup>[46]</sup> since both are equipped with  $4\pi$  electrons distributed (localized or delocalized) over three atoms.



28

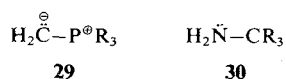
A similar formal analogy seems to exist between the formation of isocyanides (isonitriles)<sup>[46]</sup> and the formation of tetrameric iminogermynes, -stannylenes and -plumbylenes<sup>[42]</sup> [Eq. (n)]. However, whereas the reaction of the heavy carbene analogues takes place by an addition mechanism, the reaction of carbenes with primary amines has as

its first step the insertion of  $:\text{CX}_2$  into the N-H bond; a base-induced elimination of HX follows.<sup>[47]</sup> The special stability of the "inert electron pair" of the heavy main group element is obviously an important factor in determining the differing reactivities of  $:\text{ElX}_2$  and  $:\text{CX}_2$ .<sup>[48a]</sup>

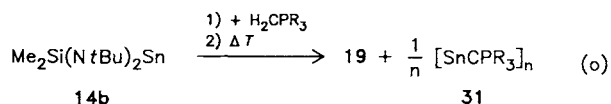


El = Ge, Sn, Pb; X = basic substituent

Methylene phosphoranes are, in the broader sense, isoelectronic with primary amines (cf. formulas **29**, **30**) (for the similar relationship between phosphorus ylides and silylamines see Ref. [48b]). It is therefore not surpris-

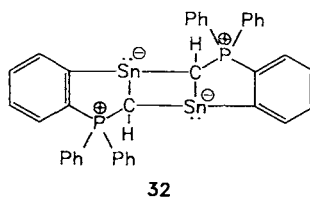


ing that methylene phosphoranes also react with the stannylenes **14b**, the addition and subsequent thermolysis leading to the bis(amino)silane **19** and the product **31** [Eq. (o)].<sup>[49]</sup> Compound **31** can be isolated in the form of

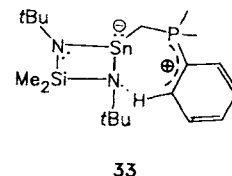


red crystals for R = Ph. The X-ray structure analysis shows that **31** does not contain a central tin-carbon cube (analogous to the iminostannylenes) but instead is a polycyclic compound (**32**).

Clearly a phenyl ligand is involved in the reaction of **14b** with the phosphorane. The reactive intermediate can be isolated and structurally characterized (as in the reaction of **14b** with *tert*-butylamine). It is an addition product that contains a tin-carbon bond and a  $\text{N}\cdots\text{H}-\text{C}$  bridge<sup>[49]</sup> (**33**). The carbanion, stabilized at the *o*-carbon of the phenyl ring, can then displace the  $\lambda^4\text{-N}$  atom at tin; this explains the formation of the five-membered ring in **32** (for the experimental verification and the further reaction steps cf. Ref. [49]).



32



33

## 4.2. Reactions between Unsaturated Element-Metal Compounds

Ethene and acetylene and their derivatives are generally stable with respect to oligomerization to cyclobutanes, tetrahedranes or cubanes; this stability is primarily kinetic<sup>[50]</sup> (see e.g. tetra-*tert*-butyltetrahedrane<sup>[51]</sup>). As mentioned in the introduction, molecules with a polar "double bond"

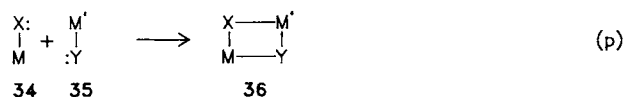
(e.g. **1** and **2**) are appreciably more reactive and therefore easily convertible into oligomers; this property can be utilized to prepare cyclic and polycyclic molecules containing metal atoms. The use of sterically demanding ligands (either on the metal or the non-metal atom) largely avoids the formation of polymers.

The polycyclic compounds described below arise from multiple acid-base reactions of unsaturated starting materials containing metal atoms. In some cases the starting materials are only obtainable as intermediates because of their high reactivity; the comments on the mechanisms involved should therefore be interpreted with caution. With this reservation we present a simple model with which the formation of the compounds can be formally described:

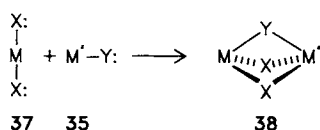
1) The starting materials always come together in such a manner that the nucleophilic and electrophilic centers are adjacent; in other words, the arrangement of atoms in the polycyclic products is such as to neutralize the polarity of the starting materials.

2) The metal atoms tend, by increasing their coordination number, to acquire an electron configuration corresponding (at least) to the next noble gas. They can act as multiple acceptors to several donors.

In our classification of these reactions, we consider the number of atoms involved; this is a loose analogy to cycloaddition reactions of unsaturated hydrocarbons.<sup>[32b]</sup> As an example, see Eq. (p); this can be described as a [2+2]-cycloaddition involving the interaction of a Lewis acid/base pair **34** with a second pair **35**. An important differ-



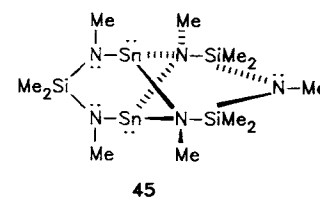
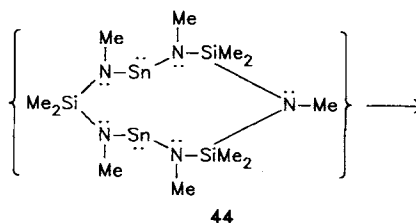
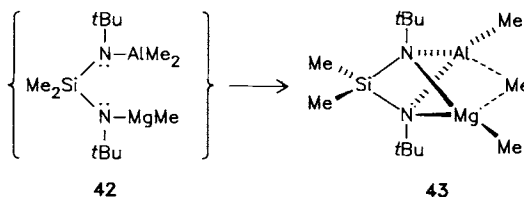
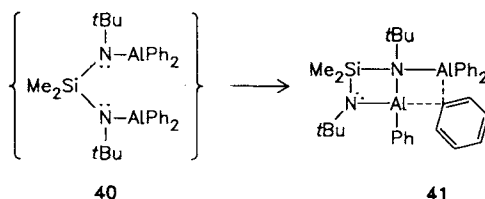
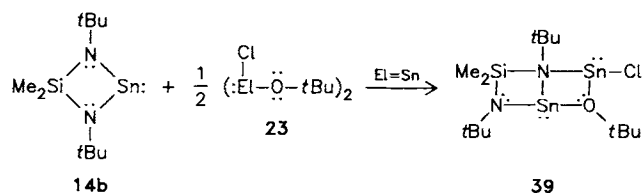
ence from the hydrocarbon reactions is that the size of the new ring is not necessarily given by the number of interacting centers in the reaction; for instance, the three centers of **37** react with the two centers of **35** to give not a simple ring system but the polycyclic compound **38**. The reason for this is the multiple acceptor nature of the metal atom  $M'$  in **35** towards the two bases X of **37**.



#### 4.2.1. [2+2]-Additions

As already mentioned, the dimers described in Section 3 can be considered to arise from [2+2]-additions of the monomeric Lewis acid/base systems. Further examples of this reaction type are given in Scheme 2.

The reaction of the bis(amino)stannylyene **14b** with the asymmetrically substituted tin(II) compound **23** proceeds by dissociation of dimeric **23** and addition of the resulting monomer to one of the tin-nitrogen bonds of **14b**, leading to **39**, which has been characterized by X-ray structure determination.<sup>[39]</sup> For steric reasons the molecule **40**, which is equipped with two acid and two basic centers, cannot



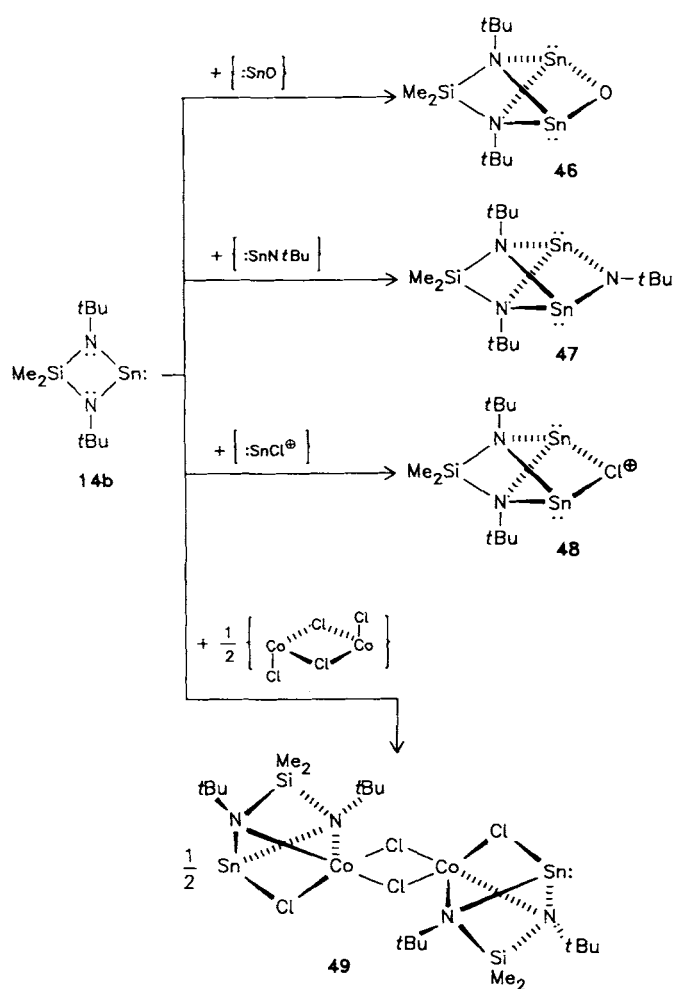
Scheme 2.

“react” intramolecularly to give a tricyclic product in which both nitrogen atoms function as bases. In **41** a three-center, two-electron bond, in which the carbon atom of a phenyl group and two aluminum atoms take part, serves to complete the coordination of the metal atoms.<sup>[29]</sup> The tricyclic product just mentioned is obtained, however, if an atomic arrangement as in **42** is provided. A three-center two-electron bond must also be assumed in **43** to complete the coordination at magnesium.<sup>[52]</sup> Another intramolecular double addition enables the tricyclic **45** to be “constructed” from **44**.<sup>[53]</sup>

#### 4.2.2. [3+2]-Additions

The ability of the  $\text{SnN}_2$  group in **14b** to coordinate through all three centers, rather than just two, has been discussed in Section 4.1. This property is particularly marked when **14b** comes into contact with extremely reactive molecules containing metal atoms with unusually low coordination number (Scheme 3).





Scheme 3.

The reaction product in each case is a hexatomic system of three rings containing as a structural element a distorted tetrahedron, two opposite edges of which are bridged by one atom each (Fig. 6). The products **46–49** all contain the starting molecule **14b**; it coordinates via both nitrogen atoms to the metal atom (Sn or Co) and its tin atom functions as acceptor. The recently discovered molecule **49** shows that transition metals can also function as accept-

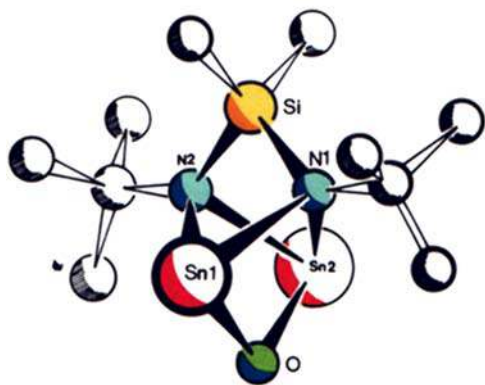
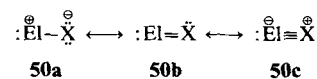


Fig. 6. Structure of **46** as a structural unit in the compounds  $\text{Me}_2\text{Si}(\text{NtBu})_2\text{Sn}_2\text{O}\cdot\text{SnCl}_2$  [43] and  $[\text{Me}_2\text{Si}(\text{NtBu})_2\text{Sn}_2\text{O}]_2\cdot\text{Me}_2\text{Si}(\text{NtBu})_2\text{Sn}(\text{O})_2\text{Sn}(\text{NtBu})_2\text{SiMe}_2$  [45].

ors.<sup>[55]</sup>  $\text{SnO}$  and  $\text{SnN-tBu}$  are probably generated as reactive intermediates in the hydrolysis<sup>[43]</sup> or *tert*-butylaminolysis<sup>[42]</sup> of **14b**, respectively, and are then trapped by excess **14b** to give **46** and **47**. The latter decomposes irreversibly at 210°C by a first-order reaction to give **14b** and  $(\text{SnNtBu})_4$ <sup>[4a]</sup>—evidence for the existence of an  $\text{SnN-tBu}$  intermediate. The polycyclic compound **48** is formed, together with the anion  $\text{SnCl}_3^-$ , in the reaction of **14b** with two mol equivalents of tin(II) chloride.<sup>[56]</sup>

The intermediates  $\text{SnO}$  and  $\text{SnN-tBu}$  can be regarded as heavy homologues of carbon monoxide or *tert*-butyl isocyanide respectively<sup>[36]</sup> (see Ref. [57] concerning the existence of  $\text{Ph-NSi}$ ). However, whereas the limiting structures **50b** and **50c**, involving multiple bonds, are clearly



El = C, Si, Ge, Sn, Pb; X = O, NtBu

dominant for carbon, the structure **50a**, which involves a single bond, is probably more important for the heavier homologues.<sup>[36]</sup> The differing bonding schemes are reflected in the properties of the compounds. Carbon monoxide and organic isocyanides are monomeric; the corresponding compounds of the higher homologues, where existent, are tetrameric (see next Section). In the compounds **46–48**, several such tin species form part of the respective molecules.

The isoelectronic substitution of the low-valent main group element and of the nitrogen in  $\text{ElN-R}$  leads formally to alkoxides of univalent elements of the third main group, which have been known for a long time.<sup>[58]</sup> These alkoxides should correspond electronically to the imino-carbene analogues (see e.g. formula **50a**). As expected, thallium(I) *tert*-butoxide reacts smoothly with tin(II) *tert*-butoxide in a [3+2]-addition [Eq. (q)].<sup>[59]</sup> The distorted trigonal bipyramidal structure of the  $\text{SnO}_3\text{Tl}$  framework of **52** is easily recognized in Figure 7.

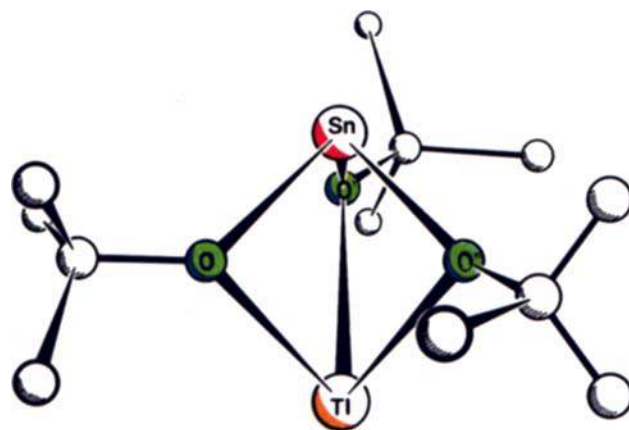
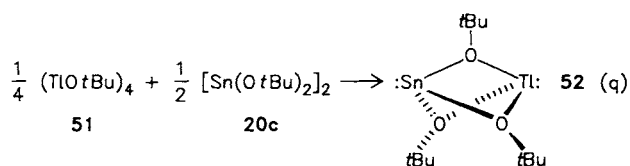
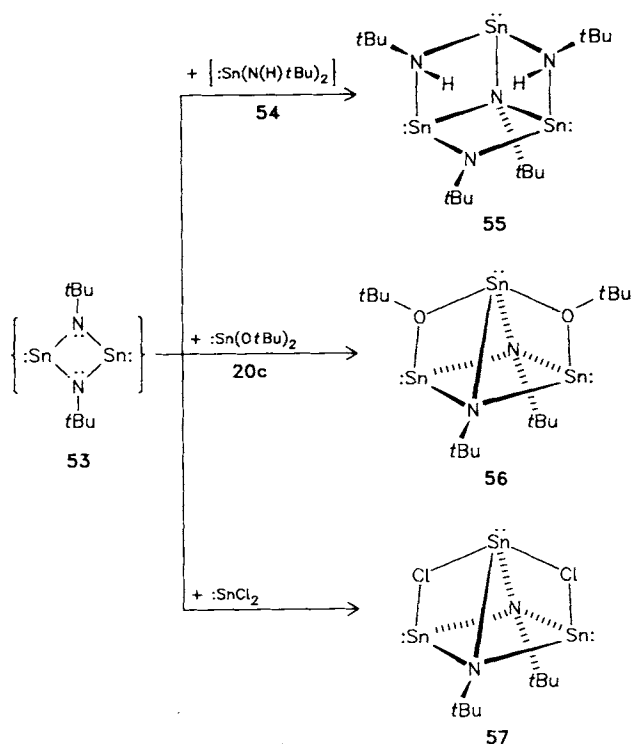


Fig. 7. Molecular structure of **52** [59].

#### 4.2.3. [3+3]- and [3+4]-Additions

Trifunctional systems containing one acid and two base functions react with the same compounds, but in a manner depending on the strength of the base. Whereas **14b**, for example, reacts with one equivalent of  $\text{SnN-tBu}$  to give stable polycyclic **47**, **20c** reacts with two equivalents of  $\text{SnN-tBu}$ . From these two equivalents one can construct the four-membered ring **53**, which formally displays two acid and two basic functions and is isoelectronic with a cyclobutadiene. As can be seen from Scheme 4, this ring can be trapped by reactions with various trifunctional molecules. The reaction of **53** with the equally unstable **54** is a [3+3]-addition resulting in a seco-norcupane skeleton **55**; <sup>[42a,60]</sup> all four centers of **53**, however, react with the three centers of **20c**, and this causes one of the tin atoms of the product **56** to be four-coordinate. <sup>[61]</sup> The structural difference between **56** (with a central seven-atom framework consisting of two bipyramids with a common face) and **55** may be attributed to the three-coordinate oxygen and four-coordinate nitrogen respectively. The preparation of **57** also depends on a [4+3]-addition. <sup>[36,56]</sup> An X-ray structure



Scheme 4.

analysis has shown that the molecular units **57** link to form a polymer; one of the chlorine atoms acts as a bridge to two adjacent  $\lambda^3$ -tin atoms, itself acquiring square planar coordination (Fig. 8).

#### 4.2.4. [2+2+2+2]- or [4+4]-Additions

There are a large number of molecules with the cubane structure whose formation can in general be attributed

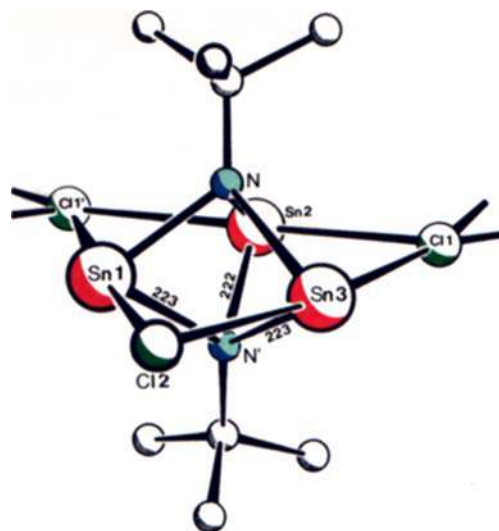
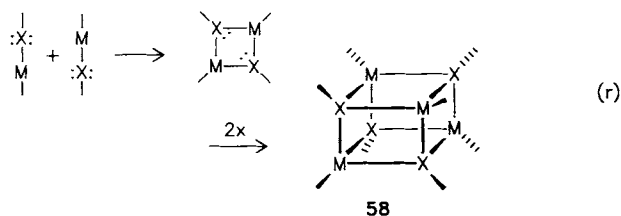


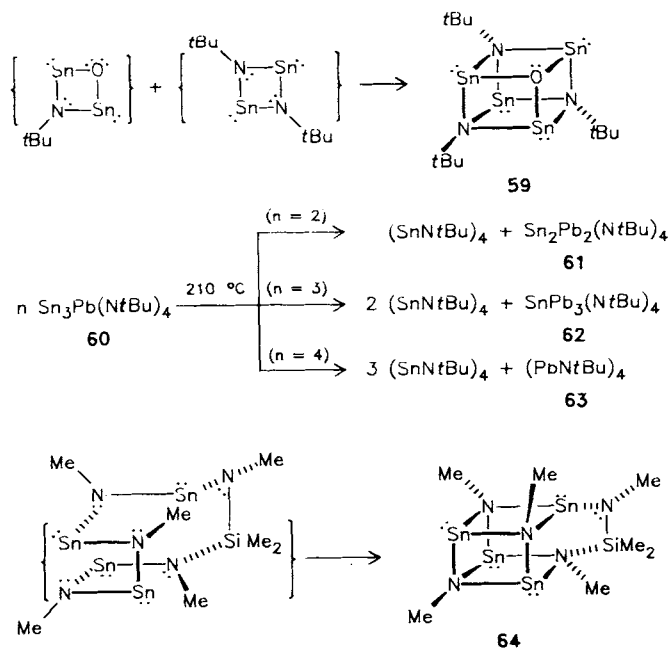
Fig. 8. Section of the crystal structure of **57** [36, 57]. The local symmetry of the  $\text{Sn}_3(\text{NtBu})_2\text{Cl}_3$  unit is close to  $D_{3h}$ .

to the reaction of doubly unsaturated acid-base systems. Examples are organoberyllium alkoxides  $(\text{RBeOR})_4$ , <sup>[62]</sup> iminoalanes  $(\text{RAlNR})_4$ , <sup>[63]</sup> and thallium(I) alkoxides  $(\text{TIOR})_4$ , <sup>[58]</sup> to name only three typical representatives. Retrosynthetic considerations lead to the assumption that monomeric units first come together in pairs to form four-membered rings, pairs of which then mutually complete their coordination spheres by forming a cubane system **58** [Eq. (r)].



With light elements and less bulky substituents, higher oligomers than tetramers can be formed, <sup>[64]</sup> whereas with heavy elements (in particular low-valent metals with an "inert" s-electron pair) the preferred use of pure p orbitals leads exclusively to cubane-type arrangements. <sup>[35b,36]</sup> The formation of tetrameric iminogermynes (e.g.  $(\text{GeN-tBu})_4$  <sup>[23a,65]</sup>), iminostannylenes  $(\text{SnNR})_4$  (R = isopropyl, 1,1-dimethylhydrazyl, <sup>[42b]</sup> tert-butyl, <sup>[42a,44]</sup> benzyl <sup>[44]</sup>) and iminoplumbylens (e.g.  $(\text{PbNtBu})_4$  <sup>[23a]</sup>) can be described in an analogous manner (cf. also Fig. 5).

Apart from these "homogeneous" oligomers of doubly unsaturated acid-base systems, there are also a series of compounds that are formed from non-identical starting materials (e.g. by "scrambling" reactions) or that formally arise from an intramolecular [4+4]-cycloaddition (e.g. to give **64**). Some of these compounds are presented in Scheme 5; for the exact preparative details the reader should consult the original references (**59**, <sup>[44,66,67]</sup> **60-63**, <sup>[23a]</sup> **64** <sup>[53]</sup>). Figure 9 shows the structure of the molecule **64**, which is analogous to basketane. <sup>[68]</sup>



Scheme 5.

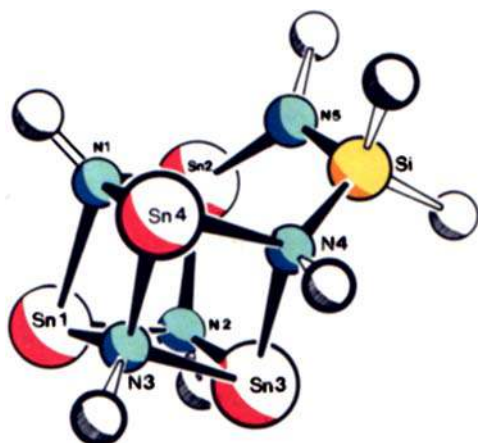
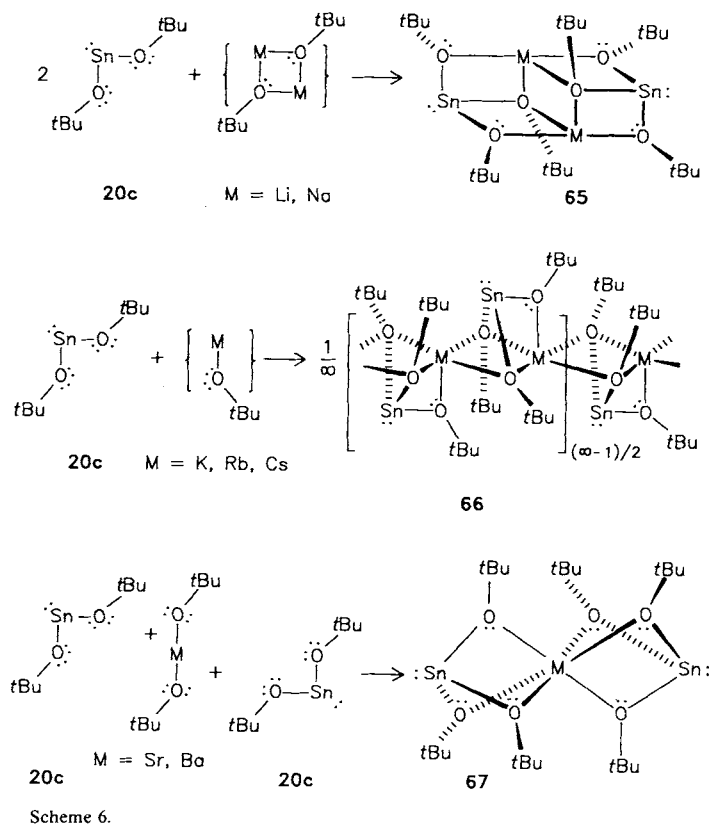


Fig. 9. Molecular structure of **64** [53].

#### 4.2.5. Additions Involving Several Acid and Base Centers

Metal alkoxides of the first and second main groups form oligomeric, in some cases molecular, compounds in which the metal atoms tend to compensate for their lack of electrons by acquiring as many oxygen donors as possible.<sup>[69, 70]</sup> they should therefore be ideal starting materials for addition reactions with trifunctional acid-base systems. This is indeed confirmed in the reactions of metal *tert*-butoxides with tin di-*tert*-butoxide (Scheme 6). An X-ray structure determination shows that the metal atoms Li and Na in molecule **65**<sup>[71]</sup> are four-coordinate, the tin atoms three-coordinate and the oxygen atoms three- or four-coordinate. The polycyclic unit  $\text{Sn}_2\text{O}_6\text{M}_2$  is composed of two *seco*-norcubane-analogous subunits that share a common face. The reaction of **20c** with the alkoxides of the heavy alkali metals leads to polymeric arrangements of trigonal bipyramidal cages  $\text{Sn}(\text{O}t\text{Bu})_3\text{M}$  (**66**), in which the alkali metal atom is coordinated by five oxygens and forms the link between the cages (cf., on the other hand, **52**).<sup>[71]</sup> The

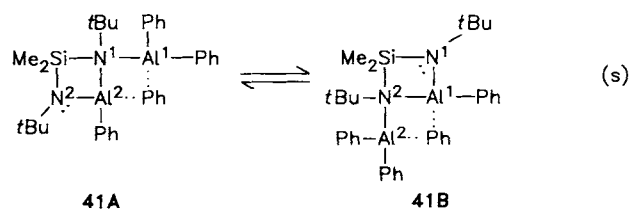
larger radius (and possibly the accessibility of d orbitals) is associated with a larger coordination number for K, Rb and Cs. The alkoxides of the alkaline earth elements strontium and barium react with the tin alkoxide **20c** to form the molecules **67**, which contain six-coordinate alkaline earths (the reaction corresponds to a [3 + 3 + 3]-addition;  $\text{Mg}(\text{O}t\text{Bu})_2$  and  $\text{Ca}(\text{O}t\text{Bu})_2$  do not react).<sup>[72]</sup>



Scheme 6.

## 5. Properties of Metallacycles

The polycyclic species described in Section 4 are thermally more stable when the point symmetry of the central framework is high and the distribution of the peripheral ligands is isotropic. Whereas  $(\text{Sn}t\text{Bu})_4$ , for example, can be heated to above  $250^\circ\text{C}$  without decomposing, **47** decomposes within a few hours at  $210^\circ\text{C}$  to **14b** and  $(\text{Sn}t\text{Bu})_4$ .<sup>[42a]</sup> Molecules that possess, in addition to the donor and acceptor functions that are bound to each other, further coordinatively unsaturated bases (e.g. the three-coordinate nitrogen atoms in **39**, **41**, **55** and **64**) can display intramolecular valency fluctuation; this is shown here for molecule **41**. The temperature-dependent  $^1\text{H-NMR}$  spectrum shows that there is an equilibrium between **41A** and **41B** [Eq. (s)]. The fluctuation within compound **41** is



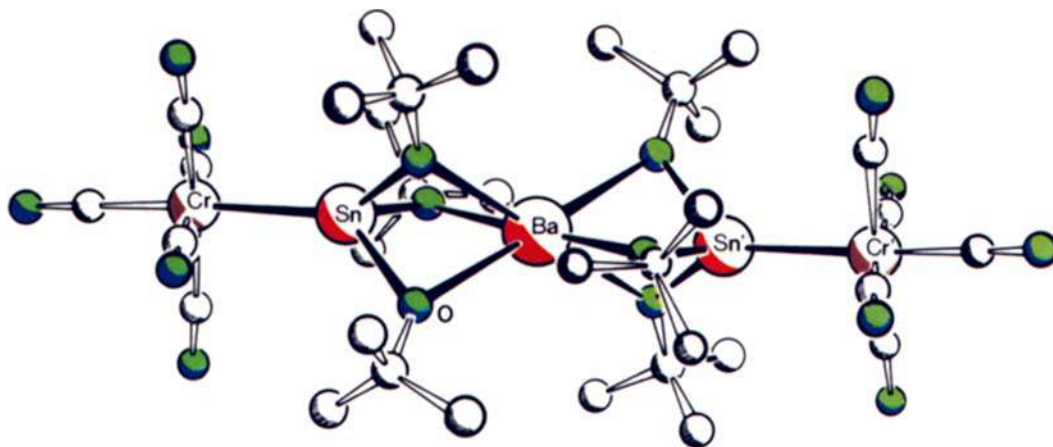


Fig. 10. Molecular structure of **70** [78].

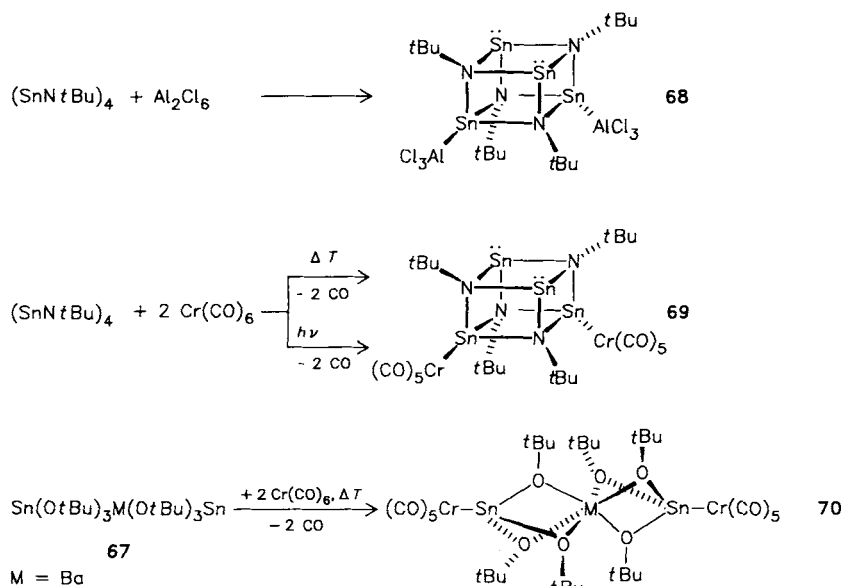
caused by the competition between the donors N2 and N1 for a coordination site at a further aluminum atom (for a more detailed discussion see Ref. [29]). Similar competition leads to intramolecular dynamic exchange of formal donors in molecules **39**,<sup>[39]</sup> **55**,<sup>[60]</sup> and **64**.<sup>[53]</sup>

Our description of the compounds presented in Section 4 as polycyclic molecules is a necessary consequence of the model we use to interpret their formation. If, on the other hand, the accumulation of metal atoms in these compounds is accentuated, then an alternative bonding model arises in which the metal cluster<sup>[73]</sup> of the central framework is described, the non-metal ligands serving only to neutralize its charge. There is however neither structural nor spectroscopic evidence<sup>[44]</sup> to give this model particular support.

Polycyclic compounds that contain low-valent metal atoms with lone pairs should be able to utilize these to act as electron donors. Since the heavy metals can additionally function as electron acceptors, it is conceivable that, under special conditions, the molecules may aggregate to form "coordination polymers" with metal-metal interactions. We have only found one compound in which different tin

atoms act as acceptors and donors (in the crystal). The crystal structure of  $(\text{SnNNMe}_2)_4$ <sup>[42b]</sup> involves an undulating ribbon of approximately equidistant tin atoms—irrespective of whether the contacts are intra- or intermolecular. The compound is a red solid (in contrast to the colorless iminostannylenes that only involve van der Waals contacts between molecules); it decomposes above 50°C to β-tin, nitrogen, methane, ethane and dimethylamine.

Compounds **68**, **69** and **70**, synthesized as shown in Scheme 7, confirm that the low-valent metal atoms can react as bases with strong Lewis acids such as  $\text{AlCl}_3$  or with transition metal fragments (the intermolecular interactions in  $(\text{SnNNMe}_2)_4$  have been discussed in terms of other models too<sup>[42b]</sup>). Compound **68** is the first chemically and structurally characterized example of an adduct of a tin(II) compound and a main group Lewis acid; the synthesis is strikingly simple considering that the compound contains a new type of metal-metal bond. The tin-chromium bond in **69**, however, is already familiar from other examples.<sup>[75,76]</sup> In both **68** and **69**<sup>[77]</sup> it is only possible to add two metal fragments to the tetrameric iminostannylene. We have not succeeded in synthesizing a molecule



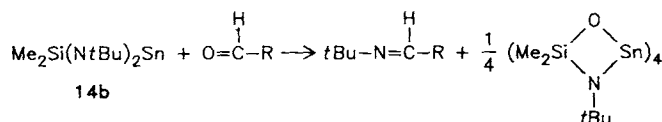
Scheme 7.

in which all four tin atoms are bound to metal fragments, either by using drastic conditions or by substituting  $\text{Mo}(\text{CO})_6$  or  $\text{W}(\text{CO})_6$  for  $\text{Cr}(\text{CO})_6$ .<sup>[177]</sup>

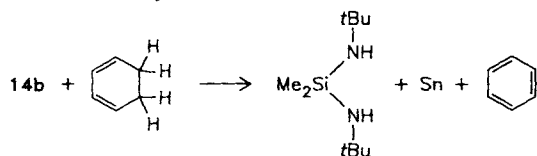
The reaction that leads to the polycyclic compound **70** (Fig. 10) seems particularly promising as a pointer to future research. The addition of two metal fragments to **67** converts the linear arrangement of three metal atoms to a chain consisting of five metal atoms.<sup>[178]</sup> Preliminary studies suggest that this principle can be arbitrarily extended.

## 6. Concluding Remarks

The technical interest in main group metals is mainly concerned with the elements themselves or with metal ions in solution or in the solid state. Except for organometallics<sup>[179]</sup> and other specialized compounds such as alkoxides<sup>[69]</sup> and metal amides,<sup>[18,69]</sup> molecular compounds of these elements play only a modest role. The cyclic and polycyclic metal compounds described in this review are noteworthy because they allow the transfer of the metal atoms to nonpolar solvents and thus satisfy one condition necessary for homogeneous reactions with other species. The synthetic potential of these compounds is illustrated in Scheme 8 by some reactions of **14b** with organic molecules; the low oxidation state of the metal atom permits both addition and redox reactions (for further redox reactions see Ref. [80]).



R = Ph, H, Alkyl



Scheme 8.

Aliphatic or aromatic aldehydes are converted into *tert*-butylimines;<sup>[81]</sup> the initial step in this quantitative reaction is the [2+2]-addition of the polar C–O bond to one of the ring tin–nitrogen bonds of **14b**.<sup>[81]</sup> The tin atom acts as a halogen acceptor (and is thus oxidized) in the conversion of bromoalkanes to ethenes.<sup>[82]</sup> The possibility of using **14b** as an oxidizing agent has been realized only in the conversion of hexadiene to benzene.<sup>[37a]</sup>

*I am grateful to my co-workers for their valuable contributions to the work described here (see References). Financial assistance was generously given, at various times, by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, the State of Lower Saxony, and by Hoechst AG.*

Received: June 6, 1986;  
revised: August 11, 1986 [A 591 IE]  
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