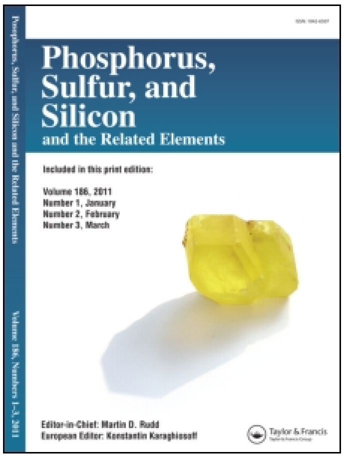

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Some Typical Properties of Cages Containing Simultaneously Main Group Metals and Non-Metals

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SOME TYPICAL PROPERTIES OF CAGES CONTAINING SIMULTANEOUSLY MAIN GROUP METALS AND NON-METALS

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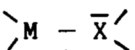
Abstract Electropositive main group elements can be incorporated into polycycles through bonding to nitrogen and oxygen atoms. The latter elements are substituted by bulky organic groups like *tert*-butyl, thereby preventing the molecules from polymerizing. The metal atoms, which behave as Lewis-acids towards the neighboring Lewis-basic ligands are generally low coordinate. In some cases temperature-dependent intramolecular rearrangements (bond fluctuations) are observed. The prominent occurance of highly strained polycycles like tetrahedra, cubes or trigonal bipyramids may be correlated to the orbitals used for bonding by the metal atoms; these are often of p- or d-type and therefore favor acute angles. These polycyclic compounds may react at either the metal or nonmetal center. The following reactions are observed: trapping of polar molecules, ligand exchange, metal exchange, redox reactions, cluster formation, metal-metal bond formation or opening of the cages.

INTRODUCTION

We have recently shown in a review[1] that a bond between a low coordinated metal atom M and an electron rich non-metal atom X can conceptively be described as unsaturated - very much like a double bond in molecules like ethylene or acetylene (Formulas 1-4).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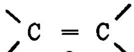
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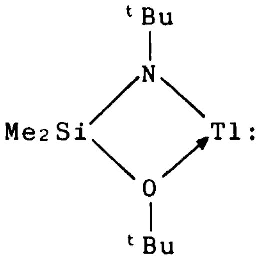
$$-\mathrm{M}-\underline{\bar{\mathrm{X}}}- \qquad -\mathrm{C}\equiv\mathrm{C}-$$

3 4

Whereas molecules like 2 and 4 are kinetically stable with respect to oligomerization, 1 and 3 are not. Because of the high polarity in the M-X-bond and the high tendency of electron lone pairs to be shifted to X rather than to M, compounds of type 1 or 3 usually tend to oligomerize or polymerize via intermolecular Lewis-acid-base-reactions[2]. The extend of polymerization will depend on the steric hindrance of the ligands at M and X. In some cases bulky substituents may even prevent polymerization, as has been found inter alia for cyclic derivatives of low valent elements from group III, IV and V (formulas 5, 6, 7)[1].



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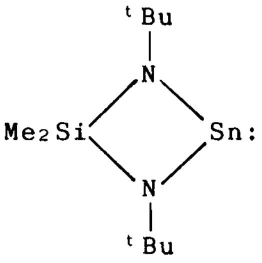

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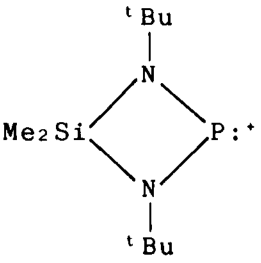

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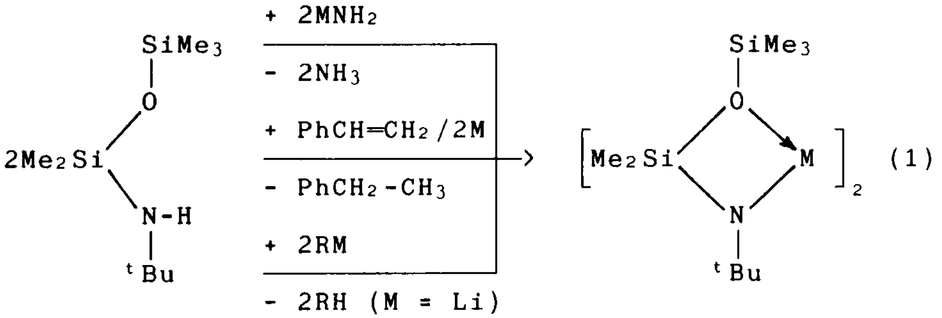
We have been able to use compounds of the general formula 1 and 3 to build up polycyclic molecules[1]. In the next chapter we will choose three recent examples in order to demonstrate the synthetic principle. The main scope of the article is nevertheless to look at the physical and chemical properties of the polycycles and cages, which we have obtained in our laboratory in the last ten years.

SYNTHETIC PRINCIPLES

Amino-Oxo-Chelated Derivatives of Alkali Elements

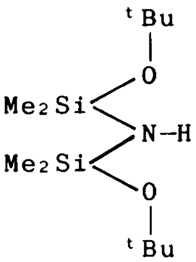
The chelating ligand $Me_3SiOSi(Me)_2N^tBu(H)$ (**8**), which is synthesized by classical methods[3,4], can be used to prepare amino derivatives of the alkali elements (**9** - **12**) as shown in equation (1).



8

M = Li (**9**), Na (**10**), K (**11**), Rb (**12**)

In all cases dimeric molecules are formed through formal intermolecular Lewis-acid-base reactions of the monomers. Even the use of a tridentate ligand, like **13**, can not prevent the dimerization as established in the compounds **14** - **17**.



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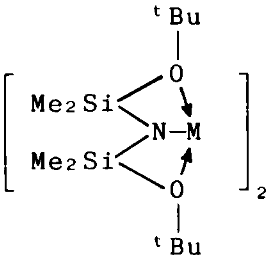


M = Li (**14**), Na (**15**), K (**16**), Rb (**17**)

The molecules **14** - **17** are prepared starting from **13** by similar methods as shown in equation (1).

Janus Type Molecules $M(O^tBu)_3M'$

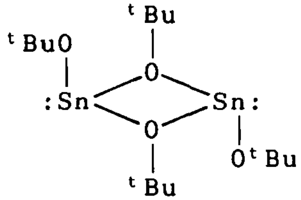
Whereas in alcoholates a low valent metal of main group III has formally only four valence electrons (see formula **18**), a low valent element of group IV has six (formula **20**). In order to raise the electron count and at the same time the coordination number at the metal, alcoholates of group III elements tetramerize (Tl_4O_4 cube)[5], while alcoholates of group IV elements dimerize[6].This is shown for Tl(I) and Sn(II) in equation (2).

$$4\ \{{}^tBu\text{–}\bar{\underline{O}}\text{–}Tl{:}\} \longrightarrow (:TlO^tBu)_4$$

18 **19**

$$2\ \{{}^tBu\text{–}\bar{\underline{O}}\text{–}\ddot{Sn}\text{–}\bar{\underline{O}}\text{–}{}^tBu\} \longrightarrow$$

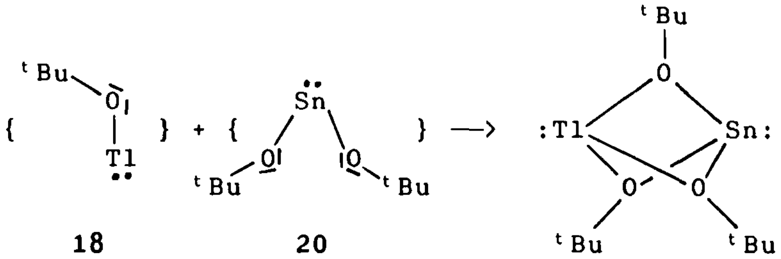
20



21

(2)

There is of course another possibility for the metallic elements Tl and Sn in **18** and **20** to become coordinatively saturated - namely by combining **18** and **20** in one molecule. The thallium atom in **18** functions as a Lewis-acid towards the two oxygen atoms in **20**, whereas the tin atom in **20** may act as an electrophilic center towards the oxygen atom in **18** (equation (3)).



18 **20** **22**

(3)

The species **22** is a molecular compound which is soluble in non-polar organic solvents; the trigonal bipyramidal structure of the TlO_3Sn cage has been proven by X-ray structure analysis[7]. We have recently prepared a number of homologous cage compounds by the method shown in equation (3) or by alternative routes, as summerized in equation (4).

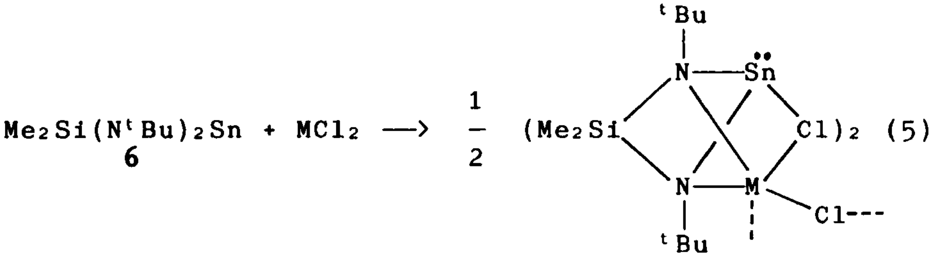
$$
\begin{array}{lll}
\frac{1}{2}\ \underset{\mathbf{23}}{[Na(O^tBu)_3M]_2} + M'Br \longrightarrow M(O^tBu)_3M' + NaBr & & \\
\underset{\mathbf{22}}{Tl(O^tBu)_3M} + M'Br \longrightarrow M(O^tBu)_3M' + TlBr & & (4)
\end{array}
$$

M = Ge, M' = In (**24**), M' = Tl (**25**),
M = Sn, M' = In (**26**)
M = Pb, M' = In (**27**), M' = Tl (**28**)

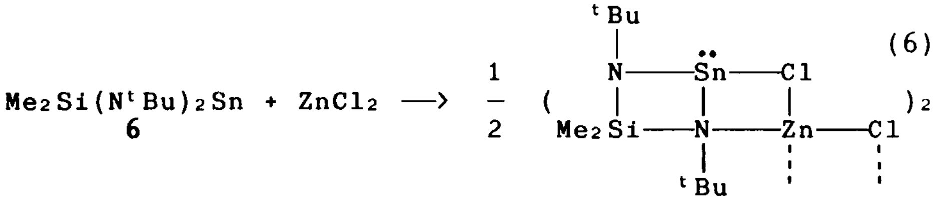
All compounds **24** - **28** can be sublimed or crystallized and are obtained in high yields[8]. They all have the common feature that the three tert-butoxyl groups are clasping the metal atoms together. As an electrophile can attack the molecule from the two metal sides with equal probability and in both cases will encounter a metal with a non-bonding electron pair, we have designated such molecules as "janus type" (see further on).

Bis(amino)stannylene Adducts of Transition Metal Halides

We have shown by numerous examples[1] that the cyclic bis(amino)stannylene **6** can behave as a dihapto- or triphapto-Lewis-acid-base ligand in different metal/non-metal systems. Halides from the 3d-elements are in this respect appropriate counterparts for **6**. When anhydrous $CrCl_2$, $FeCl_2$, $CoCl_2$ or $ZnCl_2$ are treated with a toluene solution of **6** new compounds are formed in these heterogeneous reactions (equation (5) and (6))[9].



M = Cr (**29**), Fe (**30**), Co (**31**)



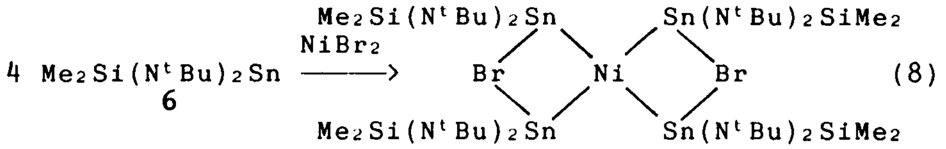
32

The compounds **29** - **32** are dimeric through chlorine bridges.

While in the case of **32** the Zn atom adopts a four-fold coordination - leading to a bicyclic connection of the ZnCl$_2$ to the cyclic bis(amino)stannylene - in the other molecules the transition metals are five-fold coordinated (three chlorine and two nitrogen ligands). A [4,2,0,0^{2,5}] cyclohexane cage (SiN$_2$SnMCl) is therefore formed. The differences in the structures from **29** - **31** to **32** stems from the availability of vacant orbitals at the transition metals.

As the tin atom in **6** is not only Lewis-acidic but also in a low oxidation state, redox reactions may occur when it is allowed to react with transition metal halides. This is exemplified by equation (7)[10] and in some respect by equation (8).

$$\underset{6}{4Me_2Si(N^tBu)_2Sn} + 2CrCl_3 \longrightarrow \underset{33}{Me_2Si(N^tBu)_2Sn(N^tBu)_2SiMe_2} + \underset{29}{[Me_2Si(N^tBu)_2SnCrCl_2]_2} + SnCl_2 \quad (7)$$



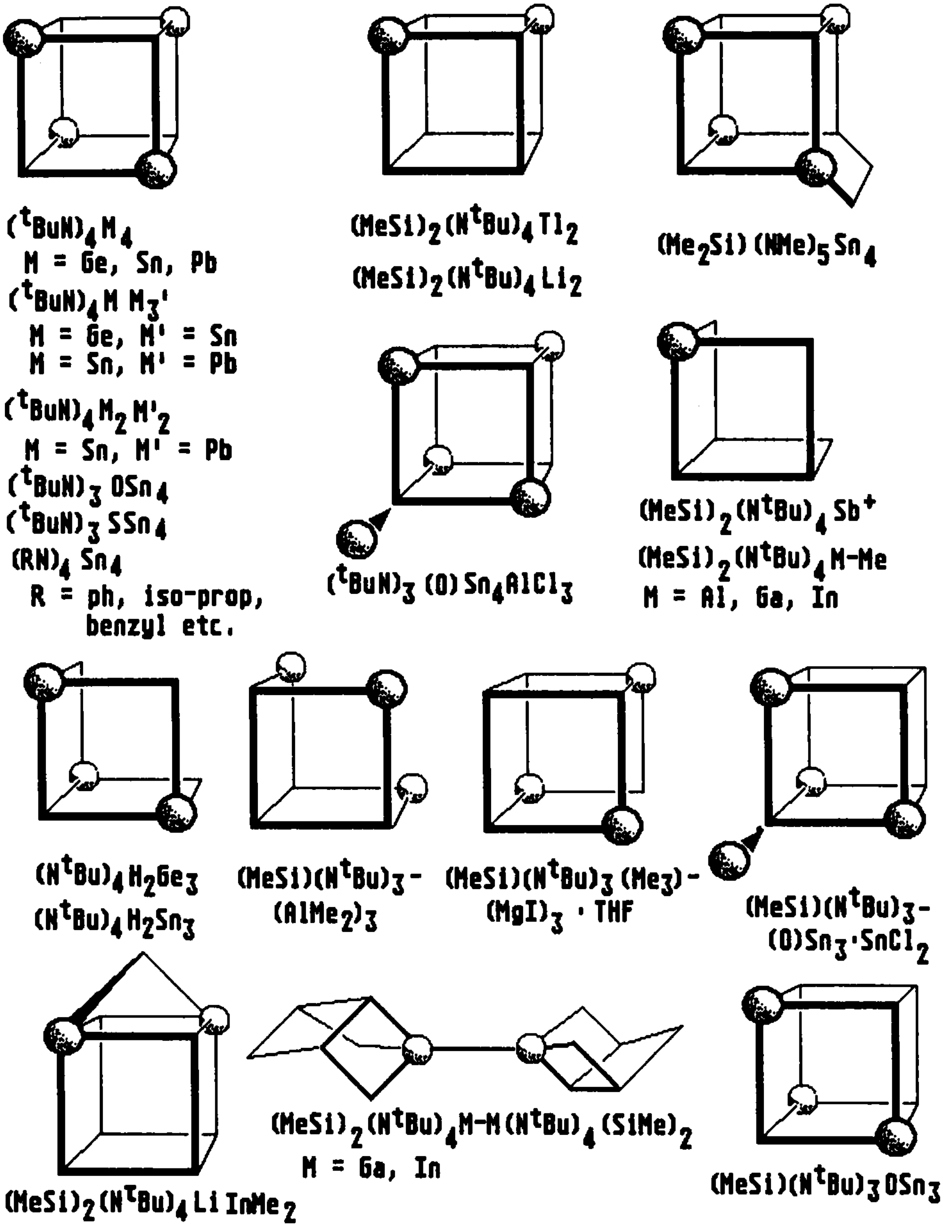
34

In the case of the reaction of 6 with chromium(III)-chloride, the Cr(III) is reduced to Cr(II), which, in turn, is trapped by 6 forming 29. Sn(II) is oxidized to Sn(IV) to give compound 33. The genesis of the polycyclic 34 can be attributed to the insertion of the stannylene into Ni-Br bonds (formally no redoxreaction). Compound 34 contains five metal atoms linked together in a distorted square with the Ni in the middle. The distortion from planarity is not severe, but significant enough (about 15°, from X-ray structure determination) that at room temperature a magnetic moment of 0.5 BM is found for the compound.

STRUCTURAL ASPECTS OF THE POLYCYCLES AND CAGES

Polyhedra and Geometrical Arrangements Used by the Polycycles and Cages

In order to discover the common structural principles for the polycycles and cages, which incorporate metal as well as non-metal atoms, we have assembled in figures 1 - 4 sketchy representations of the different molecules. In these illustrations we have used spheres



$(^tBuN)_4M_4$
M = Ge, Sn, Pb
$(^tBuN)_4M\,M_3'$
M = Ge, M' = Sn
M = Sn, M' = Pb
$(^tBuN)_4M_2M_2'$
M = Sn, M' = Pb
$(^tBuN)_3OSn_4$
$(^tBuN)_3SSn_4$
$(RN)_4Sn_4$
R = ph, iso-prop, benzyl etc.

$(MeSi)_2(N^tBu)_4Tl_2$
$(MeSi)_2(N^tBu)_4Li_2$

$(Me_2Si)(NMe)_5Sn_4$

$(^tBuN)_3(O)Sn_4AlCl_3$

$(MeSi)_2(N^tBu)_4Sb^+$
$(MeSi)_2(N^tBu)_4M\text{-}Me$
M = Al, Ga, In

$(N^tBu)_4H_2Ge_3$
$(N^tBu)_4H_2Sn_3$

$(MeSi)(N^tBu)_3\text{-}(AlMe_2)_3$

$(MeSi)(N^tBu)_3(Me_3)\text{-}(MgI)_3 \cdot THF$

$(MeSi)(N^tBu)_3\text{-}(O)Sn_3 \cdot SnCl_2$

$(MeSi)_2(N^tBu)_4LiInMe_2$

$(MeSi)_2(N^tBu)_4M\text{-}M(N^tBu)_4(SiMe)_2$
M = Ga, In

$(MeSi)(N^tBu)_3OSn_3$

FIGURE 1 Some Representative Examples of Polycycles and Cages ("Cubes")

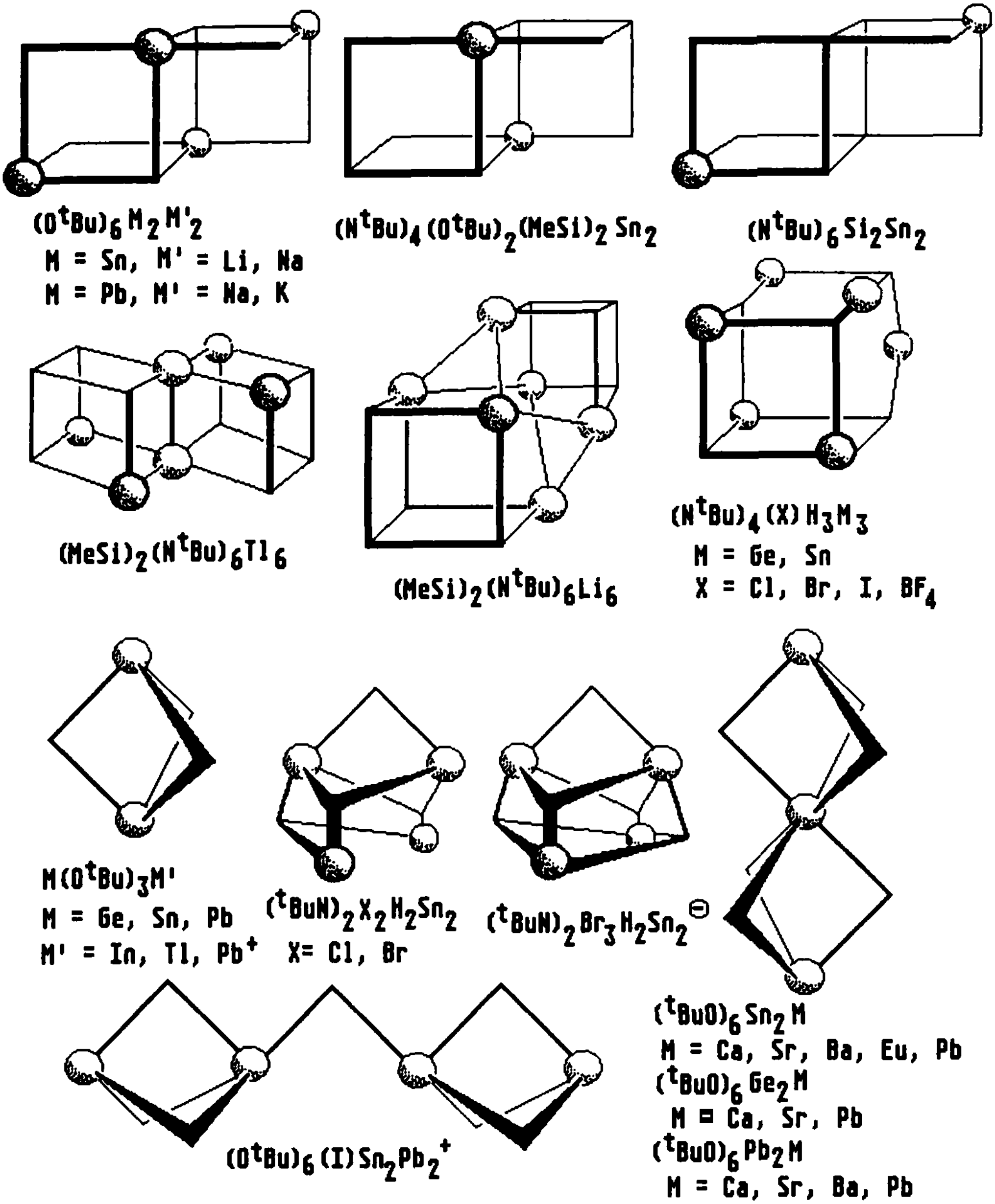
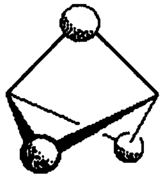
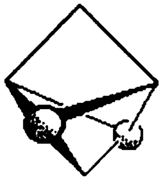


FIGURE 2 Polycycles and Cages ("Cubes, Tetrahedra and Trigonal Bipyramids")



$(N^tBu)_2(Me)_5MgAlSi$



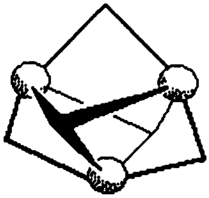
$(Me_2Si)(N^tBu)_3Sn_2$

$(Me_2Si)(N^tBu)_2OSn_2$

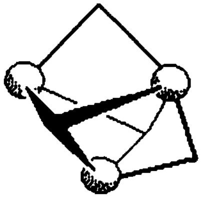
$(Me_2Si)(N^tBu)_2ClSn_2^{\oplus}$

$(Me_2Si)(N^tBu)_2BrSn_2^{\oplus}$

$(Me_2Si)(N^tBu)_2ClSnCoCl$

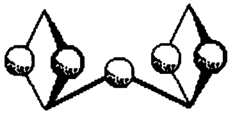


$(N^tBu)_2Cl_3Sn_3^{\ominus}$

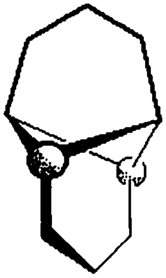


$(N^tBu)_2(O^tBu)_2Sn_3$

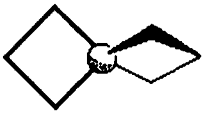
$(N^tBu)_2(O^tBu)_2Sn_2Ge$



$[(Me_2Si)(Me_2Al)(N^tBu)_2]_2Mg$



$(MeSi)_3(NMe)_5Sn_2$

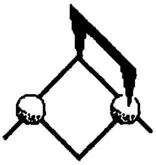


$Me_2Si(N^tBu)_2M(N^tBu)_2SiMe_2$

M = Ge, Sn, Pb

$[Me_2Si(N^tBu)(O^tBu)]_2M$

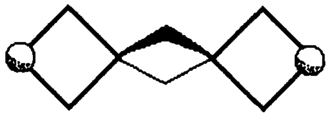
M = Mg, Zn



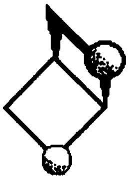
$(Me_2Si)(N^tBu)(O^tBu)Cl(HgCl)_2$

$(Me_2Si)(N^tBu)_2ClSnMCl$

M = Fe, Zn

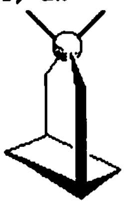


$(^tBuN)_6Si_2Ge_2$

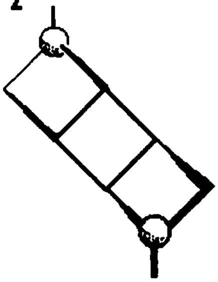


$(MeSi)(N^tBu)_2(N^tBuH)(AlMe_2)M$

M = Na, MgMe, MgI

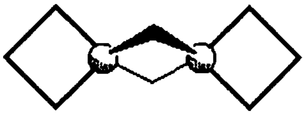


$(MeSi)_2(N^tBu)_4Mg \cdot 2THF$

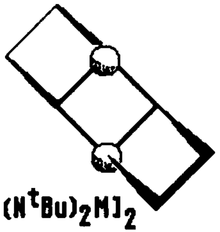


$(MeSi)_2(N^tBu)_4Li_2 \cdot 2Et_2O$

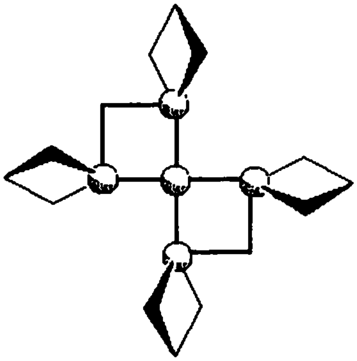
FIGURE 3 Polycycles and Cages ("Tetrahedra and Connected Four-membered Rings")



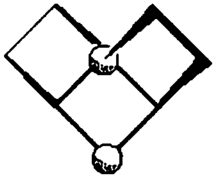
$[Me_2Si(N^tBu)_2SnX]_2$
X = O, S



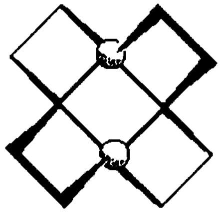
$[Me_2Si(N^tBu)_2M]_2$
M = In-Me, Al-Me, Mg $\leftarrow$ THF
$[Me_2Si(NSiMe_3)(O^tBu)M]_2$
M = K, Rb
$[Me_2Si(NSiMe_3)(O^tBu)Na \leftarrow py]_2$



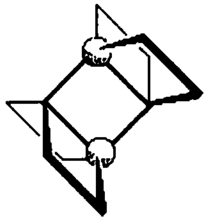
$[Me_2Si(N^tBu)_2]_4Br_2NiSn_4$



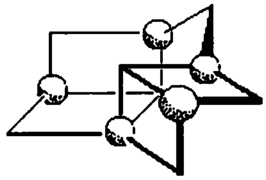
$[Me_2Si(N^tBu)(O^tBu)M]_2$
M = Li-py, Li-THF, Li-Diox
$[Me_2Si(NSiMe_3)(O^tBu)Na]_2$



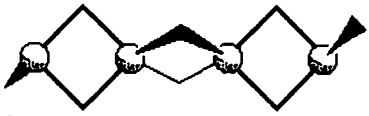
$[(Me_2Si)_2(O^tBu)_2NM]_2$
M = Li, Na



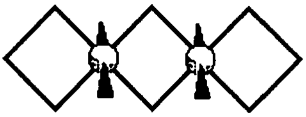
$[(Me_2Si)_2(O^tBu)_2NM]_2$
M = K, Rb



$(^tBuO)_7Ge_2Li_3$



$(O^tBu)_8Sn_2M_2$
M = Mg, Zn, Cd, Cr, Mn, Co, Ni



$[Me_2Si(N^tBu)(O^tBu)]Ca(THF)_2^{\bullet}]_2$

FIGURE 4 Polycycles and Cages ("Connected Four-membered Rings continued") to label the position of the metallic element or the hydrogen atoms, whereas all other elements within the polycycle or cage, like Si, N, O, S, Cl, Br, I etc., are drawn as simple corners of bonds. The metal atoms as well as the corners of the cages may have further ligands attached. These ligands have been omitted for clarity, but they may easily be derived from the formulas assembled below each little picture. Further details of the structures are referenced in the article mentioned above[1]; addititional articles have been published recently[11-20] and some will be published in the near future.

As can be concluded from the perusal of figures 1 - 4, the predominant structural elements of these metallacycles and cages seem to be the formation of small rings and the disposition of the ligands at right angles to each other. There are at least three reasons for these findings:

1) The bulky tert-butyl groups at the non-metals will favor small rings or small cages in order to be separated as far as possible from one another.

2) The orthogonal arrangement of the ligands at low-valent metals like In(I), Tl(I), Ge(II), Sn(II) or Pb(II) seems to rely on the fact, that these elements use exclusively non-hybridized p-orbitals for bonding - the non bonding electron pair being located in an almost pure s-orbital. Also, the additional metals present can easily adopt these geometries, as they are known to be found in the center of trigonal bipyramids or octahedra.

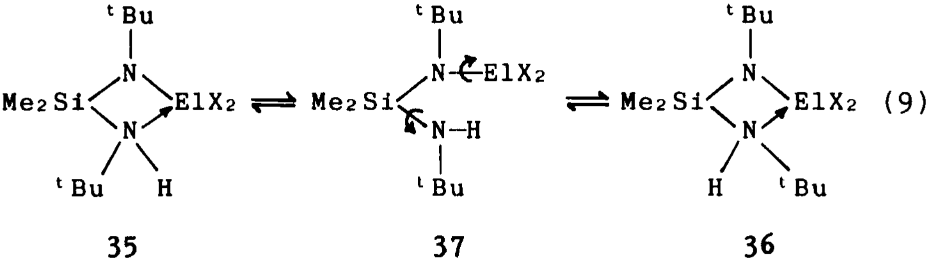
3) As the building units of the polycycles and cages are often four membered rings, it is not surprising to find this structural element again in the products.

The metallacages and polycycles can be classified as consisting of four families: (a) cages, which are derived from a cube (fig. 1, 2), (b) cages, which are derived from a tetrahedron (fig. 2 and 3), (c) cages, which have a trigonal bipyramid as central unit (fig. 2) and (d) polycycles which consist mainly of connected four-membered rings. Again the arguments given before and the synthetic route used are responsible for the different structural possibilities.

Dynamic Phenomena: Fluctional Bonds within the Polycycles and Cages

From X-ray analysis of a crystal the structural ground state of a molecule is often quite easily deduced, whereas dynamic phenomena within the molecular unit can be followed by NMR techniques. The metallapolycycles and cages are typical representatives of "fluctuating molecules" due to the incorporation of metal atoms. What is known from metal-complexes - the ligands being in equilibrium around the metallic center (complex formation constant) - can be transposed in loose analogy to molecular cages. This will be especially important in compounds where a variety of nonmetals with different coordination numbers are present. These are in competition for the metallic centers in the cages and thus provoke a redistribution of bonds (fluctuation).

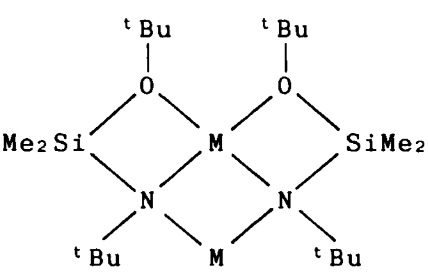
A very instructive example has been found in cyclic amino compounds of group III-elements[21].



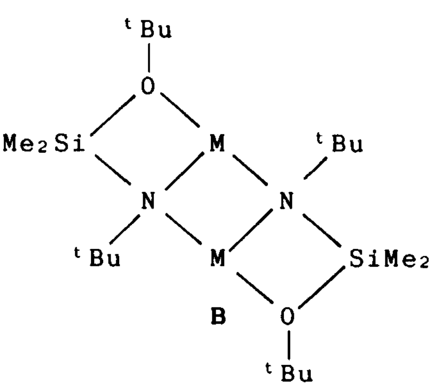
$El = Al, Ga, In, Tl, X = CH_3, Cl, Br$ (38 - 49)

The mirror images 35 and 36 are in equilibrium (equation (9)) via the intermediate open chain compound 37, in which rotation around the Si-N and N-El bond occurs. The activation energy for this process is strongly dependent on the Lewis-acidity of the element El, the electron withdrawing ability of the substituents X, as well as on steric factors[21].

The alkali compounds 9 - 12, resp. 14 - 17, which have been described in a previous chapter, have different structures in the crystal, depending on the alkali element. While the lithium and sodium derivatives 9 and 10 have as common structural element three edge-sharing four-membered rings of point symmetry C_2 (**A**), the potassium and rubidium derivatives 11 and 12 have a different structure with, again, three shared rings of point symmetry C_i (**B**).

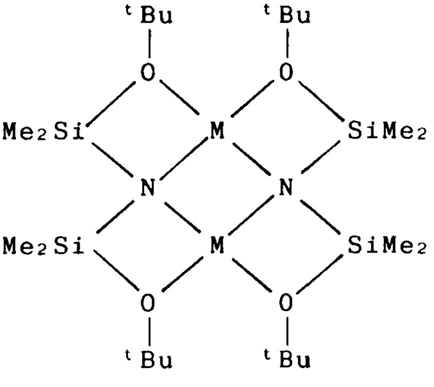


A

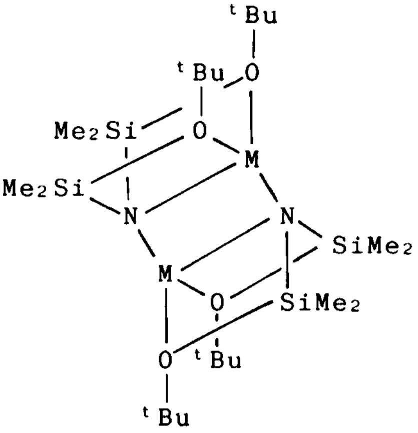


B

In analogy the compounds **14** and **15** adopt the structure depicted in formula **C**, while **16** and **17** form structure **D** in the crystal.

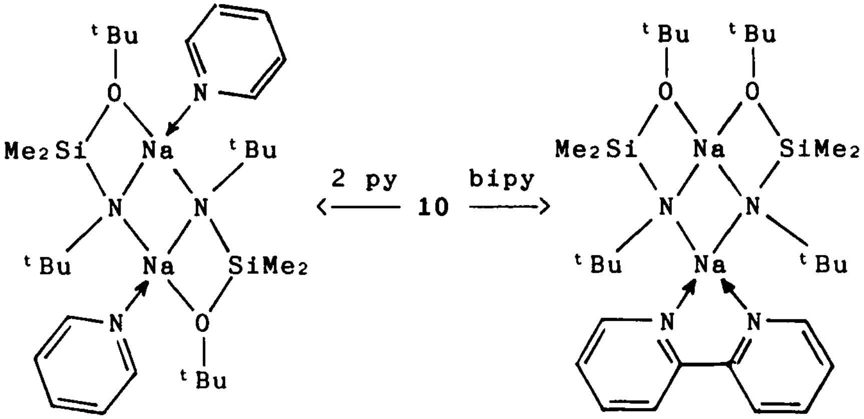


C



D

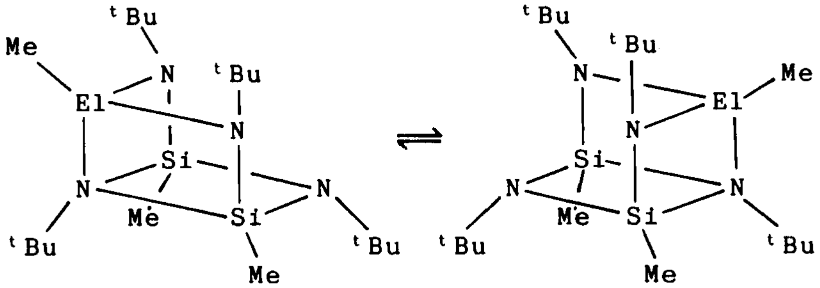
As can be shown using solution NMR-techniques, the ligands at the metal atoms "fluctuate" and a rapid interconversion from **A** —> **B** and from **C** —> **D** and vice versa occurs. Slight differences in electronegativities and in the atomic radii seem to stabilize one of the two alternative forms in the solid state. Even in solution only one of the two possible arrangements can be stabilized by the addition of a base. If the sodium compound **10** is allowed to react with the monodentate base pyridine the adduct **50** is formed, while with the bidentate bipyridine **51** is isolated from the reaction (X-ray structure determinations, equation (10)).



(10)

50 51

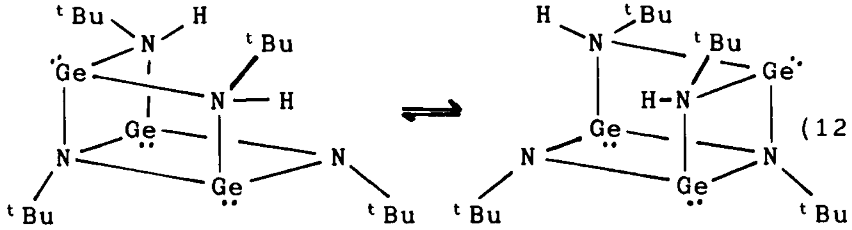
In the equations (11) - (14) further examples of rapid interchange between different structures are depicted[11,17,22]. These redistributions of bonds within the molecules have one common aspect: a nitrogen atom of coordination number 3 is in competition with another nitrogen atom of coordination number 4.



(11)

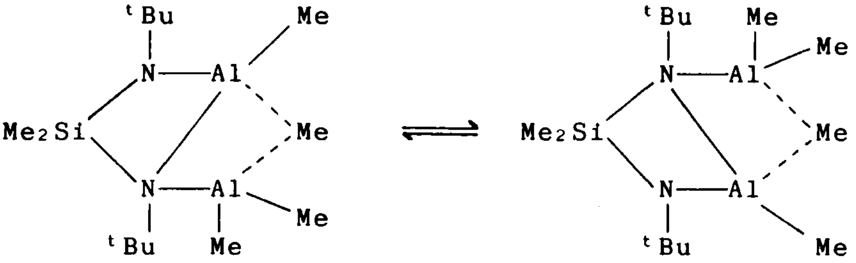
52 - 54 A 52 - 54 B

El = Al (52), Ga (53), In (54)

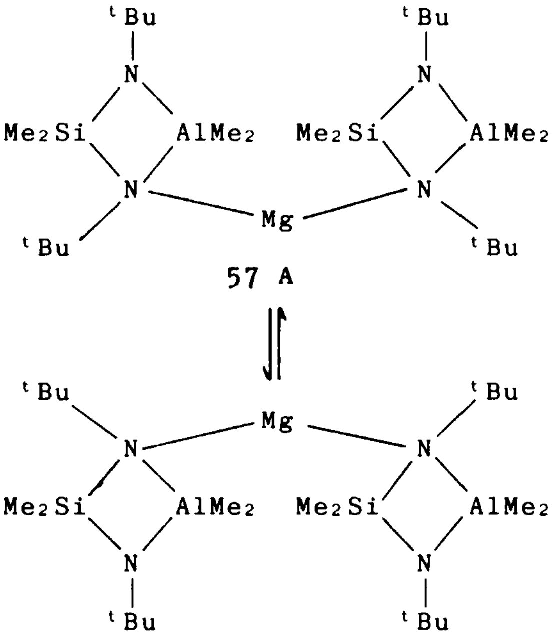


(12)

56 A 56 B



55 A 55 B (13)



57 B (14)

The "redistributions" of the ligands may occur very quickly and sometimes they are too fast for the intermediate to be detected by ^{1}H-NMR techniques at 180 K.

TYPICAL REACTIONS OF METALLACAGES

In this section we would like to list reactions which are typical for the cage compounds and which are, in part, influenced by the special steric requirements of these molecular clusters.

Substitution Reactions

Four examples of substitution of atoms within a cage compound are given in reactions (15) - (18)[1,17].

$$\underset{\mathbf{58}}{\mathrm{Sn_3(N^tBu)_4H_2}} + \underset{\mathbf{59}}{\mathrm{Ge(N^tBu)_2SiMe_2}} \xrightarrow{\Delta T} \underset{\mathbf{60}}{\mathrm{GeSn_3(N^tBu)_4}} + \underset{\mathbf{61}}{\mathrm{Me_2Si(N^tBu)_2H_2}} \qquad (15)$$

$$\underset{\mathbf{62}}{\mathrm{(MeSi)_2(N^tBu)_4InCl}} \xrightarrow{\mathrm{SbCl_3}} \underset{\mathbf{63}}{\mathrm{(MeSi)_2(N^tBu)_4Sb^+InCl_4^-}} \qquad (16)$$

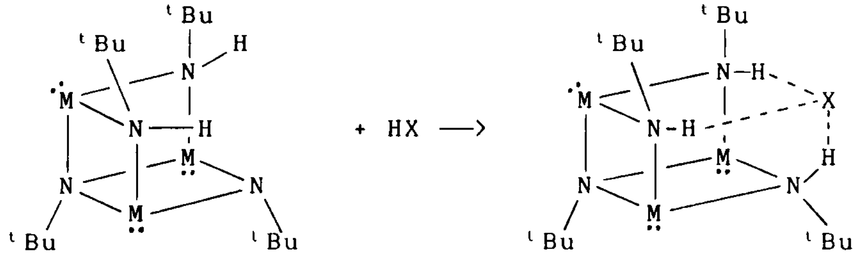
$$9\ \underset{\mathbf{64}}{\mathrm{Sn_3Pb(N^tBu)_4}} \xrightarrow{\Delta T} 6\ \underset{\mathbf{65}}{\mathrm{Sn_4(N^tBu)_4}} + \underset{\mathbf{66}}{\mathrm{Sn_2Pb_2(N^tBu)_4}} + \underset{\mathbf{67}}{\mathrm{SnPb_3(N^tBu)_4}} + \underset{\mathbf{68}}{\mathrm{Pb_4(N^tBu)_4}} \qquad (17)$$

$$4\ \underset{\mathbf{58}}{\mathrm{Sn_3(N^tBu)_4H_2}} \xrightarrow{+\ 3\mathrm{H_2O}} 3\ \underset{\mathbf{69}}{\mathrm{Sn_4O(N^tBu)_3}} + 7\ \mathrm{{}^tBuNH_2} \qquad (18)$$

In reaction (15) the hydrogen atoms of the seco-norcubane-like molecule **58** are displaced by a divalent germanium atom; the mixed-metal cage **60** ressembles a distorted cube. The displacement of indium in the seco-norcubane-like polycycle **62** by antimony is accompanied by an abstraction of a chloride ion to form $\mathrm{InCl_4^-}$ (equation (16)); **63** is a salt. The equation (17) is an example for scrambling reactions, which may occur easily if the metal atoms within the cage are heavy. The 1:3 ratio of lead to tin in **64** is redistributed in the products **65** - **68**. Not only metals but also non-metals may be substituted as shown in equation (18). The diagram demonstrates that a redistribution of the components of the cages is taking place at the same time.

Trapping of Polar Hydrogen Compounds by the seco-Norcubane-like $Sn_3(N^tBu)_4H_2$ or $Ge_3(N^tBu)_4H_2$

The seco-norcubane-like compound 58 and its homologue $Ge_3(N^tBu)_4H_2$ (70) have three different nitrogen atoms within their cages: one of the nitrogen atoms is coordinating 3 metal atoms in addition to its tert-butyl ligands, two others coordinate two metal atoms and one hydrogen atom. The fourth nitrogen atom is only bonded to two metals. This last atom is unique in having the coordination number three and may accept a further proton. This property can be used synthetically by reaction of 58 or 70 with proton donors like the hydrogenhalides or tetrafluoroboric acid (equation (19))[23].



(19)

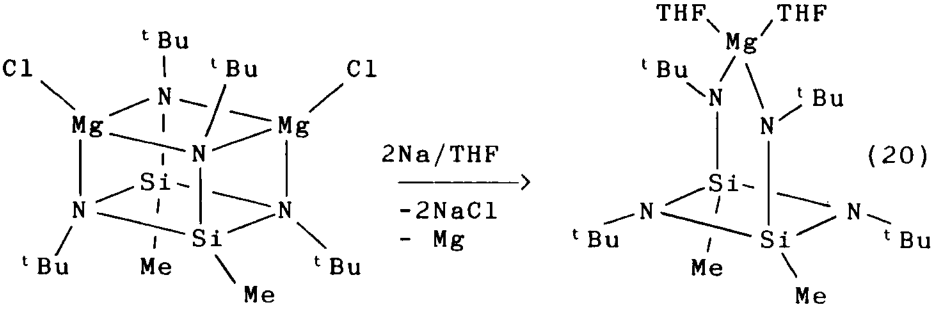
M = Sn (58), Ge (70)

M = Sn, X = Cl, Br, I, BF_4 (71 - 74)
M = Ge, X = Cl (75)

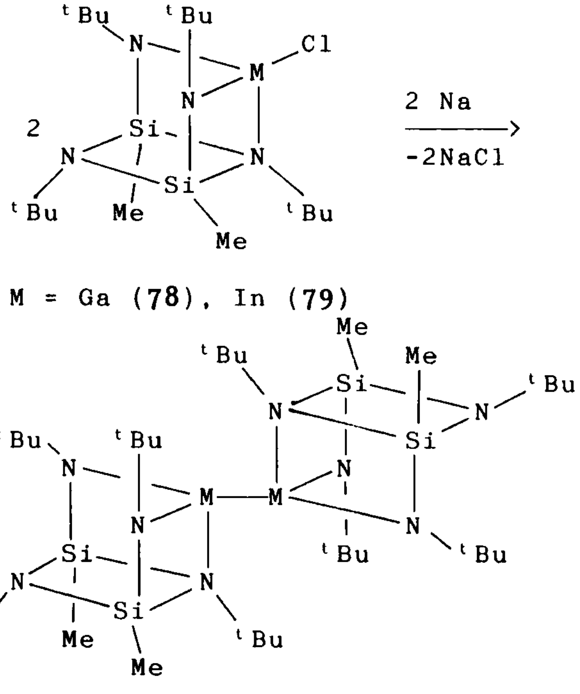
The products 71 - 76 of reaction (19) are easily obtained; they are remarkable, in that in these compounds the halide resp. BF_4 is coordinated to three hydrogen atoms. This has been established by X-ray structure determinations of 71, 74, and 75. These species are representatives of unique molecular complexes of the hydrogenhalides.

Redoxreactions of Metallacages

Metallapolycycles and cages, which have a halogen atom as further ligand at the metal centers, may be reduced in order to obtain metal-metal bonds. The reactions can proceed intra- or intermolecularly. In equations (20) and (21) two examples of redoxreactions are depicted.



76 **77** (20)



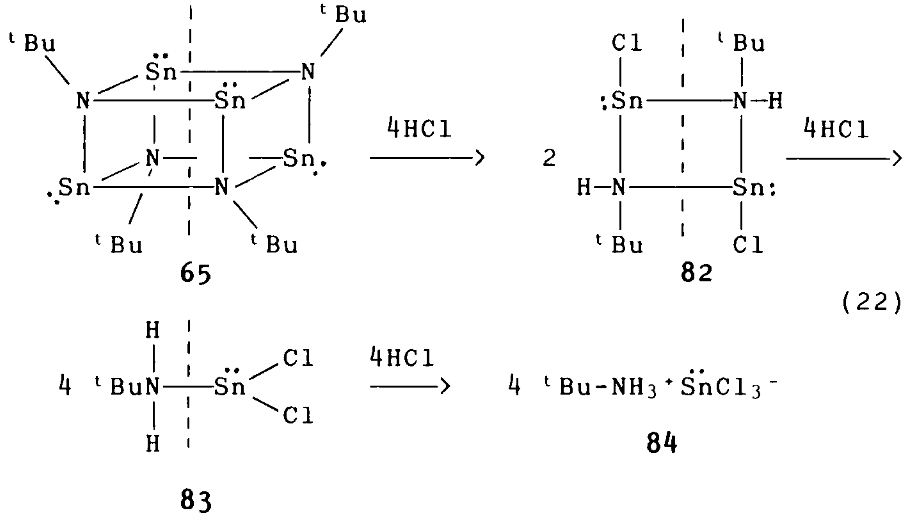
M = Ga (**78**), In (**79**) (21)

M = Ga (**80**), In (**81**)

Whereas the reduction of **76** leads to elemental magnesium and to a polycycle, **77**, containing only one metal atom, the reactions of **78** or **79** with sodium proceed in the desired direction. The compounds **80** and **81** contain Ga-Ga or In-In bonds (the metals having the formal oxidation state +II), which otherwise are known only to exist with donor-molecules coordinated to the metallic centers[24]. The inclusion of the Ga and In atoms in the cages seems to be very favorable in stabilizing these metal-metal bonds.

Controlled Decomposition of Metallacages

As we have stated several times, the cubane-like cages $({}^tBuNM)_4$ (M = Ge, Sn, Pb), may be formally described as tetramers of the corresponding iminogermylene, -stannylene, or -plumbylene[25]. It is conceivable that these compounds may add polar molecules like hydrogenhalides in a way similar to iminoboranes[26]. We have tested this hypothesis by treating $({}^tBuNSn)_4$ (**65**) with hydrogenchloride in a noncoordinating solvent like benzene or toluene[14].



(22)

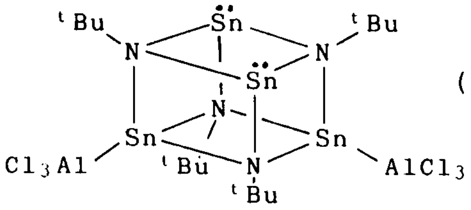
The results of this experiment, which are shown in equation (22), clearly demonstrate, that the analogy to the addition of HCl to unsaturated bonds does exist. It is obvious, however, that in our examples single bonds are cleaved by HCl (dotted lines). We have been able to separate the products of reaction (22). Compounds **82**, **83**, and **84** have also been prepared by alternative routes and have been completely characterized[14].

Metal-Metal Interactions: Low Valent Elements Embedded in Cages, Serving as Lewis Bases.

If low valent elements are incorporated in the cages described above, they are asymmetrically coordinated (normally c.n. = 3 with acute angles) and should react by means of their non-bonding electron pairs as Lewis-bases towards suitable Lewis-acids. We have been able to demonstrate by only one example, that main group Lewis-acids like $AlCl_3$ may form adducts with these elements (equation (23))[27].

$(^{t}Bu)NSn)_4$ + Al_2Cl_6 $\longrightarrow$

65



(23)

85

In compound **85** two Al-Sn-bonds are formed by mere interaction of the tin(II)atoms with the Lewis-acid $AlCl_3$.

A much more facile route to metal-metal bonds is the reaction between cage-bound low-valent elements and d-block metals - the latter serving as electron acceptors. A huge variety of such "metal adducts" have been prepared in our laboratories. The general reactions are outlined in equations (24) - (28)[8,28-30].

$$\underset{\mathbf{65}}{\mathrm{Sn_4(N^tBu)_4}} + 2\mathrm{M'(CO)_{x+1}} \xrightarrow[-2\mathrm{CO}]{} \mathrm{(CO)_xM'\text{-}Sn[Sn_2(N^tBu)_4]Sn\text{-}M'(CO)_x} \tag{24}$$

M' = Cr (**86**), Mo (**87**), Fe (**88**)

$$\begin{gathered}\mathrm{M(O^tBu)_3M'} + \mathrm{M''(CO)_{x+1}} \xrightarrow[-\mathrm{CO}]{} \underset{\mathbf{89}}{\mathrm{M(O^tBu)_3M'\text{-}M''(CO)_x}}\\ + \mathrm{M'''(CO)_{y+1}} \xrightarrow[-\mathrm{CO}]{} \underset{\mathbf{90}}{\mathrm{(CO)_yM'''\text{-}M(O^tBu)_3M'\text{-}M''(CO)_x}}\end{gathered} \tag{25}$$

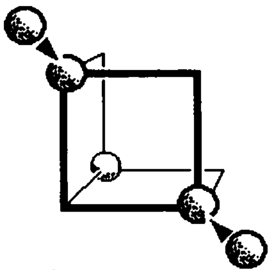
M = Sn, Ge, M' = In,
M",M'" = transition metals

$$\begin{gathered}2\ \mathrm{M(O^tBu)_3In} + \mathrm{M'(CO)_4nbd} \xrightarrow[-\mathrm{nbd}]{}\\ \underset{\mathbf{91}}{\mathrm{M(O^tBu)_3In\text{-}M'(CO)_4\text{-}In(O^tBu)_3M}}\\ + 2\ \mathrm{M''(CO)_{x+1}} \xrightarrow[-2\mathrm{CO}]{}\\ \underset{\mathbf{92}}{\mathrm{(CO)_xM''\text{-}M(O^tBu)_3In\text{-}M'(CO)_4\text{-}In(O^tBu)_3M\text{-}M''(CO)_x}}\end{gathered} \tag{26}$$

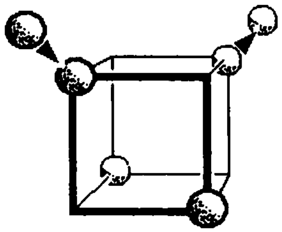
M = Ge, Sn, M' and M" = transition metals

$$\begin{gathered}\mathrm{M(O^tBu)_3M'(O^tBu)_3M} + \mathrm{M''(CO)_{x+1}} \xrightarrow[-\mathrm{CO}]{}\\ \underset{\mathbf{93}}{\mathrm{M(O^tBu)_3M'(O^tBu)_3M\text{-}M''(CO)_x}}\\ + \mathrm{M''(CO)_{x+1}} \xrightarrow[-\mathrm{CO}]{} \underset{\mathbf{94}}{\mathrm{(CO)_xM''\text{-}M(O^tBu)_3M'(O^tBu)_3M\text{-}M''(CO)_x}}\end{gathered} \tag{27}$$

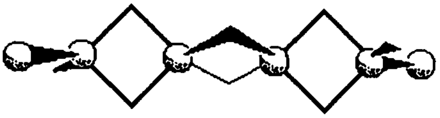
M = Ge, Sn; M' = Ca, Ba, Sr, Eu(II); M"=transition M



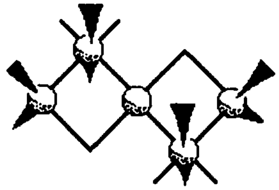
$(^{t}BuN)_4H_2Sn_3\cdot$
$\cdot 2Fe(CO)_4$



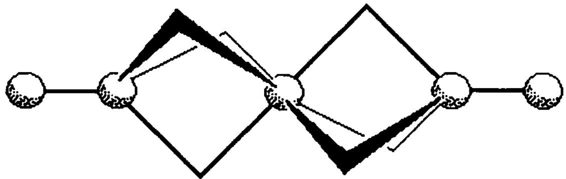
$(^{t}BuN)_4Sn_4\cdot 2AlCl_3$
$(^{t}BuN)_4Sn_4\cdot 2M(CO)_n$
$M(CO)_n = Cr(CO)_5$, $Fe(CO)_4$,
$Mo(CO)_5$, $W(CO)_5$



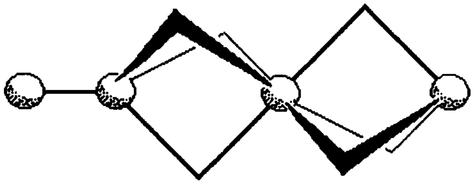
$[(CO)_xM]_2Sn\,M'_2(O^{t}Bu)_8$
$(CO)_xM = Cr(CO)_5$, $Fe(CO)_4$
$M' =$ Co, Ni



$(^{t}BuO)_6Ge_2Pb[Fe(CO)_4]_2$

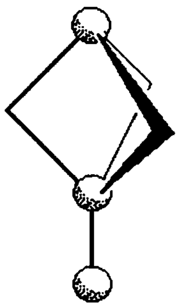


$(^{t}BuO)_6Sn_2M\cdot 2M'(CO)_x$
$M =$ Sr, Ba
$M'(CO)_x = Cr(CO)_5$, $Mo(CO)_5$ $Fe(CO)_4$

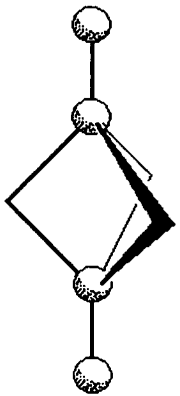


$(^{t}BuO)_6Sn_2M\cdot Cr(CO)_5$
$M =$ Sr, Ba

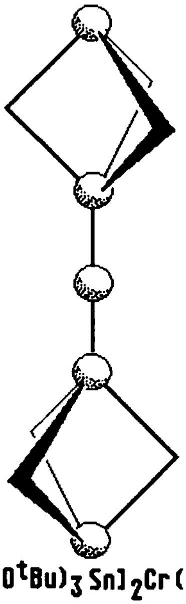
FIGURE 5 Sketchy Structures of Metal-Metal Bonded Metallacages



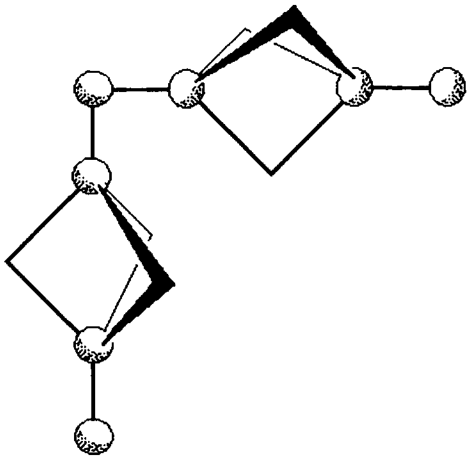
$M(O^tBu)_3M'-M''(CO)_x$
M = Tl, M' = Sn
$M''(CO)_x = Cr(CO)_5, Fe(CO)_4$



$(CO)_xM - M'(O^tBu)_3M'' - M'''(CO)_y$
M' = Sn, Ge
M'' = In
$M(CO)_x = Cr(CO)_5, Mo(CO)_5$
$M'''(CO)_y = Fe(CO)_4, Cr(CO)_5$

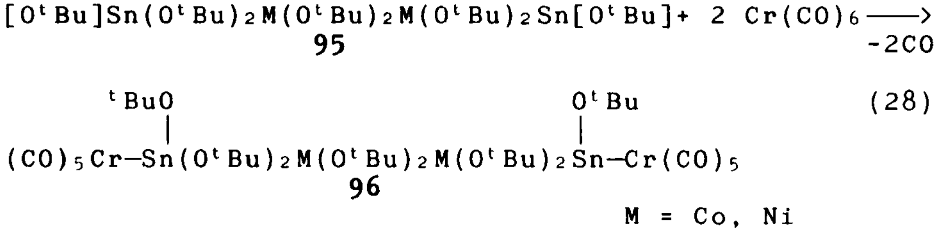


$[Tl(O^tBu)_3Sn]_2Cr(CO)_4$



$[Cr(CO)_5]_2[Sn(O^tBu)_3In]_2Cr(CO)_4$

FIGURE 6 Simplyfied Representations of Metal Connected "Janus-Type" Cages



$$[O^tBu]Sn(O^tBu)_2M(O^tBu)_2M(O^tBu)_2Sn[O^tBu] + 2\ Cr(CO)_6 \xrightarrow[-2CO]{}$$

95

$$(CO)_5Cr{-}\overset{{}^tBuO}{\overset{|}{Sn}}(O^tBu)_2M(O^tBu)_2M(O^tBu)_2\overset{O^tBu}{\overset{|}{Sn}}{-}Cr(CO)_5 \qquad (28)$$

96

M = Co, Ni

The products of reactions **86** - **94** and **96** contain metal atoms which are either held together by ^{t}Bu-N- or ^{t}BuO-groups or bonded directly through σ-bonds. In compounds of type **89** three metals, in those of type **90**, **91**, and **93** four metals and in species of type **92** and **94** five metals are arranged linearly. Even more metallic atoms are linked in compounds **96** (six) and **92** (seven), but for steric and electronic reasons these are not linearily arranged. Figures 5 and 6 contain structural sketches of these molecules.

ACKNOWLEDGEMENTS

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