

Alkyl- and Aryl-Substituted Main-Group Metal Amides

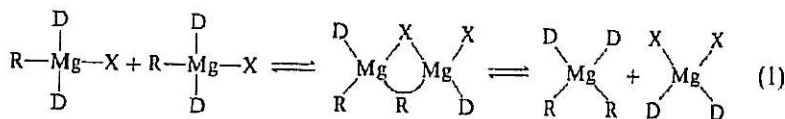
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INTRODUCTION

Main-group metal alkyls and aryls are valuable tools in preparative organic and inorganic chemistry, and many industrial applications are known for these reactive substances. In addition, they have attracted considerable attention from a more fundamental and theoretical point of view, because the high Lewis acidity at the metal center is the source of singular structures and bonding (1-3).

The formal substitution of one of the alkyl or aryl groups at the metal by nonmetallic and electronegative groups leads to compounds that have both electrophilic and nucleophilic centers in the molecule. The Grignard reagents are the best known and most important class of such compounds (4,5). Because of their high polarity and their acid/base properties, they must be handled in coordinating solvents. Moreover, they undergo exchange reactions that are known as Schlenck equilibria [Eq. (1)] (6-8). In Eq. (1), D is the donor solvent, X is the halogen, and R is the organic group.



A consequence of these complex intermolecular equilibria [Eq. (1) is only one of several occurring in solution] is that their use in preparative chemistry is somewhat limited with respect to high-yield procedures. Another limiting effect of these reagents is their dependence on the presence of coordinating solvents.

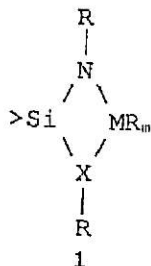
Substitution of the halogen X by another electronegative group affords compounds that are stable with respect to intermolecular ligand transfer; these compounds do not require donor solvents for stabilization. In particular, ligands with a nitrogen atom attached to the metal fulfill at least one of the

two required properties. The amide function in these metal amides (9) may be derived from alkyl or aryl amines or from trialkylsilyl amines (silazanes). Silyl amides appear to stabilize the electron deficiency at the metal center most efficiently, an effect that is ascribed to the electron-donating properties of the silyl ligands (9).

In this article we describe the syntheses, structures, and physical properties of metal alkyls or aryls that have a further "chelating" amino ligand attached to the metallic center. These substances have been mainly developed in our laboratories in order to accomplish the following objectives:

1. Suppress coordination by solvent molecules at the metal.
2. Improve their solubility in nonpolar solvents.
3. Minimize the coordination number at the metal.

The substituents at the nitrogen atoms are invariably *tert*-butyl groups (see objective 3) in combination with silicon, which simultaneously functions as an electron donor as well as a bridging atom to other intramolecular basic centers X (nitrogen or oxygen atoms). Formula I shows the general structural framework of the compounds.



In Section II, the structures of alkyl and aryl metal amides of the metallic elements Mg, Ca, Sr, Ba, Al, Ga, In, and Tl are briefly discussed from a general point of view. Some analogous compounds of other elements are included for comparison.

II

STRUCTURAL ASPECTS OF ALKYL AND ARYL METAL AMIDES

A. Compounds of the Alkaline Earth Elements

Whereas a considerable number of pure amides of Mg, Ca, and Ba are known, the alkyl or aryl amides of these elements have been little investigated (9). Compounds of the general formula RMgNR'_2 are usually coordination polymers, unless ether molecules are added to the compound or bulky R

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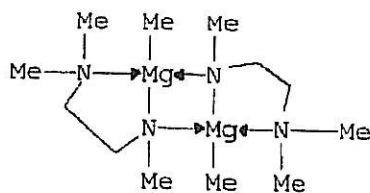
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groups are used. For example, $\text{MeMg}(\text{NMe}_2)$ seems to be polymeric, whereas $[\text{iPrMg}(\text{NiPr}_2)]_2$ is dimeric (10), and the addition of tetrahydrofuran (THF) to EtMgNPh_2 leads to the formation of monomeric $\text{EtMgNPh}_2 \cdot (\text{THF})_2$ (10). If chelating ligands such as $\text{MeNCH}_2\text{NMe}_2$ are used, dimers such as $[\text{MeMgNMe}(\text{CH}_2)_2\text{NMe}_2]_2$ (2) are obtained. The crystal structure of this compound shows that it contains a four-membered Mg_2N_2 ring as the central unit (11).



2

As can be seen from the structure, the dimerization proceeds via nitrogen-magnesium interactions. To our knowledge, dimerization via $\text{Mg}-\text{R}-\text{Mg}$ two-electron three-center bonds in alkylmagnesium amides has neither previously been found in the solid state nor proved by X-ray techniques, although the existence of such bonds has been claimed (10).

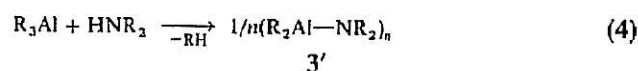
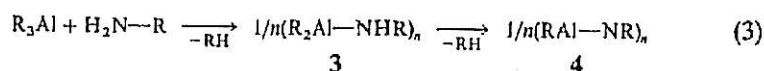
The existence of alkyl- or aryl calcium amides has not as yet been unambiguously demonstrated. One reason for this seems to be because calcium-carbon bonds are much less stable than calcium-nitrogen bonds, as is illustrated by the following reaction [Eq. (2)] (12).



B. Compounds of Aluminum, Gallium, Indium, and Thallium

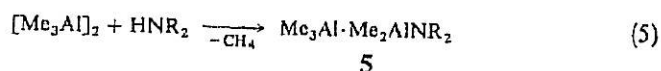
1. Simple Organometal Amides

The chemistry of alkyl- and arylaluminum, gallium, indium, and thallium amides has been investigated much more than the comparable chemistry of Group II elements (9,13-18). Alkylaluminum amides especially have a very rich and diverse structural chemistry (9,13-15). When a trialkylalane reacts with primary or secondary amines, the amides 3, 3', and 4 are formed in addition to a simple adduct [Eqs. (3) and (4)].

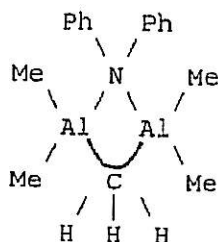


Compounds of type 3 or 3' are cyclic and those of type 4 are polycyclic, as shown by spectroscopic data or X-ray structure determinations. $(\text{Me}_2\text{-AlNMe}_2)_2$ forms a planar four-membered cycle (19) but $(\text{Me}_2\text{AlNHMe})_3$ has a six-membered Al_3N_3 ring, one isomeric form of which adopts a chair (20) and the other a skew-boat conformation (21). The two isomers interconvert, as may be seen in temperature-dependent NMR spectra (21). The six-membered Al_3N_3 ring of trimeric ethylenimino(dimethyl)alane also has a chair \rightleftharpoons boat conformation (22). In the four-membered rings, the angles at aluminum and nitrogen approach 90° , whereas in the trimers the angles are different, with the smaller value found at the heavier atom (Al, $100\text{--}108^\circ$; N, $115\text{--}123^\circ$) (14). The Al—N bond lengths (of the order $1.93\text{--}1.90 \text{ \AA}$) are quite constant and show no dependence on the ring size.

The polycyclic oligomers $(\text{RAINR})_n$ (type 4 compounds) may adopt an Al_nN_n skeleton that resembles either a cube ($n = 4$), a hexagonal prism ($n = 6$), or two more complex cages with $n = 7$ or $n = 8$ (14,23). No monomers have ever been isolated, but borazole-like $[\text{MeAl}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)]_3$ has been obtained, which has a planar $\text{Al}_3\text{N}_3\text{C}_6$ core (X-ray structure) (82). As in the compounds of type 3 or 3', both the aluminum and nitrogen atoms always have the coordination number four. When the substituents on the secondary amine in Eq. (4) are bulky or when trimethylsilyl groups are employed, compounds are isolated that have only one amide function in the product [Eq. (5), $\text{R} = \text{Ph}, \text{SiMe}_3$] (24,25).



A structure determination of compound 5 ($\text{R} = \text{Ph}$) reveals a four-membered Al_2NC ring as the central unit in which the two aluminum atoms are connected by two different bridging atoms. Whereas the nitrogen atom functions as a base (four-electron three-center bond), the methyl group forms a two-electron three-center bond ($\text{Al}\text{--}\text{N} = 2.00 \text{ \AA}$; $\text{Al}\text{--}\text{C}$ bridge = 2.14 \AA) (24). The corresponding gallium derivative has also been isolated (26).



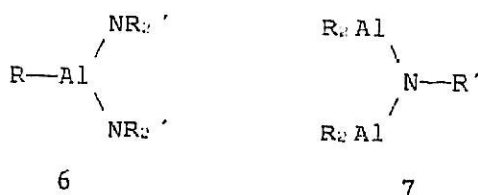
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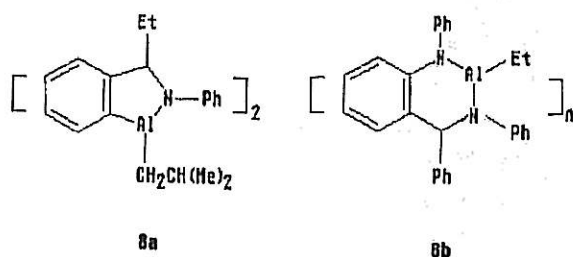
In addition to compounds of type 3 and 3', some of which have been claimed to be monomeric [e.g., $\text{Me}_2\text{AlN}(\text{SiEt}_3)_2$ (27), $\text{Me}_2\text{Al}-\text{NPhSiMe}_3$ (28), and $i\text{Bu}_2\text{AlN}(\text{SiMe}_3)_2$ (29)], compounds of type 6 and 7 have also been synthesized but have been poorly characterized structurally (9, 15).



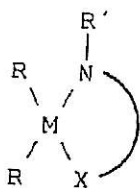
Many of the structural principles found for organoaluminum amides also hold for the corresponding compounds of gallium, indium, and thallium (15-18). As in the case of the aluminum compounds, the amides tend to oligomerize through intermolecular Lewis acid/base interactions. There are nevertheless remarkable differences. Whereas Me_2AlNHEt in benzene is a cyclic trimer (30), the corresponding thallium compound Me_2TlNHEt appears to be dimeric, as assessed by spectroscopic methods (31). In order to obtain a compound that is monomeric, all the alkyl groups in an alkyl metal amide need to be substituted by very bulky groups, for example, $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ (32) and $\text{Tl}[\text{N}(\text{SiMe}_3)_2]_3$ (33). In both these species the metal has the low coordination number three.

2. Cyclic and "Chelated" Organometal Amides

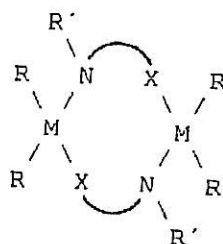
Aluminum, gallium, indium, and thallium have been successfully incorporated in cyclic systems, although little structural information has been obtained (15). Hoberg (34) has prepared many such ring compounds, including, for example, 8a and 8b, and has demonstrated the former to be dimers from molecular mass determinations and from mass spectra.



There are numerous examples of chelating ligands that have been used to obtain monometal-centered rings (15). However, a problem that arises from such attempts is that chelation may not necessarily take place at the same metal center and may lead to an intermolecular chelate, as is shown in formula 10, rather than to the form 9.



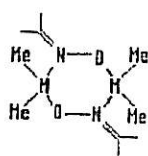
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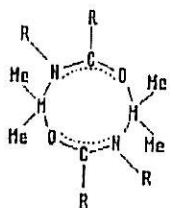
The two forms 9 and 10 may, however, be in equilibrium, as has been demonstrated in some cases. Some representative examples of the "intermolecular chelate" 10 are depicted in formulas 11-16. Many of these structures have

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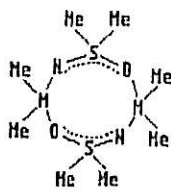
M = Al, Tl

11 [35]



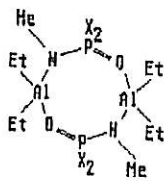
M = Ga, In
R = Me [36], R = Ph [37,38]

12



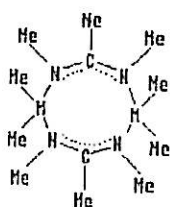
M = Ga, In

13 [39]

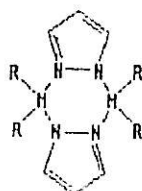


X = OEt, OCH₂CHMe₂, NMe₂

14 [40]



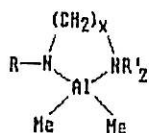
M = Al, Ga
15 [41,42]



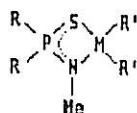
M = Al, Ga, Tl
R = Me, Cl
16 [43-47]

been confirmed by X-ray diffraction determinations. Although the ring systems of the six-membered cycles are planar, the corresponding eight-membered rings may be significantly distorted (see references).

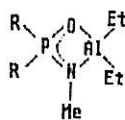
In addition to these dimeric molecules some mononuclear metal compounds of type 9 have been found either by molecular weight determinations in noncoordinating solvents or by X-ray structure analyses (17-21). Some of



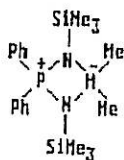
R = Me, R' = Me, x = 3
R = Et, R' = Me, Et, x = 2
17 [48]



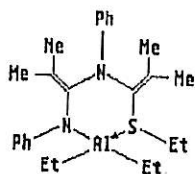
M = Al, R = CHMe2, R' = Et
M = Al, R = tBu, R' = Et
M = Al, Ga, In, R = R' = Me
18 [40,49,50]



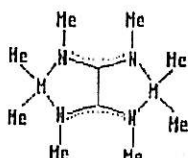
R = Me2CHCH2O
R = CHMe2
19 [48]



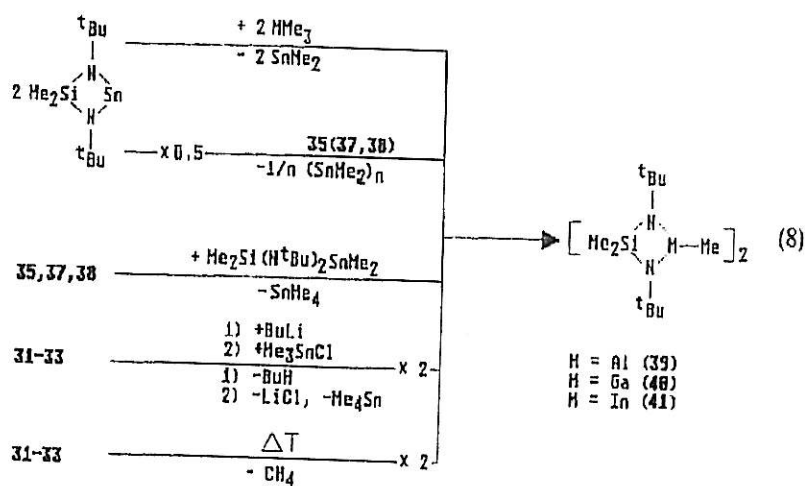
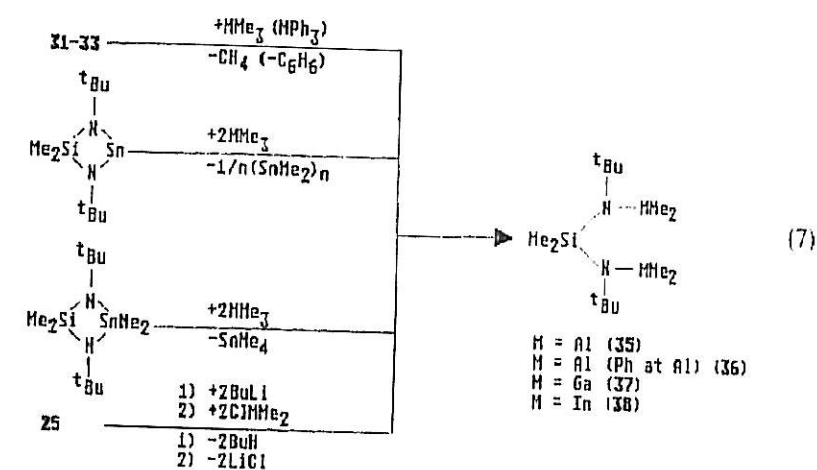
M = Al, Ga
20 [50]



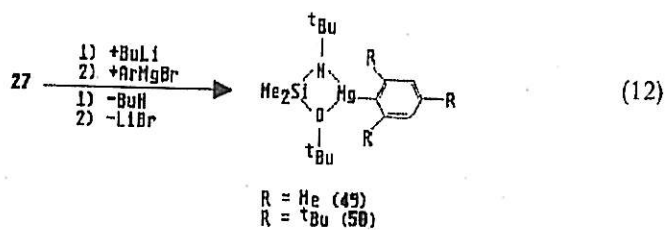
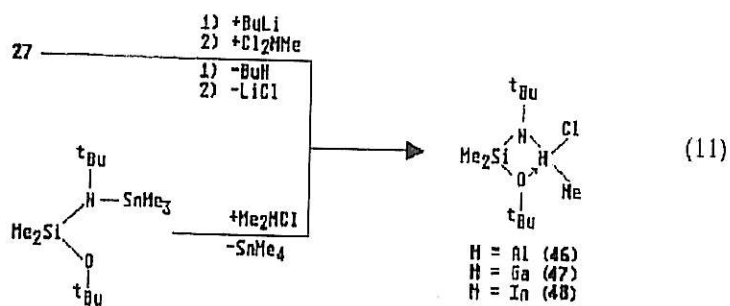
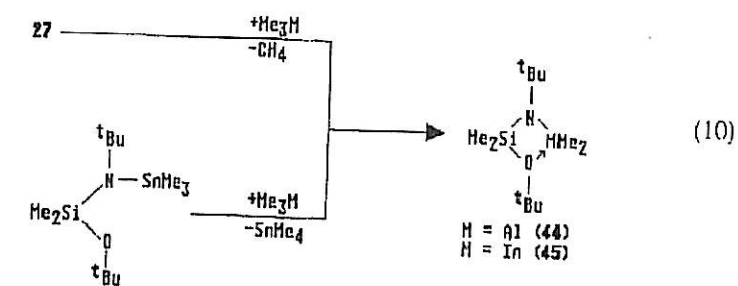
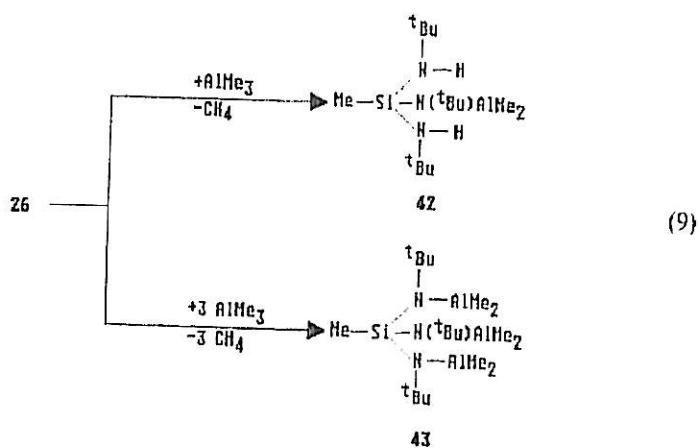
21 [51]

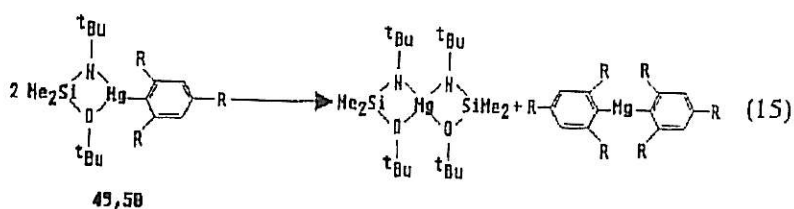
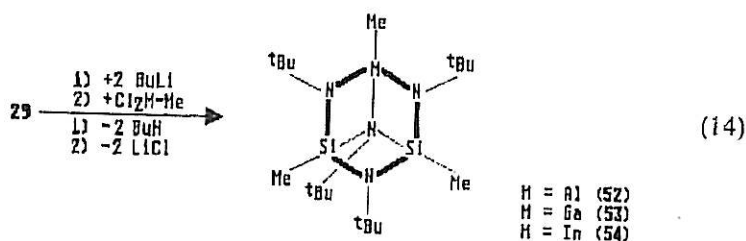
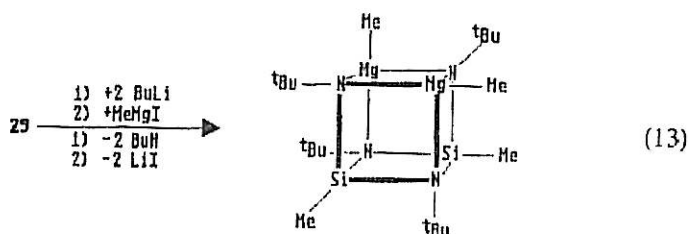


M = Al, Ga, In
22 [52]



The products 31-54 of these reactions can be handled under dry nitrogen and they analyze correctly, are soluble in nonpolar solvents such as pentane, cyclohexane, benzene, and toluene, and are often sublimable without decomposition under reduced pressure. They may be prepared in high yields and large quantities. The synthetic procedures starting with a stannazane [30, Me₂Si(N^tBu)₂Sn or Me₂Si(N^tBu)₂SnMe₂] afford high yields of product. The reaction temperature in Eq. (12) must be strictly controlled, because compound 49, and to a lesser extent compound 50, tend to disproportionate into the symmetrical products [Eq. (15)] (67).





B. Structures of the Compounds

The structures of compounds 31–54 may be deduced indirectly by spectroscopic methods (NMR, IR, or MS) or may be determined by X-ray crystallography. Frequently the structures found in solution are different from those existing in the crystalline state due to intramolecular bond fluctuations, as explained in Section III.D.

The molecules 31–34 are all monomeric and cyclic, as shown by infrared and ^1H and multinuclear NMR spectra (63,70). Unfortunately, the quality of crystals of these compounds was not sufficient for X-ray diffraction studies and therefore we used a derivative of 31, $\text{Me}_2\text{Si}[\text{tBu}(\text{H})\text{N}](\text{NtBu})\text{AlCl}_2$, to establish unambiguously the structural details (64). As depicted in Fig. 1, a four-membered SiN_2Al ring is the central unit. The two nitrogen atoms N1 and N2 differ in their coordination numbers (three and four), the trigonal-planar coordinated N1 effecting shorter bonds to Al and Si than those effected

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Fig. 2.
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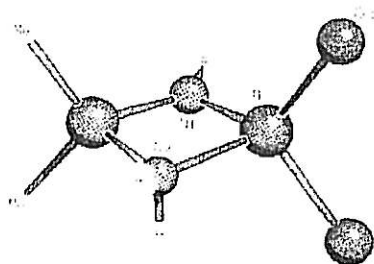


Fig. 1. The four-membered ring in $\text{Me}_2\text{Si}(\text{NtBu})[\text{NtBu}(\text{H})]\text{AlCl}_2$. As in Figs. 2-14, the *tert*-butyl groups are denoted by R and the methyl groups are denoted by Me.

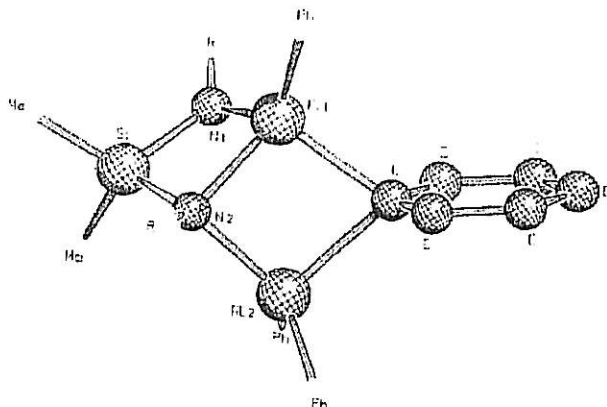
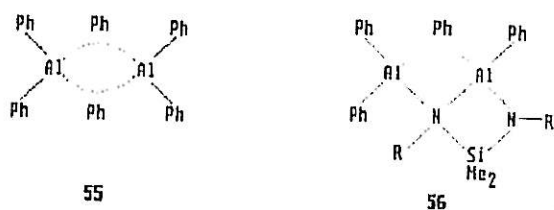


Fig. 2. The polycycle in $\text{Me}_2\text{Si}(\text{NtBu})_2(\text{AlPh}_2)_2$ (36). The hydrogen atoms at the bridging phenyl group are not shown.

by the tetrahedrally distorted N2, as expected [$\text{N1}-\text{Al} = 1.830(2) \text{ \AA}$, $\text{N1}-\text{Si} = 1.712(2) \text{ \AA}$, $\text{N2}-\text{Al} = 1.994(2) \text{ \AA}$, and $\text{N2}-\text{Si} = 1.861(2) \text{ \AA}$] (64).

The dimetallasilazanes 35, 37, and 38 are not suitable for X-ray structure determinations because they form plastic crystalline phases, as shown for 35 (cubic crystal system, point symmetry for 35 $m\bar{3}m$ or $43m$) (63). In contrast, the structure of the phenyl derivative 36 has been established, and the central skeleton is shown in Fig. 2 (64). Two four-membered rings (Si, N1, N2, Al1 and Al1, N2, Al2, and C29) share an edge, and C29 connects a four-membered with a six-membered ring as a spirocenter (64). The bonding in this compound can be derived from Al_2Ph_6 (71), where one bridging and one terminal phenyl group have been replaced by nitrogen atoms (formulas 55 and 56).



The Al1-C29-Al2 and Al1-N2-Al2 bridges are almost symmetrical with an Al-C distance of 2.18(3) Å and an Al-N distance of 1.99(1) Å. As expected, the bond distances to the terminal atoms are remarkably shorter (64). Although C29 may be visualized as the center of a two-electron three-center bond, N2 uses two electron pairs to coordinate to the aluminum atoms.

Figure 3 represents the only dimer formed in this series of metallacycles. The coordination number of the indium atom is increased by interaction with the nitrogen atom of a second molecule. The dimer 41 has a center of inversion and three edge-fused four-membered rings. This type of structure is very common in metallacycles that are derived from the ligand 25 (56). The central N_2In_2 ring is almost square-planar [$In-N = 2.27(1)$ Å] and the In-C dis-

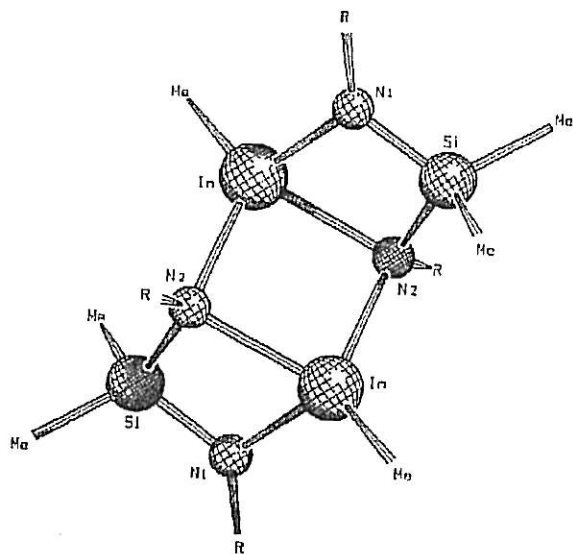


FIG. 3. The escalator structure of the three fused four-membered cycle in $[Me_2Si(NtBu)_2In-Me]_2$ (41).

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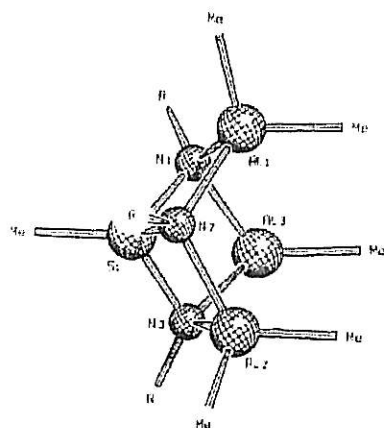


FIG. 4. The open cage of $\text{McSi}(\text{N}(\text{tBu})\text{AlMe}_2)_2$ (43). The second methyl group of Al3 is hidden behind this atom.

tance is 2.153(5) Å. The homologous compounds 39 and 40 are also dimeric, 39 forming crystals isomorphous with 41 (63,64).

Compound 43 is a polycycle that can be derived from a cube having one corner missing (Fig. 4). The distortion from the point symmetry $3m$ (C_{3v}) is small, the pseudo-threefold axis passing through the Si—C bond. All atoms of the ring have the coordination number four in a tetrahedrally distorted environment (65). The Al—N distances are almost the same [2.02(1) Å], whereas the Al—C distances are slightly shorter in the direction of the threefold axis [1.95(1) Å] than those that are almost perpendicular to it [1.98(1) Å]. The chelates 44–48 have been shown by cryoscopy in benzene to be monomeric. Their ring structure can be deduced from NMR spectra (66) (see also Section III,D).

No suitable crystals have been obtained of compound 51. Nevertheless, we have been able to synthesize the corresponding bromine derivative (the methyl groups at the aluminum being replaced by bromine atoms) (69) and have determined its crystal structure by X-ray diffraction. Figure 5 shows the central $\text{Si}_2\text{N}_4\text{Mg}_2$ cage, which may be derived from a cube, the corners being occupied alternatively by metals and nonmetals. The Mg—N distances are different [Mg—N2 = 2.210(6) Å and Mg—N1(N1') = 2.147(6) Å] and are considerably longer than the Si—N distances [1.72–1.78 Å], which accounts for the distortion from ideal cubic geometry.

Of compounds 52–54, the aluminum and gallium derivatives have been fully characterized in the solid state by X-ray diffraction (62,69). In Fig. 6, the

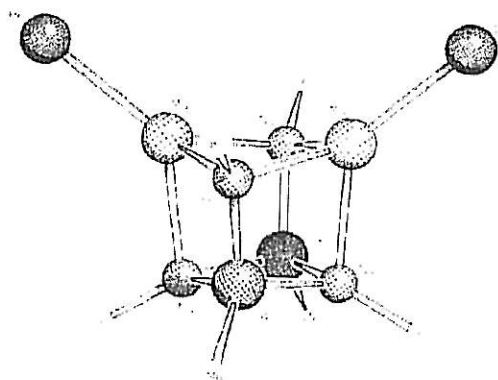


FIG. 5. The cube arrangement of the noncarbon atoms in $(\text{MeSi})_2(\text{BrMg})_2(\text{NtBu})_4$ (59).

polycyclic $\text{Si}_2\text{N}_4\text{Ga}$ skeleton of **53** is depicted; it resembles the skeleton of the aluminum compound **52**. The gallium atom is in fourfold coordination by three nitrogen atoms and one carbon atom of the methyl group. As expected, the N3—Ga donor bond is significantly longer than are the N(2,4)—Ga bond distances [$\text{Ga}-\text{N3} = 2.119(3) \text{ \AA}$ and $\text{Ga}-\text{N}(2,4) = 1.927(2) \text{ \AA}$]. In the aluminum derivative **52**, the corresponding distances are $\text{Al}-\text{N3} = 1.795(7) \text{ \AA}$ and $\text{Al}-\text{N}(2,4) = 1.733(6) \text{ \AA}$ (62,69). The Ga—C bond in **53** [$2.009(4) \text{ \AA}$] is again longer than the Al—C bond in **52** [$1.85(1) \text{ \AA}$].

C. Synthetic Uses; Polymetal Silazanes

Reactive centers in a cyclic or chelated alkyl or aryl metal silazane, such as compounds **31–54**, are (1) the polar metal—carbon bond, (2) the polar metal—nitrogen bond, and (3) other bonds in the silazane, especially nitrogen—hydrogen bonds. We have been interested in reaction centers (1) and (3) and have

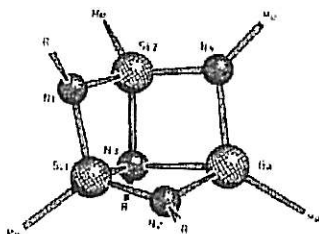
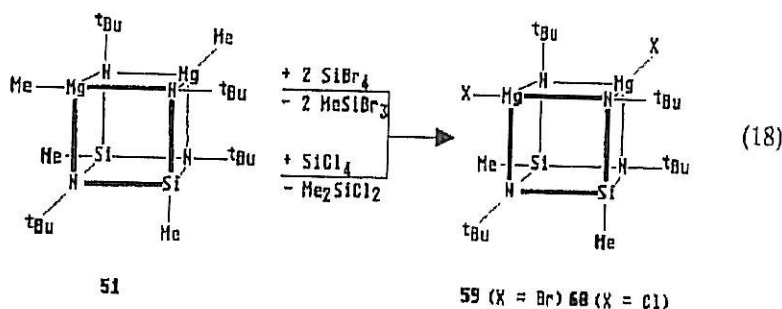
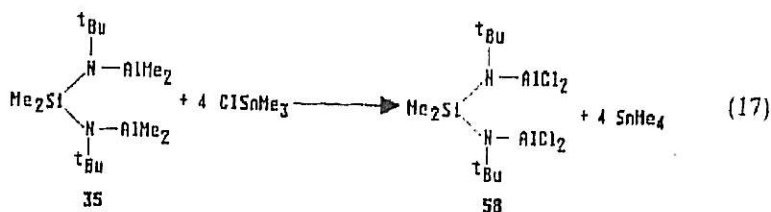
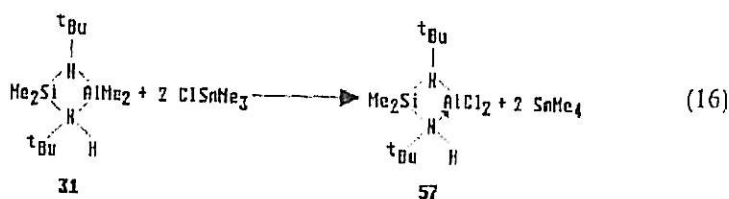


FIG. 6. The seco norcubane-like polycycle in $(\text{MeSi})_2(\text{MeGa})(\text{NtBu})_4$ (53).

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performed several reactions to evaluate their synthetic use. As expected, compounds of types 31–54 are very efficient alkylating reagents. Some selected examples are shown in Eqs. (16)–(18).

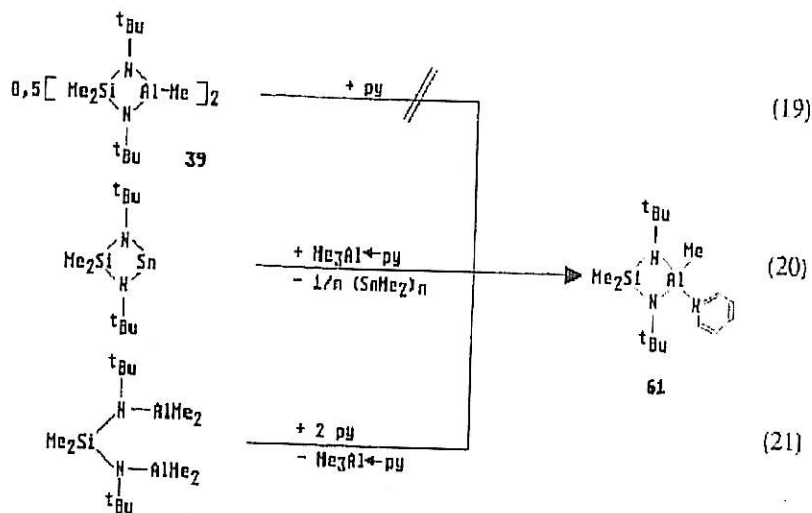


The procedures given by Eqs. (16)–(18) may be used either to alkylate silicon halides or tin halides in very high yields (90–100%), or to substitute the alkyl functions in the metallacycles by halogen atoms. The two products in these reactions can be easily separated from one another and compounds 57–60 are isolated in high yields (63,69).

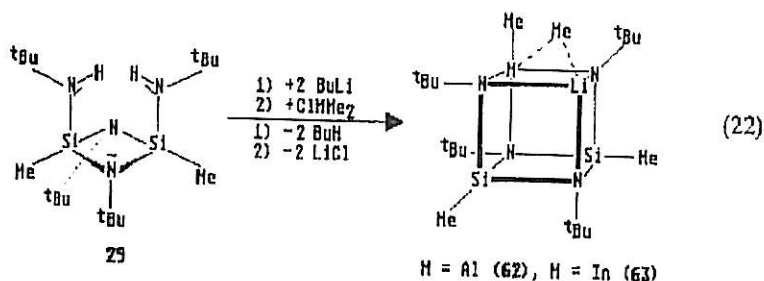
The dimers 39–41 are stable toward base addition, and there is no way to transform by coordination of pyridine compound 39 to the monomeric base adduct 61 [Eq. (19)]. The species 61 can only be prepared by other routes, as indicated in Eqs. (20) and (21).

In order to visualize the reaction path of Eq. (21), the reader should be reminded that intramolecular methyl bridges between the two aluminum atoms in 35 need to be invoked (see Section III,D).

The metallacycles 31–54 can also simultaneously function as acceptors and

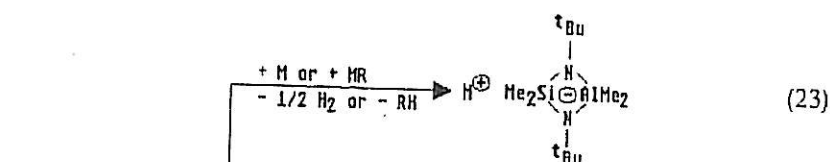


donors and may accommodate different metallic elements. Starting with 29, a dilithium derivative can first be synthesized [the core structure of this compound has been established to be a distorted $\text{N}_4\text{Li}_2\text{Si}_2$ cube (68)], which then can react with only one equivalent of ClAlMe_2 or ClInMe_2 to form 62 and 63 [Eq. (22)].

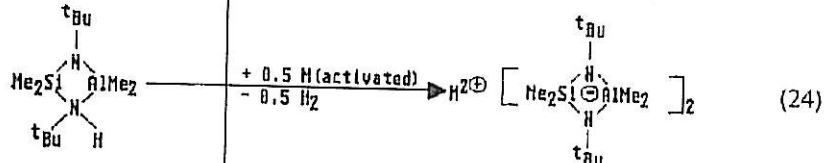


The structures of 62 and 63 can be established by ^1H NMR spectra, the bridging methyl group between aluminum or indium and/or lithium showing up as a broad signal at high field [$\delta = -0.35$ ppm (vs. tetramethylsilane for 62)]. In this series, 62 and 63 are the first compounds that contain two different metals in a silazane. Such poly(metal)silazanes may be prepared by different routes, starting with alkyl metal silazanes that still have a hydrogen atom bonded to one of the nitrogen atoms. Several examples are summarized in Eqs. (23)–(29).

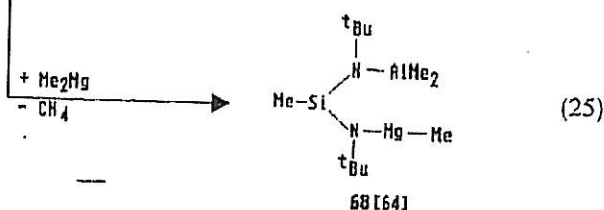
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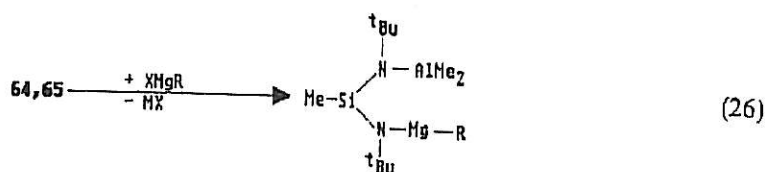
64 (M = Li), 65 (M = Na) [64]



66 (M = Hg), 67 (M = Ca) [73, 73]



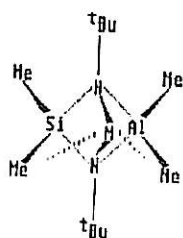
68 [64]



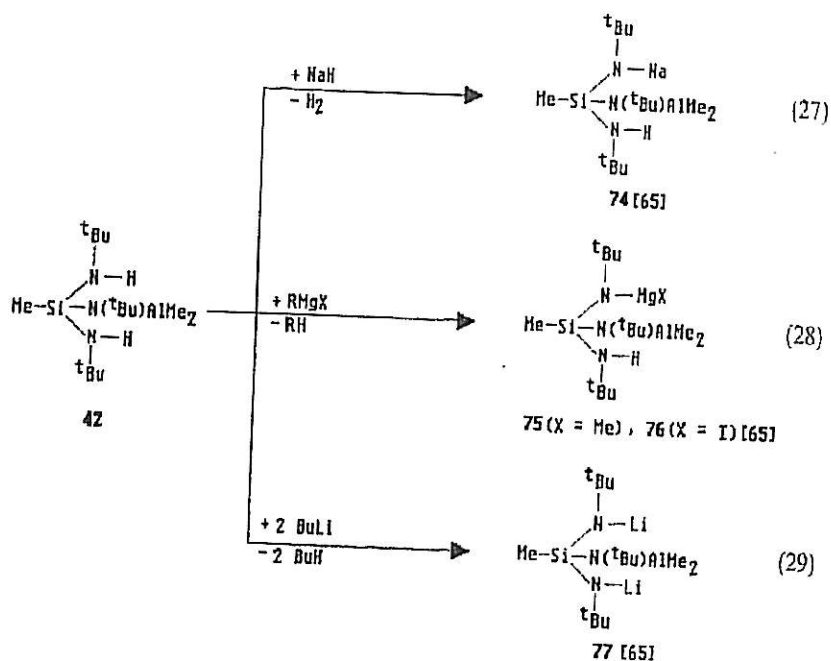
69 (R = tBu), 70 (R = CH₂-Ph)
 71 (R = Ph) [64], 72 (R = CPh₃) [73]
 73 (R = I) [64]

The poly(metal)silazanes 62–77 are isolated usually as colorless crystals. They are unstable with respect to water and oxygen and are soluble in non-polar solvents (with the exception of compound 77). The formulas drawn for 64–67 are merely formal and do not imply that these substances have a considerable ionic character. They are soluble in benzene and are monomolecular as found by cryoscopic molecular weight determinations. The ¹H NMR spectra of 64 and 65 (64) demonstrate that the metal atoms are coordinated by methyl groups, the most reasonable structure being depicted in the formulas 64 and 65. The trigonal-bipyramidal arrangement of the N₂SiAlM

M. VEITH



64, 65

FIG. 7.
magnesium

fragment has been found for some compounds in the solid state. In Figs. 7 and 8, N_2SiAlMg and N_2SiAlCa bipyramids, respectively, are observed as the central skeletons. Whereas two of the bipyramids in 73 are linked via iodine bridges, with the magnesium atom situated in an almost square-planar environment, in 67 two bipyramidal N_2SiAlCa cages are connected by the common calcium atom. Compound 67 can also be visualized as a sandwich in which the calcium atom lies between the two SiN_2Al rings. Compared to calcium, magnesium seems to be too small to fit between these four-membered SiN_2Al rings. As is apparent from Fig. 9, the "sandwich" in 66 is more open,

FIG. 9.
at AlI and

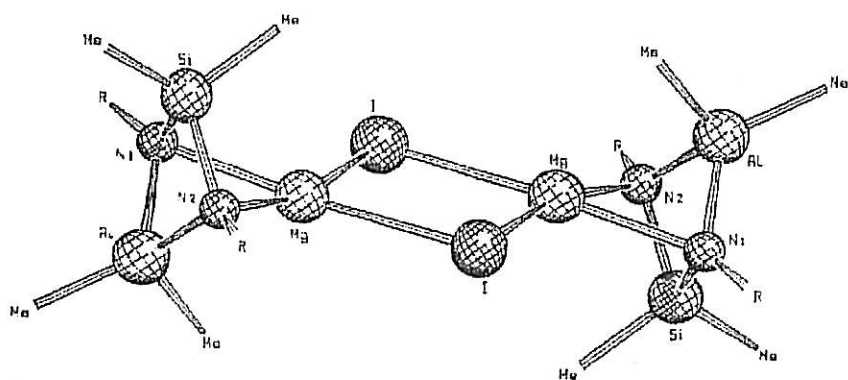


FIG. 7. The dimeric structure of $(\text{Me}_2\text{Si})(\text{Me}_2\text{Al})(\text{IMg})(\text{NtBu})_2$ (73). The coordination at the magnesium atom is distorted square-planar.

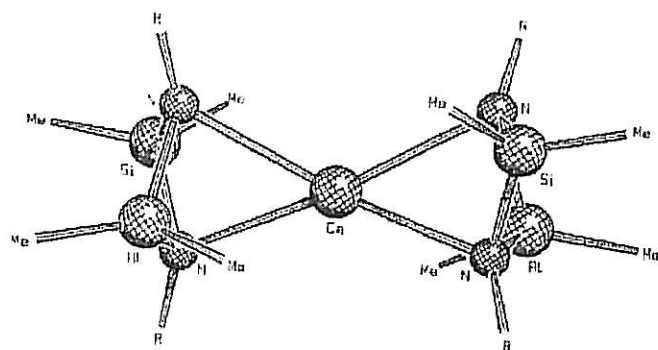


FIG. 8. The sandwich-structure of $\text{Ca}[\text{Me}_2\text{Si}(\text{NtBu})_2\text{AlMe}_2]_2$ (67).

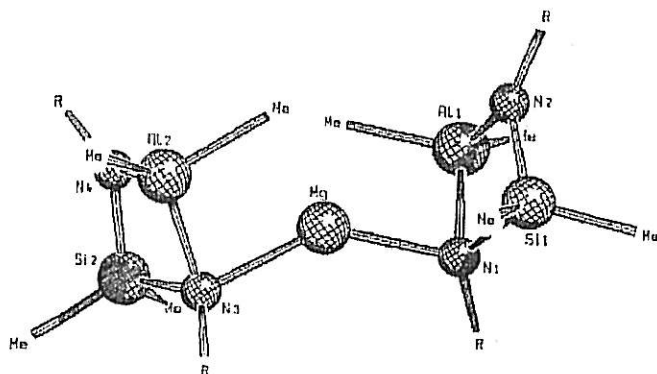


FIG. 9. Two-coordinate magnesium in $\text{Mg}[\text{Me}_2\text{Si}(\text{NtBu})_2\text{AlMe}_2]_2$ (66). The methyl groups at A11 and A12 have weak interactions with the magnesium atom (2.60 Å).

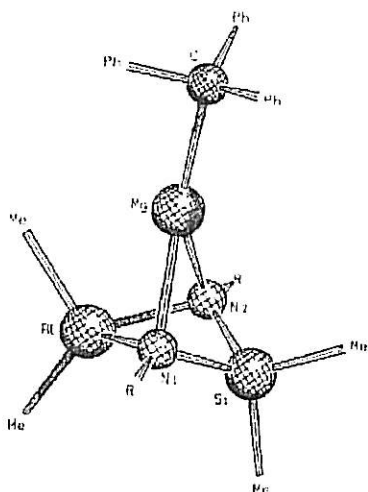
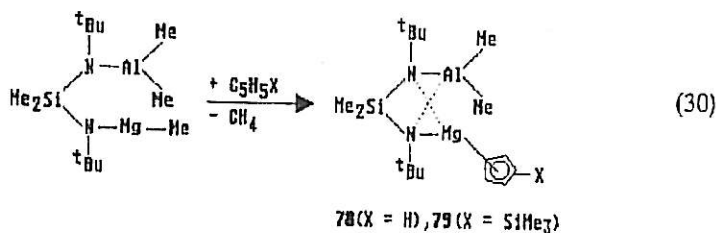


FIG. 10. The trigonal coordinated magnesium atom in $(t\text{BuN})_2(\text{Me}_2\text{Si})(\text{Me}_2\text{Al})\text{MgCPh}_3$ (**72**).

the magnesium atom being almost two coordinate (there is also some intramolecular methyl interaction (**72**,**73**)). Only the trityl compound in the series **68**–**72** is suitable for a crystallographic study. Figure 10 shows the skeleton of **72**, which again is a distorted N_2SiAlMg bipyramid (**73**). The magnesium atom is in trigonal-planar coordination by two nitrogen atoms and a carbon atom.

The distances within the SiN_2Al unit for the compounds **66**, **67**, **72**, and **73** vary in the range 1.70–1.79 Å for Si–N and 1.85–1.97 Å for Al–N. The aluminum–carbon distances are in the range 1.97–2.06 Å. The magnesium carbon distance in **72** is quite elongated [2.20(1) Å], a feature that might be related to some extent to the triphenylmethyl group.

It was of interest to determine which of the metal–carbon bonds, Mg–C or Al–C, in alkyl poly(metal)silazanes such as **68** would be the more reactive. This was probed by treating **68** with cyclopentadiene or trimethylsilylcyclopentadiene [Eq. (30)] (**73**).



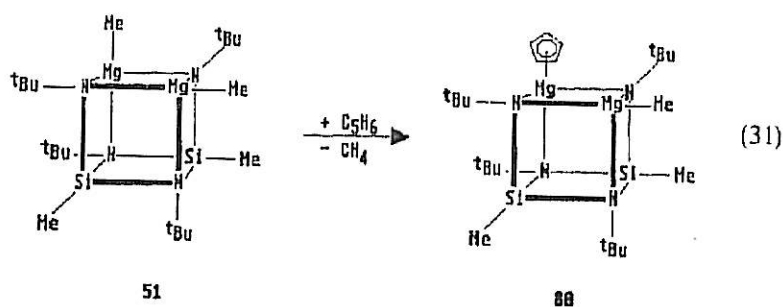
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NMR spectra showed that in these reactions the $\text{Me}_2\text{Si}(\text{NtBu})_2\text{AlMe}_2$ portion of the molecules remains unchanged, and in each case, the methyl group of the magnesium atom is replaced by the cyclopentadienyl ligand, indicated by a singlet in the ^1H -NMR spectra of **78** and **79** ($\delta = 6.35$ and 6.54 ppm for **78** and **79**, respectively).

The same type of reaction can be used to replace one of the two methyl groups in **51** by a cyclopentadienyl moiety, according to Eq. (31).



Compound **80** was unambiguously characterized by elemental analysis and ^1H NMR. The singlet of the cyclopentadienyl group has a comparable chemical shift ($\delta = 6.52$ ppm) to the same ligand in **78**. Compound **80** is a very rare example of a silazane containing two magnesium atoms with different organic ligands, and it resembles tetrameric cubanelike $(\text{cpMgOEt})_4$ (**74**).

The products of Eqs. (27) and (28) have been studied by single-crystal X-ray diffraction, and the skeleton core structures of the compounds **74**–**76** are illustrated in Figs. 11–13 (65). Surprisingly, **74** is monomeric even in the

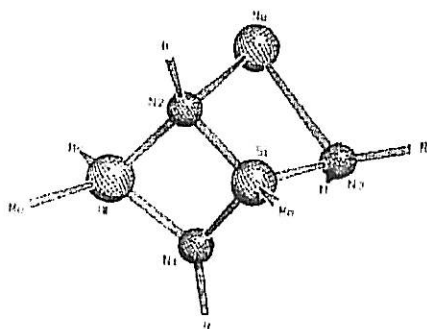


FIG. 11. The two fused four-membered rings in $\text{MeSi}(\text{NtBu})_3(\text{H})(\text{Na})\text{AlMe}_2$ (**74**). Even in the crystal, the sodium atom has no further contacts.

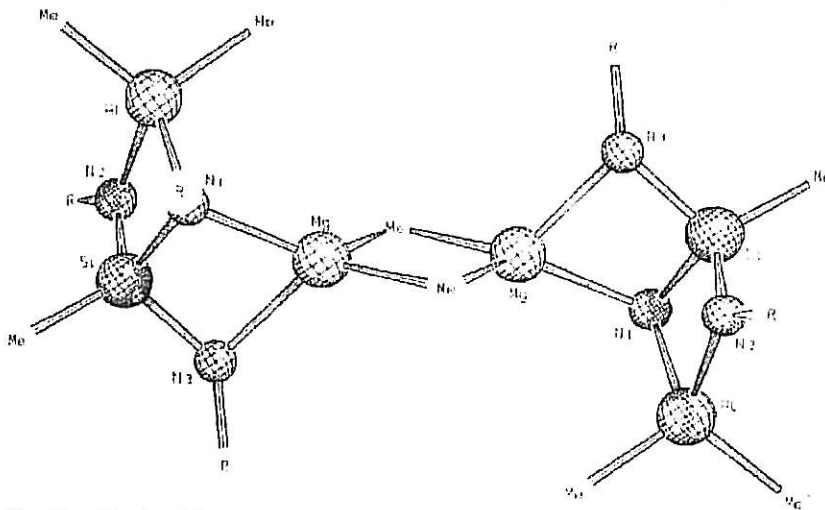


FIG. 12. Five fused four-membered cycles with magnesium atoms as spiro centers and methyl bridges in the dimeric $[(\text{MeSi})(\text{NtBu})_3(\text{AlMe}_2)(\text{H})\text{MgMe}]_2$ (75).

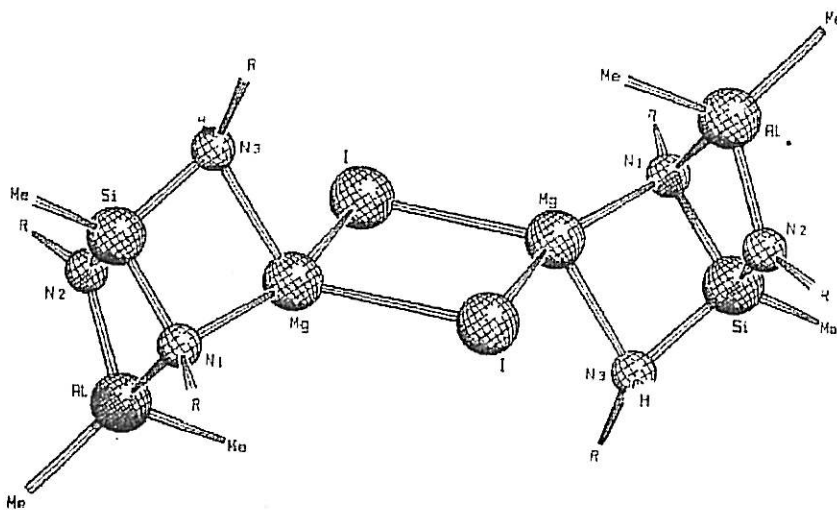


FIG. 13. The iodine compound corresponding to 75 (compare Fig. 12) $[(\text{MeSi})(\text{NtBu})_3(\text{AlMe}_2)(\text{H})\text{MgI}]_2$ (76).

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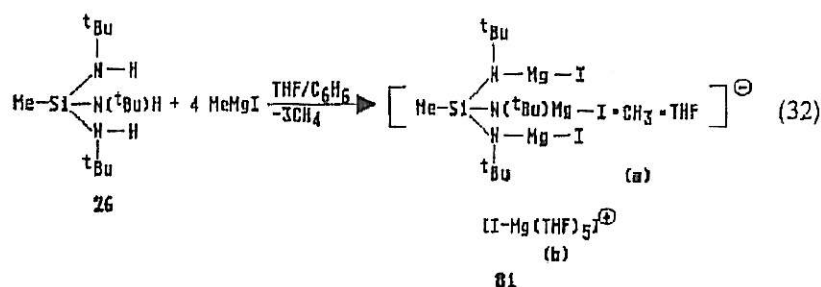
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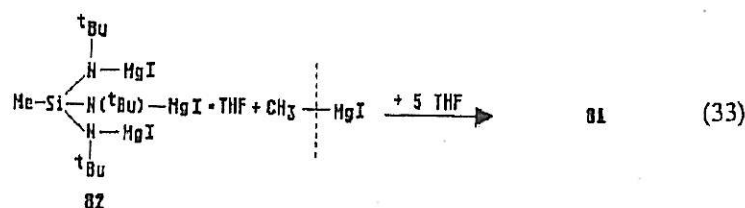
solid state, whereas **75** and **76** are dimeric through Mg-Me-Mg or Mg-I-Mg bridges. In both **75** and **76**, the magnesium atom adopts a distorted tetrahedral coordination.

Compound **74** is one of the few compounds yet characterized by X-ray diffraction that contains a two-coordinate sodium atom (61,75). The bonding distances to nitrogen, Na-N2 = 2.476(8) Å and Na-N3 = 2.523(9) Å, are comparatively long, indicating a decreased polar character of the bond. The common skeleton of compounds **74**-**76** is two edge-sharing four-membered rings that are almost mutually orthogonal. Whereas the methyl bridge in **75** is involved in a three-center two-electron bond [Mg-C = 2.24(2) Å], the iodine bridge in **76** uses two electron pairs [Mg-I = 2.771(1) Å and Mg-I' = 2.900(1) Å] and is unsymmetrical. The Mg-C distances compare well with the corresponding distances in Me₈Al₂Mg [2.21 Å (76)], as does the average Mg-I value (2.84 Å) in **76** with the corresponding Mg-I distance in **73** (2.83 Å).

To close this section, we describe our observations on the reaction of MeSi(NtBu[H])₃ (**26**) with the Grignard reagent CH₃MgI in benzene/tetrahydrofuran (**65**). According to Eq. (32), four equivalents of the Grignard reagent always react with the silazane (**26**), even if the molar ratios are changed.



We have been able to show by spectroscopic methods and by an independent preparation of MeSi(NtBuMgI)₃·THF that the reaction proceeds via the intermediate compound **82**, which seems to function as a very strong Lewis acid toward CH₃MgI [Eq. (33)] (**65**).



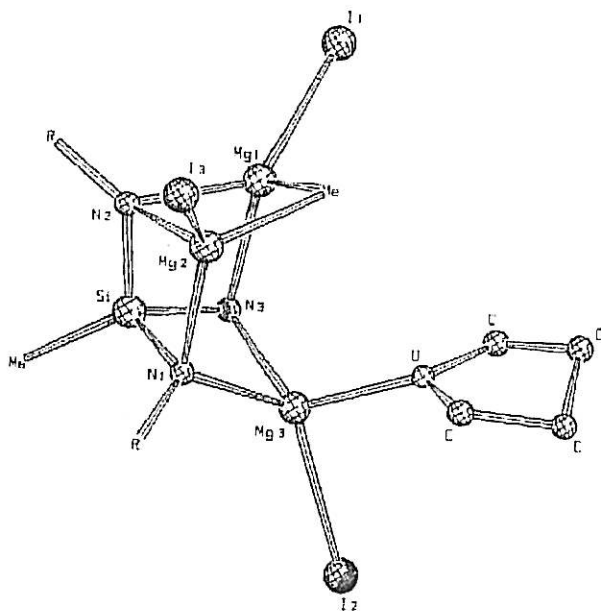


FIG. 14. The anion $\text{MeSi}(\text{NtBu})_3(\text{MgI}) \cdot \text{CH}_3 \cdot \text{THF}^-$ in compound 81. The methyl anion lies between the magnesium atoms Mg1 and Mg2. The magnesium atom Mg3 is stabilized by an added THF molecule.

The Grignard reagent is thus cleaved into a cation, $\text{IMg}(\text{THF})_3^+$, and the anion **81a**, which contains the methyl anion. We have been able to perform a structure determination on single crystals of **81**. In Fig. 14, the anion is represented as part of this structure. The two magnesium atoms coordinate the methyl group $[\text{Me}]^-$, and the third magnesium in the polycycle is coordinated by a tetrahydrofuran molecule. All metal atoms adopt fourfold distorted tetrahedral coordination. The skeleton of the polycycle is thus derived from a cube with one opened edge. The $\text{Mg}-\text{C}$ distances in **81** are of the order of 2.32 Å, which is in good agreement with other magnesium complexes that have R_3Mg^- or R_6Mg_2^- anions and a cation stabilized by a crown ether (77–80).

D. Intramolecular Bond Fluctuations

The alkyl and aryl metal silazanes and poly(metal) silazanes described so far are representatives of an unusual class of compound containing simultaneously electron-deficient and electron-rich centers that can interact with one another. The interaction may be of the two-electron donor type (Lewis acid/

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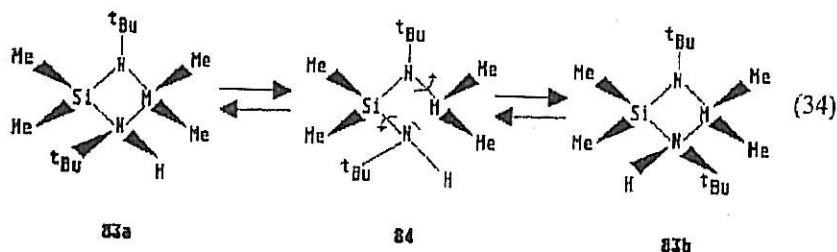
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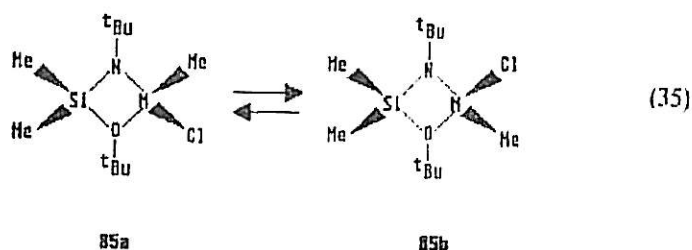
base interaction) or may be part of a two-electron three-center bond (see the two preceding sections). It is evident that such interactions can be quite labile, and that bond fluctuations, rotation of groups, inversions, etc. need to be considered, especially when several bases are competing for an acidic center in the molecule.

We have used temperature-dependent NMR spectroscopy in order to characterize the "movements" within these molecules. For reference, we generally start with the structures determined in the solid, because they should always represent an energy minimum in a fluctuation process. Such intramolecular rearrangements are not only observed in silazanes of the type described in this article, but are common to all metal-containing silazanes (56,81). The following examples have been selected to illustrate different aspects of these "motions."

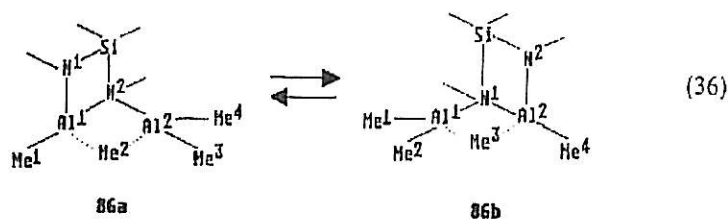
The chelates 31–34 have been extensively studied with respect to intramolecular rearrangements (70). From a comparison of the (N–H) frequencies in the different compounds, a series of increasing Lewis acidity of the MMe_2 group can be established: $TiMe_2 < GaMe_2 \approx InMe_2 < AlMe_2$. The λ^4 N–M bond in these compounds is subject to opening, and its frequency can be followed by temperature-dependent 1H NMR techniques. Intra- and intermolecular hydrogen transfers can be excluded by comparing the rate constants k_H for 31–34 with k_D of the deuterated compounds. The free energy of activation for bond breaking and the rotation of the $NHtBu$ group is of the order 61–84 kJ/mol at 298 K. The process can be described best by the following model [Eq. (34)].



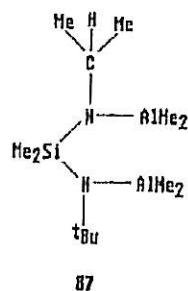
The enantiomeric forms 83a and 83b are related by the intermediate 84, in which rotation around both the N–M and the Si–N bonds may occur. Rotation around the Si–N bond is associated with an inversion at the pyramidal nitrogen atom. In a similar manner, in the chelates 46–48 the breaking of the O–M bond is accompanied by rotation around the respective bonds, and a very rapid transformation of one enantiomeric form (85a) into the other (85b) is observed [Eq. (35)] (65).



A very interesting "ligand exchange" at the metal atoms is observed in compounds of types 35–38. The two metal atoms within the molecule are in competition for the two nitrogen atoms, of which only one is attainable for steric reasons. As a consequence, one aluminum atom becomes electronically unsaturated and has to participate in a three-center two-electron bond (see also Fig. 2). This bonding situation can be rapidly inverted by an exchange of ligands as shown in Eq. (36) for compound 35 (64).



We have been able to demonstrate by synthesizing the unsymmetrical compound 87 and recording its temperature-dependent ^1H NMR spectra that, in addition to the equilibrium between the enantiomers 86a and 86b, further ligand rearrangements need also to be considered.



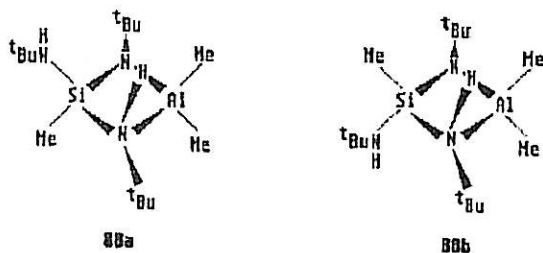
The model presented so far indicates a difference between the methyl groups Me^1 and Me^4 compared with Me^2 and Me^3 . This is the case for compound

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35, which has two discrete signals at lower temperatures for the four methyl groups of aluminum. At higher temperatures ($> -40^{\circ}\text{C}$) the two signals collapse to a single resonance, indicating "free rotation" of the AlMe_2 groups around the $\text{Al}-\text{N}$ bond. According to the structures drawn in Eq. (36), the whole process can be described as follows: (1) At high temperatures the aluminum atoms Al^1 and Al^2 exchange ligands N^1 and N^2 and may be bridged by methyl groups Me^1-Me^4 . (2) At lower temperatures the exchange of N^1 and N^2 continues, whereas the methyl groups are separated into terminal (Me^1 and Me^4) and bridging (Me^2 and Me^3) groups. (3) At very low temperatures (-70°C in compound 87) all movement is stopped, and the enantiomers 86a and 86b no longer interconvert at rates fast enough to be observed on the ^1H NMR time scale (64).

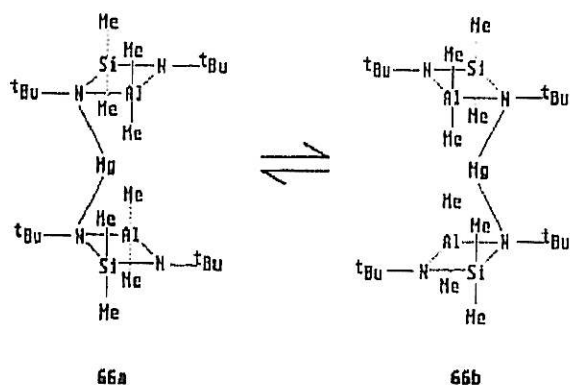
^1H -NMR techniques have also been used to show that the aluminasilazane 42 exists in two different conformers (65). At 308 K in toluene, the spectrum of 42 may be interpreted as a 3:1 mixture of the isomers 88a and 88b. If the temperature is raised to 365 K, however, the six signals for *t*Bu groups (three for 88a and three for 88b) collapse to two in a ratio 1:2, indicating that the



two *t*Bu groups within the molecule have now become chemically equivalent and a mixture of isomers is no longer observed. The best explanation for these observations seems to be that a rapid intramolecular ligand exchange of the *t*BuNH groups occurs at the aluminum atom, making impossible a distinction between the isomers 88a and 88b. Similar ligand exchanges also appear to occur in the metalla derivatives 74–76 (65).

The final example of bond rearrangement in solution is the magnesium amide 66. Examination of Fig. 9 shows that the nitrogen atoms $\text{N}1$ and $\text{N}3$ are coordinated to the magnesium, whereas the atoms $\text{N}2$ and $\text{N}4$ do not interact with the metal (the molecule has the approximate C_2 point symmetry). The *t*Bu groups at $\text{N}1$ and $\text{N}3$ should thus be different from those at $\text{N}2$ and $\text{N}4$, and therefore two resonances should be observed for *t*Bu in the ^1H -NMR spectrum. This, however, is definitely not the case, and the spectrum of 66 shows only one signal in the *tert*-butyl region down to -88°C (the methyl

groups of aluminum and silicon are all different, as expected) (73). To explain these observations it is necessary to assume a "rapid rocking" of the four-membered rings with respect to the magnesium, in which the nitrogen atoms N2 and N4 displace the nitrogen atoms N1 and N3 from the coordination sphere of the magnesium [see also Eq. (37)].



IV CONCLUSION

The sophisticated silazanes 25-29 can be used to stabilize (in a coordinative sense) metal atoms that have further organic ligands. There is, of course, no limit to other metallic or nonmetallic elements that can be incorporated in such silazanes (23,56,81). The organic groups attached to the metals should exhibit reactivity patterns different from those of Grignard reagents or aluminum alkyls. Little comparative work in organic synthesis has yet been carried out in this field, but studies are planned for the future. From a structural point of view, these compounds have a very diverse and interesting coordination chemistry. The very prominent bond fluctuations observed for these molecules are often due to competitive reactions between bases for the same acidic center. Multinuclear NMR experiments in solution and in the solid phase are planned for these compounds to complete the investigations.

ACKNOWLEDGMENTS

I am indebted to my co-workers for their help in exploring this field of chemistry. Their names can be found in the references. I also express my thanks to the people of the Fonds der Chemischen Industrie, who have supported our work. Finally I thank Dr. P. G. Harrison, Nottingham, England, for critically reading the manuscript.

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