Chapter 8

New Heterometallic Silylamides with Polycyclic and Cage-Like Structures

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Abstract

The octamethyltrisilazane, $Me_2Si[N(H)SiMe_3]_2$, can be used to ligate several metallic elements by substitution of the hydrogen atoms at nitrogen. In general it has been found that, in the absence of basic solvents, two octamethyltrisilazyl ligands act as a "chelating entity", coordinating a variety of metal centers. The formal charge in these centers is $4+$. Simple displacement reactions allow the synthesis of a great variety of heterometallic silyl amides, a class of compounds until now only poorly described in the literature.

The compounds can be classified by three general formulae: $[Me_2Si(NSiMe_3)_2]_2$-$M^{III}M^I$ (M^I = Li, M^{III} = Al, Fe, In; M^I = Na, K, In, Tl, M^{III} = In), $[Me_2Si(NSiMe_3)_2]_2M^{II}M^I_2$ (M^{II} = Pb, M^I = Li) and $[Me_2Si(NSiMe_3)_2]_2M^I_2M^{I'}_2$ (M^I = Li, $M^{I'}$ = Tl). So far we have been able to synthesize only one compound with more than two octamethyltrisilazyl (omts) ligands: $[Me_2Si(NSiMe_3)_2]_3Cd_2Li_2$. The new compounds have been characterized by spectroscopic methods (^{1}H-NMR, MS) and their solid state structures have been elucidated by single crystal X-ray diffraction analyses. The metallic elements tend to optimize their coordination numbers by Lewis acid-base interactions with ligand nitrogen atoms, resulting in the formation of bicyclic, tricyclic, tetracyclic and cage structures. The greater the number of metallic centers present, the more the nitrogens are involved in coordination.

1. INTRODUCTION

We have previously reported that the hydrogen atoms in bis(amino)silanes such as $Me_2Si[NtBu(H)]_2$ can be replaced by metallic centers, e. g. Ge(II), Sn(II) or Pb(II) [1-3], or by cationic fragments like $P(III)^+$, $As(III)^+$, $Sb(III)^+$ [4] to give 4-membered metallacycles. Such species have been shown to be monomeric in non-coordinating solvents. If more electropositive metallic elements or metal fragments such as Mg, Al-Me or Ga-Me are used [5, 6], the molecules occur as dimers. Dimerization of the diazasilastannetidines is also observed if the bulky t-

butyl group on the nitrogen atom is replaced by the less sterically demanding isopropyl group [7]. The dimerization may be described as a double Lewis acid-base interaction between the metallic elements and a nitrogen center of the second heterocycle and *vice versa*. This results in a structure containing three fused 4-membered rings, each sharing at least one common edge with the other cyclic unit.
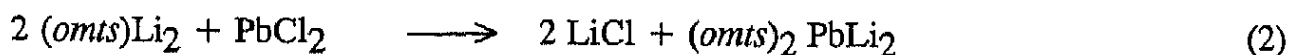
Such dimeric molecules may be regarded as homometallic amides containing two metallic elements at a short distance to one another. We were interested to know whether *different* metals could be incorporated into such amides, as heterometallic silylamides are very rare and poorly characterized, the only well documented example that we are aware of being $[(Me_3Si)_2N]_3NaM$ (M = Eu, Yb) [8]. Therefore, to our knowledge, a detailed and systematic investigation on the synthesis and properties of heterometallic amides has not yet been reported. Considering the potential value of these species as ceramic precursors and the fundamental interest in their preparation and properties, such a study is long overdue.
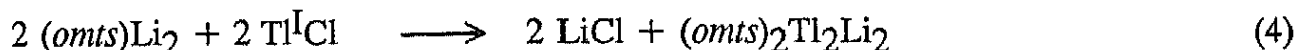
Our initial investigation into the synthesis of heterometallic amides centered on the bis(amino)silane $Me_2Si[NtBu(H)]_2$. However, it proved possible to bind two different metal centers only in a few instances, and these were restricted to metal fragments, rather than naked metal centers, e. g. $Me_2Al-N(tBu)-Si(Me)_2-(NtBu)-MgMe$, $Me_2Al-N(tBu)-Si(Me)_2-N(tBu)-M$ (M = Li, Na) [9]. Several other slightly modified silylamines were examined without significant success before we discovered the apparently unique chelating abilities of octamethyltrisilazane.

In this paper we describe the syntheses and structures of the new heterometallic amides derived from the dilithium salt of octamethyltrisilazane. The ligand had previously been prepared by U. Wannagat and coworkers [10]. The dilithium salt of the corresponding $Me_2Si[NtBu(H)]_2$ is, according to H. Bürger and co-workers, dimeric with a central Li_4N_4-cage [11], while the disodium salt of octamethyltrisilazane is trimeric [12]. Therefore, it can be assumed that $Me_2Si-(NSiMe_3)_2Li_2$ is at least dimeric.

2. SYNTHESES OF HETEROMETALLIC OCTAMETHYL-TRISILAZYLS

The dilithium salt of octamethyltrisilazane, $[Me_2Si(NSiMe_3)_2Li_2]_x$ (the formal dianion of octamethyltrisilazane being abbreviated "*omts*" hereafter), serves as an excellent starting material for the synthesis of heterometallic silylamides. It reacts with a number of metal halides (eqs. (1)-(4)) under partial loss of lithium in the form of LiCl and the incorporation of the metallic element in the amide.

$$2 \ (omts)Li_2 + M^{III}Cl_3 \longrightarrow 3 \ LiCl + (omts)_2M^{III}Li \tag{1}$$
$$M^{III} = Al, In, Fe$$

$$2 \ (omts)Li_2 + PbCl_2 \longrightarrow 2 \ LiCl + (omts)_2 \ PbLi_2 \tag{2}$$

$$3 \ (omts)\text{Li}_2 + 2 \ \text{CdCl}_2 \longrightarrow 4 \ \text{LiCl} + (omts)_3\text{Cd}_2\text{Li}_2 \tag{3}$$

$$2 \ (omts)\text{Li}_2 + 2 \ \text{Tl}^{\text{I}}\text{Cl} \longrightarrow 2 \ \text{LiCl} + (omts)_2\text{Tl}_2\text{Li}_2 \tag{4}$$

All reactions require the strict exclusion of water and oxygen.

Some of the newly synthesized molecules can be used for similar metal exchange reactions as may be seen from equations (5) and (6).

$$(omts)_2\text{InLi} + \text{M}^{\text{I}}\text{X} \longrightarrow \text{LiX} + (omts)_2\text{InM}^{\text{I}} \tag{5}$$
$$\text{M}^{\text{I}} = \text{In} \ (\text{X} = \text{Br}), \ \text{Tl} \ (\text{X} = \text{Cl})$$

$$(omts)_2\text{InTl} + \text{M}^{\text{I}}\text{I} \longrightarrow \text{TlI} + (omts)_2\text{InM}^{\text{I}} \tag{6}$$
$$\text{M}^{\text{I}} = \text{Na}, \ \text{K}$$
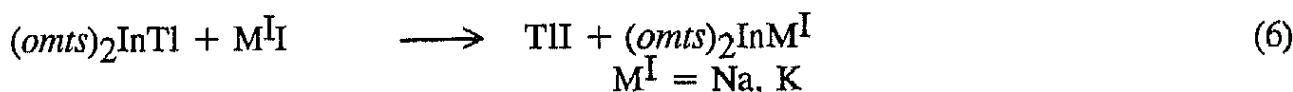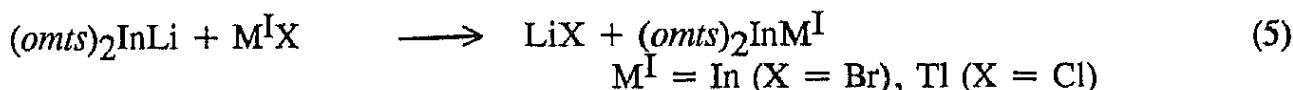
All new compounds give correct elemental analyses and have been characterized by ^{1}H-NMR and mass spectroscopy. Most of these compounds can be isolated in crystalline form and crystal structure determinations have been performed. Details are given in Table 1 and the structures are discussed in the next section.

A comparison of the structures in the solid and in solution (^{1}H-NMR) reveals fluxional solution behavior. Taking $(omts)_2\text{InLi}$ as an example: its ^{1}H-NMR spectrum at ambient temperature consists of only two resonance lines (one for the Me_3Si group and one for the Me_2Si group). Based on its structure in the solid state four NMR lines are expected (two for each group). Apparently the bonds in the molecule are involved in an exchange process which is fast on the NMR time-scale.

The compounds are highly soluble in organic solvents such as benzene, toluene or xylene with the exception of $(omts)_2\text{InK}$ which is only slightly soluble in benzene. This is not unexpected, as $(omts)_2\text{InK}$, unlike the other compounds, is strictly ionic in the solid state. The compounds are all volatile under reduced pressure and molecular ions for all species are obtained in their respective mass spectra. Characteristically all spectra contain also masses higher than the molecular ion peak due to the addition of M^+ (mostly of the monovalent metal) to the molecule.

As can be seen from the formulae of the products there are always two $omts$ units associated with the metals, the only exception being $(omts)_3\text{Cd}_2\text{Li}_2$ which has three $omts$ ligands attached to the four metals. This ligand to metal ratio is independent of the molar ratios which are used during the synthesis (see equ. (3)).

3. MOLECULAR STRUCTURES OF HETEROMETALLIC OCTAMETHYLTRISILAZYLS IN THE SOLID

This section outlines the different structures of the heterometallic amides and is followed in the next section by a more general structural classification. X-ray structure analyses on single crystals have been performed on $(omts)_2$InLi, $(omts)_2$FeLi, $(omts)_2$InK, $(omts)_2$PbLi$_2$, $(omts)_3$Cd$_2$Li$_2$ and $(omts)_2$Tl$_2$Li$_2$ (see also Table 1).

Table 1
Crystal Data and R-values of Heterometallic Octamethyltrisilazyls

Compound	Crystal system Space group	Crystal data (a, b, c [Å])	R-value
$(omts)_2$InLi	monoclinic C2/c	11.814(9),16.986(18),16.719(18) ß = 104.63(9)°; Z = 4	0.033
$(omts)_2$FeLi	monoclinic C2/c	20.091(13),10.163(6),19.427(13) ß = 122.59(5)°; Z = 4	0.045
$(omts)_2$InK	orthorhombic P2$_1$2$_1$2$_1$	10.688(6),17.525(9),18.125(9) Z = 4	0.044
$(omts)_2$PbLi$_2$	monoclinic P2$_1$/n	9.424(9),19.801(20),17.783(17) ß = 93.59(9)°; Z = 4	0.049
$(omts)_3$Cd$_2$Li$_2$	triclinic P$\bar{1}$	11.526(2),11.925(2),19.061(3) α = 86.88(1)°, ß = 82.02(1)°, γ = 74.93(1)°; Z = 2	0.037
$(omts)_2$Tl$_2$Li$_2$	triclinic P$\bar{1}$	11.575(9),12.329(9),14.273(9) α = 90.94(8)°, ß = 107.74(8)°, γ = 113.95(8)°; Z = 2	0.069

As can be seen from Figures 1 and 2, the two compounds $(omts)_2$InLi and $(omts)_2$FeLi are remarkably similar, their structures both displaying three 4-membered cycles with two common edges and one common corner.

The trivalent metal, In or Fe, respectively is coordinated by four nitrogen atoms while the lithium atoms achieve only 2-fold nitrogen coordination. While N1 in the two compounds is bonded quasi tetrahedrally to four atoms, N2 is bonded only to three in an essentially trigonal planar bonding arrangement. A crystallographic 2-fold axis passes through the two metallic elements in each compound (point symmetry of the molecules: C_2(2)).
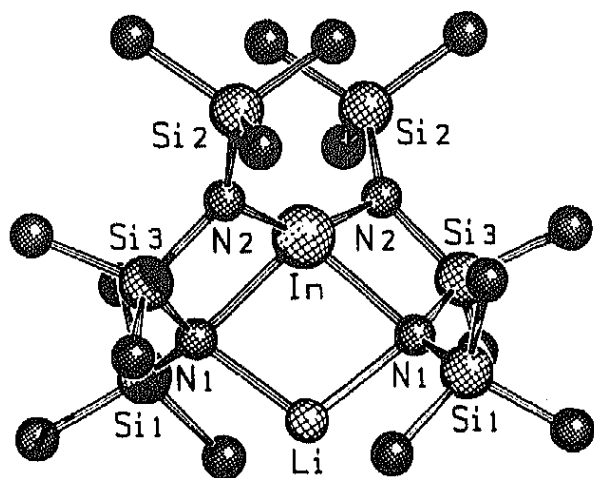
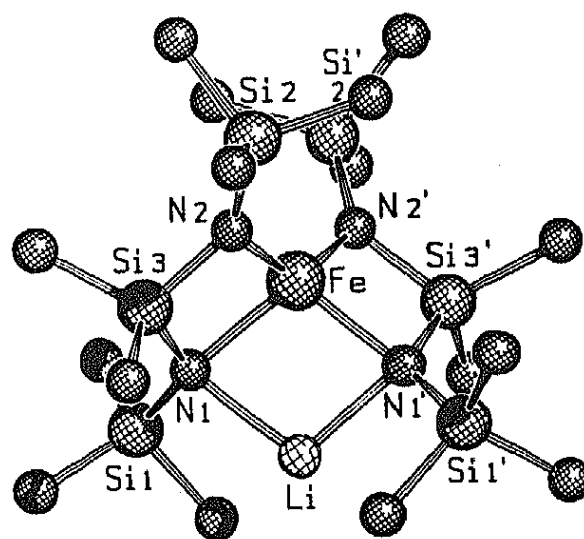Figure 1. The Molecular Structure of (*omts*)$_2$InLi

Figure 2. The Molecular Structure of (*omts*)$_2$FeLi

The metal-nitrogen distances can be split into 2 groups, depending on the coordination number of the nitrogen: small ones, viz. M-N2 (In-N2 = 2.055(3), Fe-N2 = 1.913(3) Å) and larger ones, viz. M-N1 (In-N1 = 2.223(3), Fe-N1 = 2.017(3) Å). This correlates well with the coordination numbers of the nitrogens; nitrogen atoms with higher coordination numbers display the longer bond distances. The Li-N1 bond lengths in both compounds are comparable (2.064(6) Å in (*omts*)$_2$InLi vs. 2.032(9) Å in (*omts*)$_2$FeLi).However, the M^{III}--Li distance is significantly longer in the indium derivative (In--Li = 2.748(9) Å) than in the iron compound (Fe--Li = 2.57(1) Å). This observation nicely reflects the difference in the cationic radii of In^{3+} (0.81 Å) and Fe^{3+} (0.64 Å) [13].

The two metallic elements, Li and In or Li and Fe respectively, are close to one another but this is better explained by the electronegative N1 nitrogen atoms acting as connecting links between the two electropositive elements, rather than by a direct bond. Furthermore, the formal charge of Fe and In is reduced by bonding to N2 while the lithium atoms coordinate through secondary bonds to methyl groups of the trimethylsilyl moiety (interactions which are not explicitly drawn in Figures 1 and 2).

The Li--C distances are on the order of 2.64 Å in (*omts*)$_2$InLi and 2.37 Å in (*omts*)$_2$FeLi. Such bonding to methyl groups is known from LiBMe$_4$ [14], LiAlEt$_4$ [15] and (MeLi)$_4$ [16], in which the Li--C distances are between 2.21-2.36 Å. As can be seen from our heterometallic silazyls, the closer the metal(III) atoms approach the Li atoms, the shorter are the Li--C distances. The coordination number at lithium may be described as 2+2 or, if the hydrogen atoms of the methyl groups are considered, as 2+4. Figure 3 shows the coordination sphere of lithium in (*omts*)$_2$InLi with the hydrogen atoms involved in the bonding (Li--H =
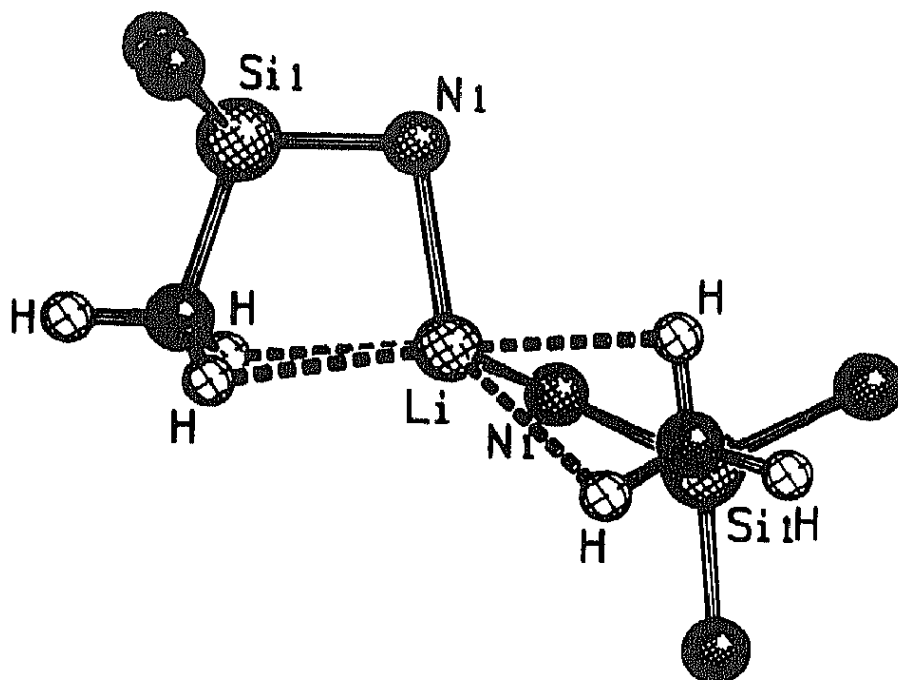
2.39-2.48 Å).

Figure 3. The coordination sphere of Li in (omts)₂InLi.
The secondary bonds to the hydrogen atoms are drawn as
dotted lines (see also text).

The three four membered cycles in (*omts*)₂InLi and (*omts*)₂FeLi are almost planar, the interplanar angles in the two compounds approaching 120°.

While (*omts*)₂InNa crystallizes isotypically to (*omts*)₂InLi (crystal data of (*omts*)₂InNa: monoclinic, space group C2/c, a = 11.83(2), b = 16.56(3), c = 17.25(3) Å, ß = 104.2(3)°; compare Table 1), the potassium compound (*omts*)₂InK is completely different in its solution behavior (see before) and its crystal data (see Table 1). This is also reflected in its solid state structure (Figure 4) which differs significantly from the sodium and lithium analogues.

The crystal structure of (*omts*)₂InK consists of [(*omts*)₂In]⁻ anions, in which two *omts* units are spirocyclicly bonded by the central indium, and of potassium cations which are situated in interstices of the lattice. As the [(*omts*)₂In]⁻ anions have a nearly closed methyl surface the potassium atoms are coordinated mostly by the hydrogen atoms of the methyl groups (Fig. 4 shows only the carbon atoms of the methyl substituents) and by the two nitrogen atoms N1 and N3. The distances from these atoms to K are relatively long (K--N1 3.26(1), K--N3 3.18(1), K--C 3.21-3.47 Å) compared to (Me₃Si)₂NK · 2 C₄H₈O₂ (K-N 2.70 Å) [17], [(Me₂SiN)₄H₂K₂(thf)₄]₂ (K-N: 2.75-3.11 Å) [18], [Me₂Si(OtBu)(NSiMe₃)K]₂ (K-N: 2.76-2.87, K--C: 3.38-3.42 Å) [19] or KCH₃ (K--C 3.20 Å) [20].
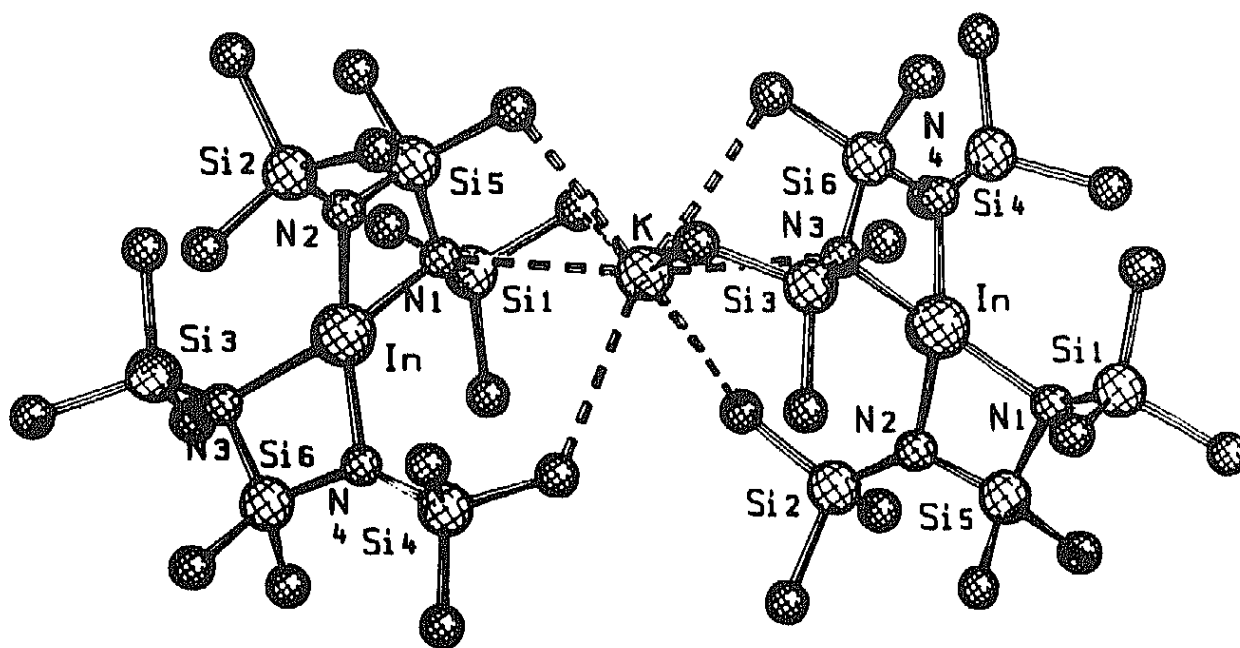
Figure 4. A section of the crystal structure of $(omts)_2InK$. The crystal consists of isolated $[(omts)_2In]^-$-anions which are interlinked by methyl and nitrogen bridges to the K^+ cations.

In a very simple description, the potassium atom can be considered as an 8-fold coordinated potassium cation with loose contacts to its neighbours. The anion $[(omts)_2In]^-$ is isoelectronic and isostructural to $[Me_2Si(NtBu)_2]_2Sn$ [2], at least as far as the heavy atom skeleton is concerned. The indium has an approximate $\overline{4}2m(D_{2d})$ point symmetry, the N2-, N4-In bonds displaying distances of 2.11(1) Å and the N1-, N3-In distances 2.17-2.18 Å. These bond lengths are typical for In^{III}-N bonds ($[Me_2Si(NtBu)_2InMe]_2$: In-λ^3N 2.11 Å, In-λ^4N 2.27 Å [6], $[^iPr(Cl)InNHtBu]_2$: In-λ^4N 2.18-2.19 Å [21], $[Me_2InNR_2]_2$: In-λ^4N 2.23-2.28 Å [22]). The longer In-N1, -N3 bonds reflect the secondary bonds to potassium (see before); in the same way N2 and N4 are essentially trigonal planar while the sum of the angles on N1 and N3 are found to be 349.9° and 349.1°, respectively.

Three, instead of two, metallic elements are combined in $(omts)_2PbLi_2$, the trivalent metal Fe or In in $(omts)_2MLi$ being formally replaced by Li and Pb, a mono- and divalent element, respectively. As can be seen in Figure 5, the skeletal atoms form a polycyclic, cage-like structure in the crystal.

Whereas all nitrogen atoms attain a 4-fold coordination sphere, the metal atoms are 3-fold (Pb, Li1) or 2-fold coordinated (as in the other lithium compounds discussed so far, methyl groups are in the vicinity of lithium atoms completing the coordination number of Li1 to four (Li--C 2.87 Å) and that of Li2 to six (Li--C: 2.72-3.11 Å)).
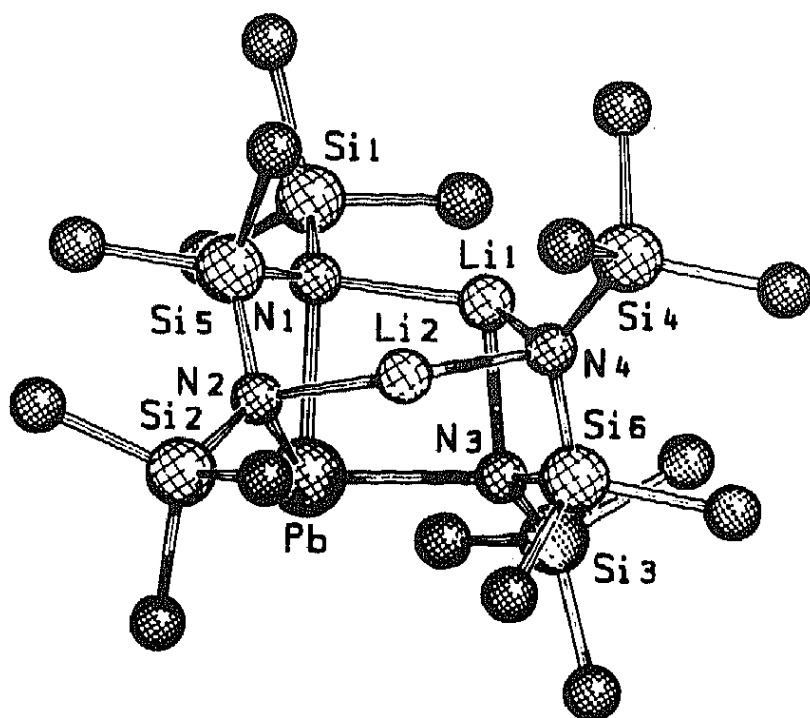
Figure 5. The molecular structure of $(omts)_2PbLi_2$.

It is interesting to note, that the lead atom is in a trigonal pyramidal position with Pb-N distances from 2.31(1) to 2.36(1) Å, which are somewhat longer than in $Pb[N(SiMe_3)_2]_2$ with a λ^2-Pb (Pb-N: 2.20 Å [23]). As stated before, the lithium atoms have different coordination numbers, Li1 bonded to three nitrogen atoms and hence displaying longer distances (Li1-N1 2.06 Å, Li1-N3 2.13 Å, Li1-N4 2.02 Å) than the two-coordinate Li2 (Li2-N2 2.02 Å, Li2-N4 1.95 Å).

The observed Li-N values nicely fit into a series of compounds with λ^2Li-N $((PhCH_2)_2NLi)_3$ [24], $[LiN(SiMe_3)_2]_2$ [25], $[LiN(SiMe_3)_2]_3$ [26]) or λ^3Li-N $([(Ph-CH_2)_2NLi-hmpa]_2$ [24], $[Me_2Si(OtBu)NtBuLi]_2-thf$ [27], $[LiN(SiMe_3)_2-Et_2O]_2$ [28]).

The polycyclic structure of $(omts)_2PbLi_2$ can be described as a central cage, which is formed from three edge-sharing four membered cycles connected at two corners by a bridging lithium atom. Looking at Figure 5, one may place a formal 2-fold axis through the "bridging" lithium atom Li2 (perpendicular to the drawing plane) which transforms half of the molecule into its symmetry related equivalent except for the atoms Li1 and Pb1. This quasi 2-fold axis seems to be responsible for disorder problems concerning the positions of Pb1 and Li1. The inner $PbLi_2N_4Si_2$ cage is almost tetrahedrally surrounded by the four trimethyl-silyl groups.

If Pb(II) is formally replaced by the divalent cadmium, the analogous compound $(omts)_2CdLi_2$ is not obtained. Instead three $omts$ units combine with two cadmium and two lithium atoms to form $(omts)_3Cd_2Li_2$. In Figure 6 a graphic representation of the molecular structure of $(omts)_3Cd_2Li_2$ is depicted.
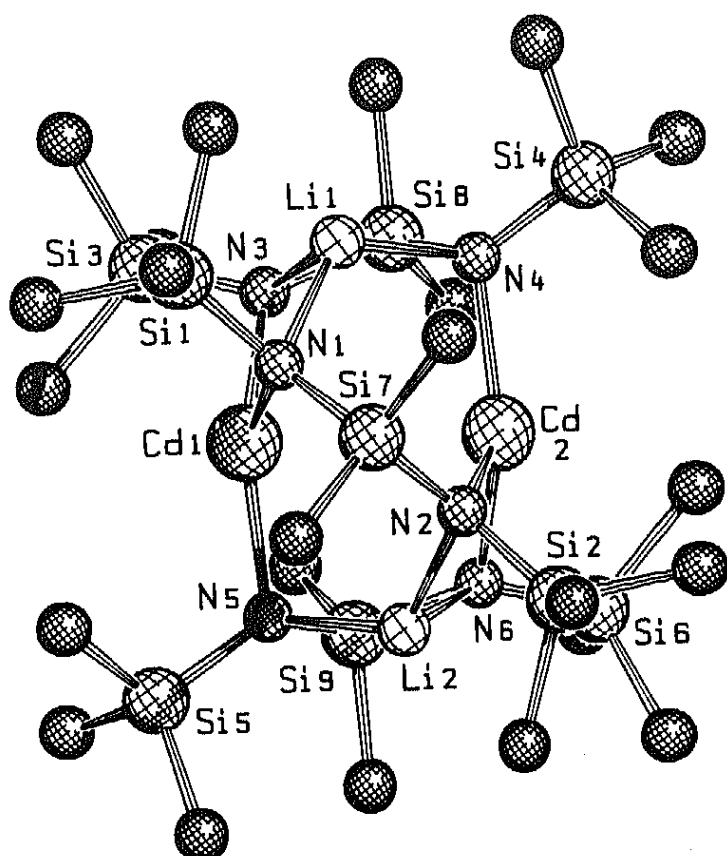

Figure 6. The molecular structure of $(omts)_3$-Cd_2Li_2. View along the quasi twofold axis (see text).

The most remarkable feature of this compound is its 13 atom cage. This is constructed from two entities, consisting of two edge sharing four membered cycles ($CdLiN_3Si$), which are connected by two N-Cd bonds and a dimethylsilyl bridge. The molecule has a pseudo 2-fold axis, which passes through the central Me_2Si group of Figure 6 and which runs perpendicular to the drawing plane. All nitrogen atoms are 4-fold coordinated while the metallic elements Li and Cd each have three nitrogen neighbours. Whereas the coordination polyhedra at the nitrogen are all distorted tetrahedra, the threefold metal coordinations are very different: Cd1 and Cd2 are almost in a planar environment (sum of the angles at Cd 353.8° and 353.6°, respectively). The lithium atoms occupy the apical positions of trigonal pyramids (sum of the angles at Li1 305°, Li2 308°).

The deviations from planarity at the cadmium atoms may have two reasons: There are two methyl groups from the trimethylsilyl substituents on N3 and N6 which are close to the metals (Cd1--C 3.09 Å, Cd2--C 3.13 Å) and the Cd1--Cd2 distance (3.099(1) Å) is extremely short. The slightly pyramidal cadmium atoms are pointing away from each other; a feature which, at first sight, might be explained in terms of a repulsion between the two metals. On the other hand the distances in metallic cadmium vary from 2.973 Å to 3.287 Å [13] and d^{10}-d^{10} interactions, which are usually weak, cannot be ruled out. While such interactions are well documented for transition elements of group 11 [29, 30], they are less discussed for group 12 transition elements [31]. In Figure 7 $(omts)_3Cd_2Li_2$ is again plotted, but this time the viewer is looking directly along the Cd--Cd axis. From this representation it becomes clear that all omts ligands are involved in bridging the two cadmium atoms, the lithium atoms functioning as interstitial links.
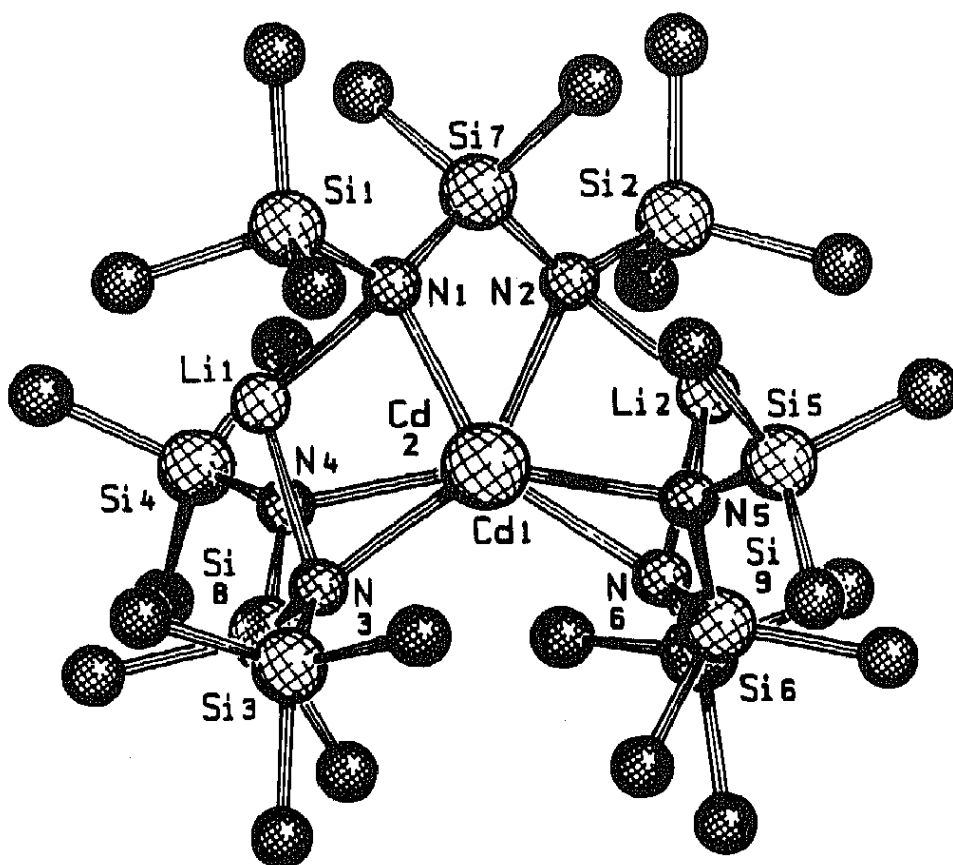

Figure 7. View down the Cd--Cd "axis" in $(omts)_3Cd_2Li_2$.

Cadmium(II) usually tends to be four coordinate and the coordination number three is quite rare for this element. Trigonal planar arrangements are found in $[Cd(P(SiMe_3)_2)_2]_2$ [32] or in $[Cd(SC_6H_2tBu_3)_2]_2$ [33] as well as in $[MeCdP(tBu)_2]_3$ [34] and in the anion $[Cd(SC_6H_2iPr_3)_3]^-$ [35]. So far, to our knowledge, no three coordinate cadmium amide has been described although two coordinate Cd has

been found in $Cd[N(SiMe_3)_2]_2$ [36].

The bond distances Cd–N in $(omts)_3Cd_2Li_2$ (Cd–N 2.154(3)-2.232(3) Å) are therefore longer than in $Cd[N(SiMe_3)_2]_2$ (Cd–N 2.03 Å) [36] but shorter than in $[Cd(N_3)_2(py)_2]$ (Cd–N 2.34-2.35 Å) [37] which has a 6-fold coordinated cadmium atom.

The lithium atoms in $(omts)_3Cd_2Li_2$ are, as stated before, situated at the apex of a trigonal pyramid which is quite acute (mean angle: 102°). As in the other structures discussed so far, a methyl group of a $SiMe_3$ ligand is pointing towards the lithium with remarkably short distances (2.43 and 2.46 Å, respectively).

The last crystal structure of an heterometallic silylamide we want to describe is that of $(omts)_2Tl_2Li_2$ which has a maximum number of metal atoms connected by omts units. From the graphic representation in Figure 8 it is obvious, that in this example metal-metal interactions (between Tl1 and Tl2) are present, as the metals are pointing at one another.
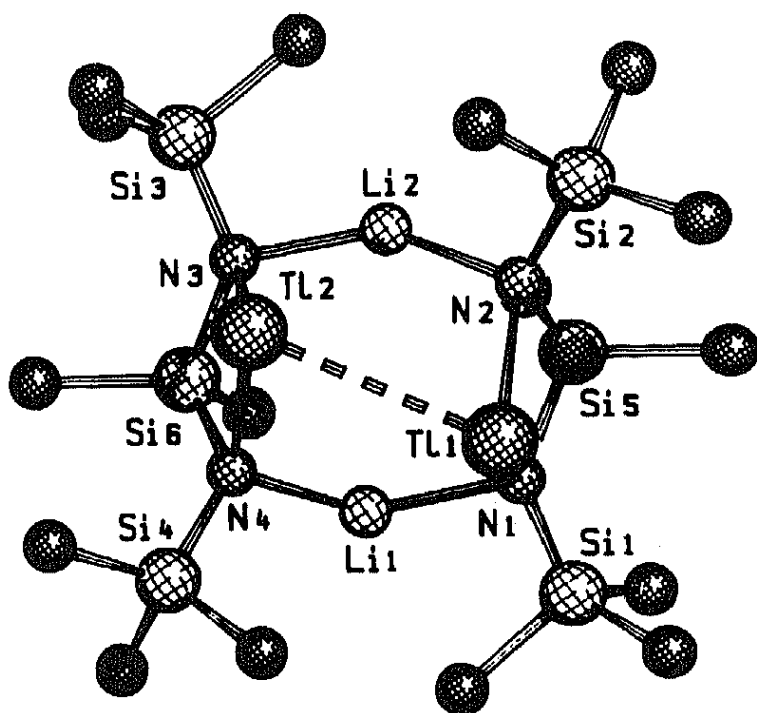

Figure 8. The molecular unit of $(omts)_2Tl_2Li_2$.

The crystal is composed of molecular units (figure 8) which are interlinked by intermolecular Tl--Tl contacts forming a one dimensional polymeric arrangement. Figure 9 shows a section of this polymer with almost all thallium atoms occupying the plane of the graphic representation.

The intramolecular Tl1-Tl2 distance (3.454(1) Å) is much shorter than the intermolecular ones (3.809(1) and 3.781(1) Å, respectively) and is similar to the distances in elemental thallium (Tl(bcc): Tl--Tl 3.36 Å; Tl(hcp): Tl--Tl 3.44 Å [38]).
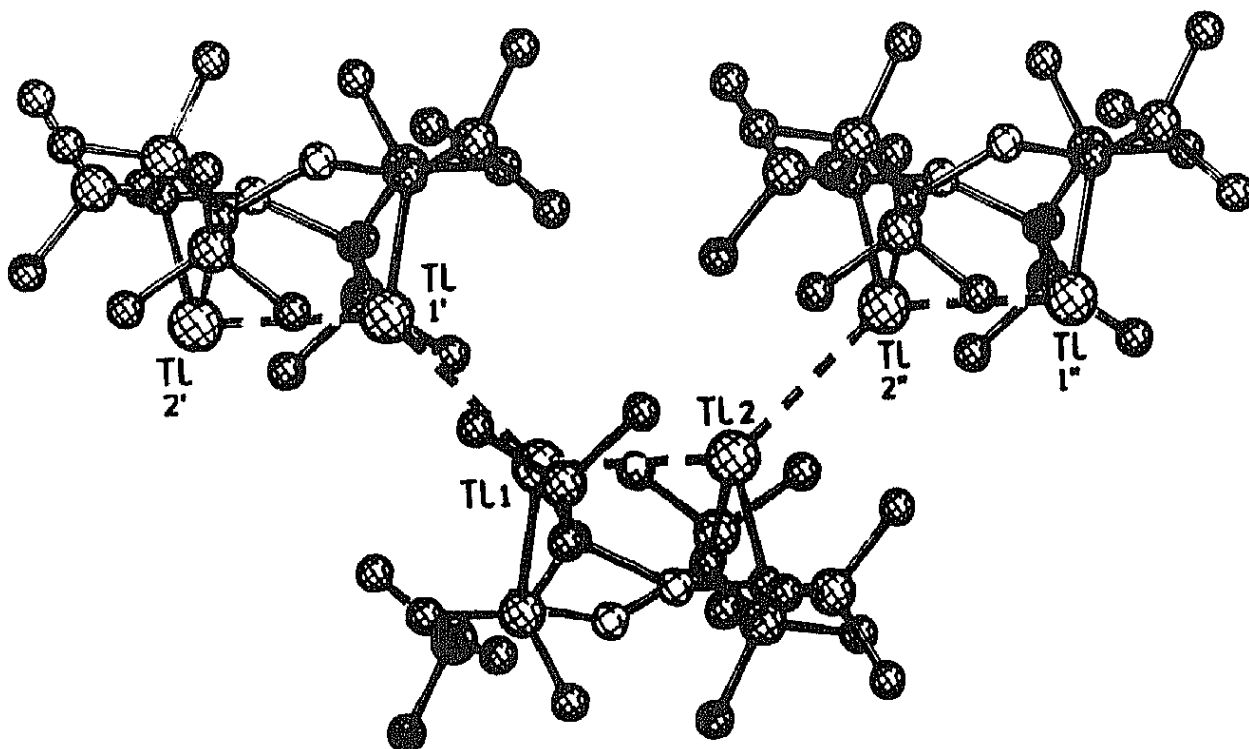
Figure 9. A section of the one dimensional arrangement of the molecular $(omts)_2Tl_2Li_2$ units in the crystal structure.

In the dimeric $[(PhCH_2)_5C_5Tl]_2$, the Tl-Tl distance is found to be 3.63 Å [39], while in $Tl_8(StBu)_8$ the intermolecular Tl--Tl distances (3.75 and 3.86 Å [40]) are in the same order as in $(omts)_2Tl_2Li_2$.

The molecular unit of $(omts)_2Tl_2Li_2$ has an approximate C_2 symmetry, the pseudo twofold axis passing perpendicular to the plane of figure 8. The cage which is formed by the metals and the *omts* ligands, can be described as being composed of two almost parallel four membered SiN_2Tl cycles which are inter-linked by two lithium atoms and the metallic Tl--Tl interaction. As in the structures discussed so far, the lithium atoms have further contacts to methyl groups but at quite long distances (2.63 and 2.73 Å). The N-Li-N angles are remarkably large (136°), whereas the mean Li-N distances (2.00 Å) correlate well with two coordinate lithium (see before). The Tl-N distances found in $(omts)_2Tl_2-Li_2$ (2.46-2.50 Å) are comparable to Tl(I)-N distances in other molecules, such as $(MeSi)_2(NtBu)_4Tl_2$ (Tl-N 2.52-2.66 Å) [41] or $HB(3-tBu-pyrazolyl)_3Tl$ (Tl-N 2.58 Å) [42].

4. GENERAL DISCUSSION OF THE STRUCTURAL DETAILS IN HETEROMETALLIC OCTAMETHYLTRISILAZYLS

Comparing the results in the previous sections it becomes clear that almost all heterometallic octamethyltrisilazyls obtained so far may be classified by the general formula $(omts)_2M_xM'_y$. With the exception of $(omts)_3Cd_2Li_2$, there are always two omts units combined with a variable number of metal atoms, the maximum number of metallic elements being equivalent to the valency of $(omts)_2$ which is four. Otherwise expressed, the following simple equation holds good (Ox(M) and Ox(M') designating the oxidation states of the metals in $(omts)_2M_x$-M'_y):

$$x \cdot Ox(M) + y \cdot Ox(M') = 4 \tag{7}$$

What is the reason for the outstanding stability of $(omts)_2M_xM'_y$ compared to $(omts)MM'$ or $(omts)_nM_xM'_y$ $(n \geq 3)$? In the absence of other bases like pyridine, bipy or divers ethers, it is clear that a compound of the composition $(omts)MM'$ (in this case M and M' are monovalent) cannot exist as a monomer as the omts dianion has only two nitrogen atoms with two nonbonding electron pairs each. The coordination site at the two metals M and M' will thus be extremely under-populated (the maximum coordination number in this case being two), and, even more important, as the two nitrogen atoms are interlinked by the Me_2Si group in a sterically fixed position, the N-M interactions will result in two four membered cycles with acute N-M-N angles:

(A)
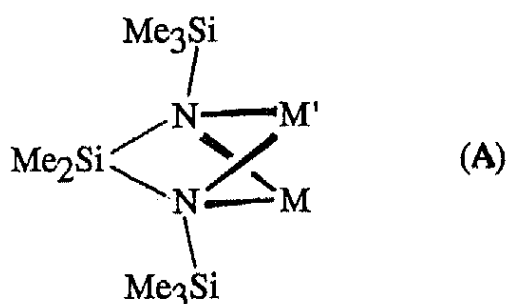
Moreover, the arrangement, which is sketched in formula A, is made difficult by the fact, that the two metal atoms will tend to be separated as much as possible as they are equally charged. The only stabilizing effect of formula A may be an attractive metal-metal interaction or lone pairs at the metallic elements (or both effects). Such lone pairs at metallic elements can be (in a simplified picture) considered as a further ligand; the monomeric 1,3-di-tert-butyl-2,2-dimethyl-1,3,2,4λ^2-diazasilaelementetidines (element = Ge, Sn, Pb, P^+, As^+, Sb^+) [43] may be taken as examples.

Upon consideration of these effects, the structure of $(omts)_2Tl_2Li_2$ (see before) is the "result of an optimization": the lithium atoms are in a less strained position (compared to structure A); they are disposed far from the thallium atoms and the secondary bonding from the methyl groups to lithium can easily be achieved.

Similar arguments may be used to explain the stability of $(omts)_2PbLi_2$ compared to $(omts)Pb$ and $(omts)Li_2$. The last compound is presumably dimeric (see above) and does not exist as a monomer! In compounds of the type $(omts)_2M^{III}M^I$, it is obvious that two omts units at least must be present as one of the metallic elements is trivalent.

The existence of $(omts)_3Cd_2Li_2$ instead of $(omts)_2CdLi_2$ can be explained as follows. Consider the latter compound to be similarly built as $(omts)_2PbLi_2$, then the cadmium atom should have trigonal pyramidal geometry. This is an excellent geometry for Pb(II) [43], but a very bad one for Cd(II) as this element prefers a trigonal planar environment when coordinated by three ligands. We believe that this electronic effect might be the driving force for the formation of $(omts)_3$-Cd_2Li_2 instead of $(omts)_2CdLi_2$ (see chapters before).

Table 2.

Structures of Polycycles of the General Formula $(omts)_2M_xM'_y$ and of $(omts)_3$-Cd_2Li_2

Number of atoms forming the Polycycle	Number of Metals	Number of N	M-N Bonds	Polycycle	Example
7	1	4	4	bicyclic	$[(omts)_2In]^-$
8	2	4	6	tricyclic	$(omts)_2FeLi$
9	3	4	8	tetracyclic	$(omts)_2PbLi_2$
10	4	4	8	tetracyclic	$(omts)_2Tl_2Li_2$
13	4	6	12	hexacyclic	$(omts)_3Cd_2Li_2$

A survey of the structures of heterometallic octamethyltrisilazyls is given in Table 2. As is clearly demonstrated, an increasing number of metallic elements is reflected in an increasing number of M-N bonds and cycles within the polycycle. In the compounds $(omts)_2Tl_2Li_2$ and $(omts)_3Cd_2Li_2$, the maximum number of M-N bonds is reached.

In Table 3 the heterometallic octamethyltrisilazyls of the general formula $(omts)_2M_xM'_y$ are compared to similar homometallic compounds. A classification of the compounds can be made by using the oxidation states of the metals. It may be noted that this list can be tested for completeness by using the simple equation (7). It is obvious from this compilation that heterometallic silazanes of the general formula $(omts)_2MM'$ (M and M' are divalent elements) or $(omts)_2$-M_3M' (M and M' are monovalent elements) are lacking, but until now we have not been able to synthesize such molecules. Of course, if more than two different metals are considered, formulae of the type $(omts)_2MM'M''$ or $(omts)_2M_2$-$M'M''$ and $(omts)_2MM'M''M'''$ may also be envisaged.

Table 3.

Homo- and Heterometallic Silylamides of the General Formula $(Me_2Si(NR)_2)_2M_x$
(R = tBu or Me_3Si)

Valency of the Metals	x	R	c.n.M[a]	c.n.N[a]	References
M(IV) Compounds					
M = Si, Ge, Sn, Ti, V, Zr, Hf	1	$SiMe_3$	4	3	44, 45
M = Si, Ge, Sn, Ti, V, Zr, Hf	1	tBu	4	3	43, 44, 45
M = "In⁻" (from $(omts)_2InK$)	1	$SiMe_3$	4	3	this work
M(III)/M(I) Compounds					
M(III) = In, M(I) = Li, Na, In(I), Tl(I)	2	$SiMe_3$	4,2	4,3	this work
M(III) = Al, M(I) = Li					
M(III) = Fe, M(I) = Li					
M(II)/M(II) Compounds					
M(II) = Sn, AlX, GaX, InX, Mg(thf) (X = Cl or CH_3)	2	tBu	3[b]	4,3	43, 46
M(II)/M(I) Compounds					
M(II) = Pb, 2 M(I) = Li	3	$SiMe_3$	3,2	4	this work
M(I) Compounds					
4 M(I) = Li	4	tBu	3[c]	5[c]	11
2 M(I) = Tl, 2 M(I) = Li	4	$SiMe_3$	(3),2[d]	4	this work

a) c.n. = coordination number of ligands around the central M or N atom. This number does not include secondary bonds from the methyl groups to the metallic elements.

b) The ligand X or (thf) is not counted in this number.

c) The formal electron pair bonding number at M is 2 and at N 4. As there are quasi ionic interactions to be considered, the geometrical c.n. is closer to 3 for M and 5 for N without considering possible M--M interactions.

d) The c.n. at Tl in brackets takes into account the intramolecular Tl--Tl contact.

There are only two compounds structurally characterized so far which do not fit into Table 3. These are $(omts)_3Cd_2Li_2$ (discussed before) and the homometallic compound $(omts)_3Na_6$ [12], which formally belong to the M(II)/M(I) and M(I) compounds, using the classification of Table 3.

The most interesting classes of compounds due to their structural variety are those which may be derived from the general formulae $(Me_2Si(NR)_2)_2M(III)M(I)$ and $(Me_2Si(NR)_2)_2M(II)M(II)$. The molecules of the first category have a tetrahedral spirocyclic center which is occupied by M(III) and consist of an eight atomic skeleton $Si_2N_4M(III)M(I)$, forming three four membered cycles sharing a common corner and being attached to each other by common edges (see Figures 1 and 2). The point symmetry of this polycycle is $C_2(2)$. The molecules of the second category also have an eight atomic skeleton $Si_2N_4[M(II)]_2$ and are composed as above of three four membered cycles, but are attached to one another in a different way: to a central $[M(II)]_2N_2$ ring two equal SiN_2M four membered cycles are centrosymmetrically added resulting in two common M-N edges with the central ring (Figure 10).
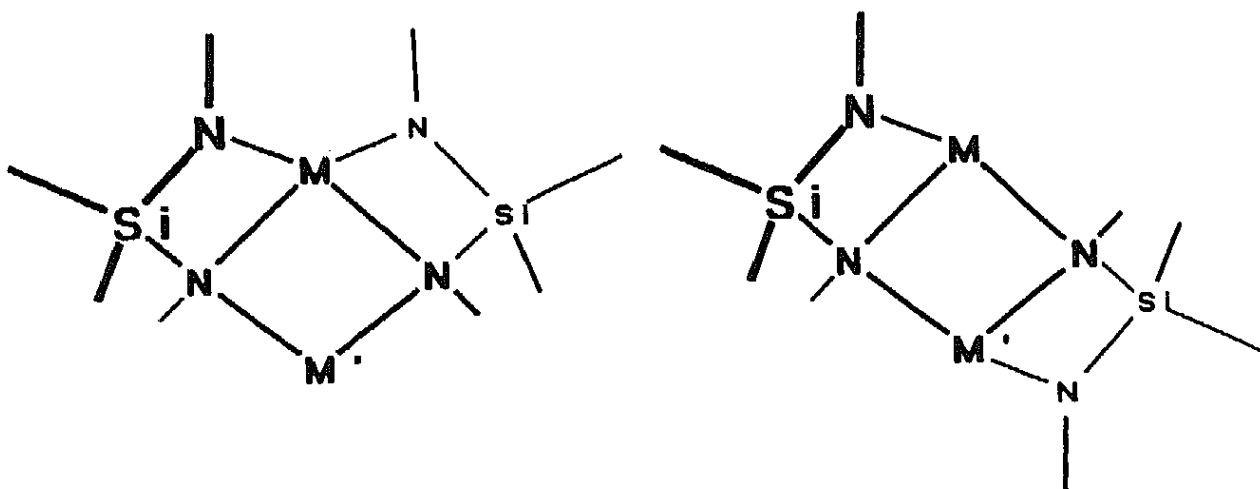

Figure 10. The different structures adopted by $[Me_2Si(NR)_2]_2M(III)M(I)$ and $[Me_2Si(NR)_2]_2M(II)_2$ molecules, designated as "butterfly" and "staircase" structures.

It seems straightforward to assume, that the two different structures (which we may designate as "butterfly" and "staircase" structures (see ref. [27])) are dependent on the oxidation states of the metallic elements involved in the polycycles, the "butterfly" structure being characteristic of the heterometallic molecules $[Me_2Si(NR)_2]_2MM'$ and the "staircase" structure of the homometallic compounds $[Me_2Si(NR)_2]_2M_2$. This conclusion should be drawn only with great caution as it does not hold for alkoxysilazyls of the general formula $[Me_2Si(OtBu)(NR)]_2M_2$ (R = tBu or $SiMe_3$), of which only homometallic species are

known [19]. The $[Me_2Si(OtBu)(NtBu)]^-$ anion is monovalent and isoelectronic to $[Me_2Si(NtBu)_2]^{2-}$. Whereas the sodium derivative $[Me_2Si(OtBu)(NSiMe_3)]_2Na_2$ has a "butterfly" structure, the potassium and rubidium analogues $[Me_2Si(OtBu)(N-SiMe_3)]_2M_2$ (M = K, Rb) adopt the "staircase" structure in the crystal [27]. Moreover, it can be shown by temperature dependent NMR techniques that, in the case of the alkoxysilazyls, the "butterfly" interconverts easily in solution into the "staircase" structure and *vice versa* [27]. Also, in the case of the $[Me_2Si(Ni-Pr)_2Sn]_2$, we have been able to show by multinuclear NMR methods that intramolecular rearrangements are taking place [47].

Are there other possibilities for the construction of three four membered cycles containing a total of 8 atoms? As there are 8 atoms the three cycles must have two common edges. A graphic solution of this problem is depicted in Figure 11.

If a seven atomic norcubane-type agglomeration of four membered cycles is cut once, an eight atom agglomeration I results which has the point symmetry $C_s(m)$. Moving the two four membered cycles attached to the central ring in opposite directions results in the two (nonidentical and thus enantiomeric) forms II and III, which are of point symmetry $C_2(2)$. A single case is the equiplanar arrangement of the cycles IV which has $C_{2v}(mm2)$ symmetry. If the starting polycycle is cut twice and one of the common edges recombined by chosing a different edge of the central ring the centrosymmetric tricycle V (point symmetry $C_i(\bar{1})$ or the tricycle VI are obtained, which has the point symmetry $C_2(2)$. If V or VI are flattened the equiplanar arrangement of cycles VII results with point symmetry $C_{2h}(2/m)$.

So far, we have not considered the nature of the components of the polycycles nor the substituents on them. If we do so, we have to account for the bulky substituents on the nitrogen atoms (and the tendency of four coordinate nitrogen to approach a tetrahedric coordination sphere in $[Me_2Si(NR)_2M]_2$ (R = tBu, SiMe_3)) and we therefore must exclude the structures IV and VII. Of the remaining possibilities I, II, III, V and VI, the structures I and VI should again be quite unstable as the substituents will be in close contact with one another. We note in passing that a type VI structure is known and may be easily connected to our systems, when in $[Me_2Si(NtBu)_2Sn]_2$ the Me_2Si group is formally exchanged by the electrophilic and smaller B-Me group and tBu by Me_3Si resulting in $[MeB(NSiMe_3)_2Sn]_2$ [48]. After exclusion of the different possibilities, we end up with the "butterfly" structures II and III and the "staircase" structure V which are found experimentally. We only need to check, if enantiomeric pairs like II and III are present in the crystal. Indeed we always find that two enantiomers are related to one another by the inversion centers of the space group in $(omts)_2InLi$ and in $(omts)_2FeLi$ (see also Table 1). In solution, it is very likely that II interconverts to III and *vice versa* as from the ^{1}H-NMR-spectra of $(om-ts)_2InLi$ and $(omts)_2AlLi$ intramolecular rearrangements have to be considered (see before).
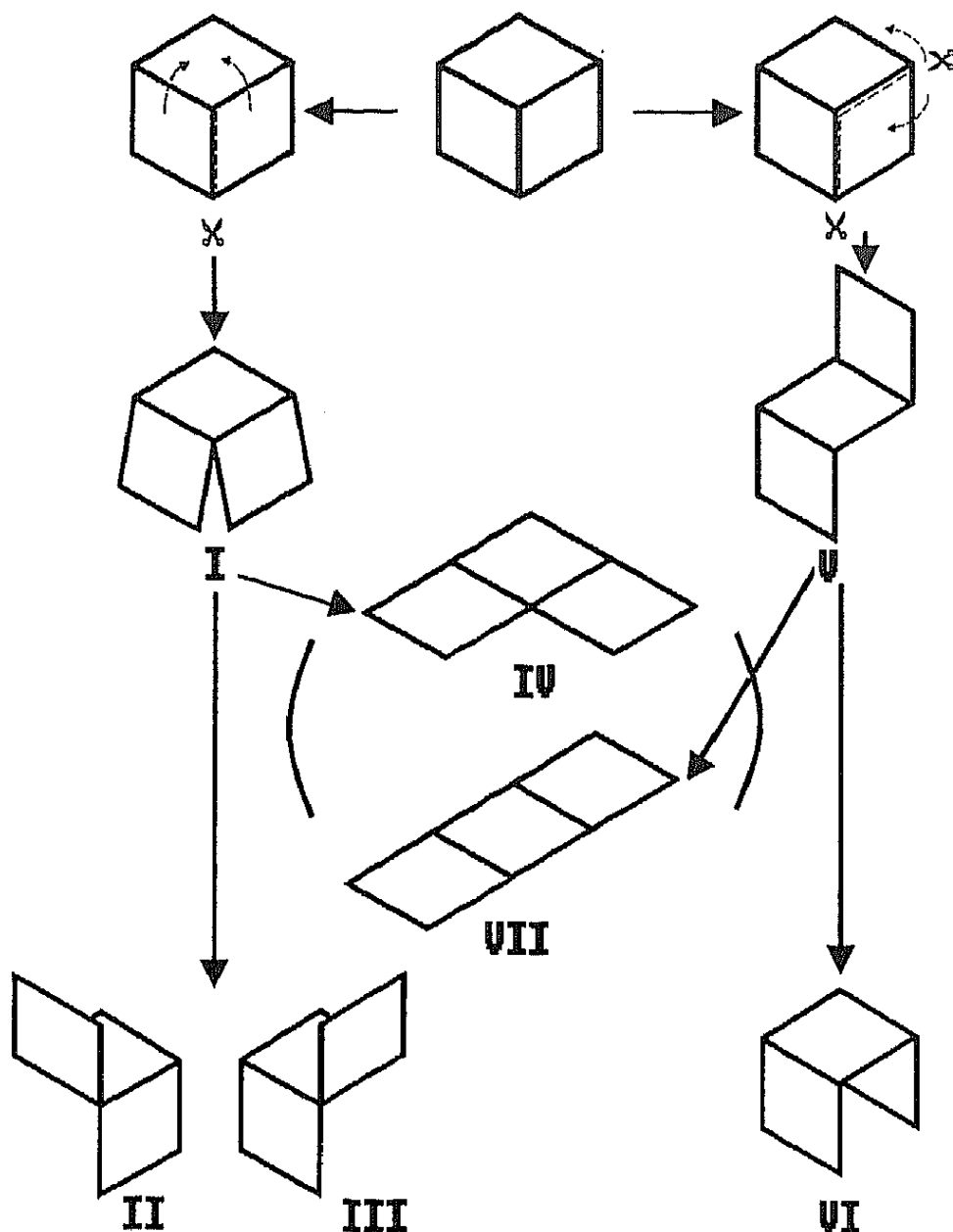
Figure 11. Conceivable bond scissions of a seven atomic norcubane-type agglomeration resulting in eight atomic polycycles I-VII all composed of three four membered cycles with two common edges.

The more facile use of $Me_2Si(NSiMe_3)_2$ as a ligand in heterometallic compounds compared to $Me_2Si(NtBu)_2$ may have its source in different effects. First of all, the Si-N bond is longer than C-N by about 0.30 Å. Secondly the methyl groups in the trimethylsilyl groups are more electronegative than the methyl groups of the tert-butyl substituent which should result in a more efficient secondary bonding to the alkali metals. Finally, the different reactivity of N-H bonds in alkylamines compared to silylamines might be of importance. It is well known

that silylamides react more efficiently with metals than alkylamines in the formation of metalamides.

5. ACKNOWLEDGEMENTS

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