ELSEVIER

Coordination Chemistry Reviews
189 (1999) 199–278

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Chemistry of the organodiamides of magnesium, aluminum and mixed Mg–Al systems. A review of the heterocumulene reactivity on the Mg–Al centers

Chung-Cheng Chang [a,b,*], Mohammed Sardar Ameerunisha [a]

[a] *Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan, ROC*
[b] *National University of Kaohsiung in preparation, Kaohsiung, Taiwan, ROC*

Received 13 January 1999; accepted 29 March 1999

Contents

Abstract

The organoamides of magnesium, aluminum and Al–Mg bridged oligomers demonstrate an exceptional utility and a bright future for further research, for example, as reagents in organic synthesis and potential precursors for aluminum nitride in semiconductor systems and ceramics. Some transformations that can be achieved with these reagents include the reduction of ketones and aldehydes, ring opening polymerization of epoxides, ortho magne-

---

[*] Corresponding author.

PII: S0010-8545(99)00135-6

siation, reductive α-substitution of sulfoxides etc. The ideal reagents for the catalytic reactions mentioned above are the coordinatively unsaturated ones. In spite of their interesting structural features and reactivity pattern the chemistry of these noteworthy main group metal complexes has not been reviewed adequately for a long time. Hence, a critical review article will help scientists push the current research to a higher level. The main focus is on the heterocumulene reactivity and this is compared with the same in transition metal complexes.

Keywords: Metal amides; Magnesium; Aluminum

---

1. Introduction

Organomagnesium chemistry is dominated by the synthesis and usage of halogenoorganomagnesium derivatives which are popularly known as the Grignard reagents. Many papers appear concerning this subject, although all of these relate to synthetic applications in organic chemistry [1–3]. Hauser bases (R_2NMgBr) and (Amido) magnesium (R_2NMgX, where X = organyl, amide, alkoxide etc.) are well known and this chemistry is becoming an increasingly active area of study of reagents in synthesis [4–6]. *o*-Magnesiation followed by quenching with carbon dioxide, acidification and esterification yielded *o*-substituted esters. *o*-Magnesiation has some advantages over *o*-lithiation in stability at elevated temperatures, yields etc. For example, diisopropylamido and tetramethylpiperidino magnesium amide bases are stable in refluxing THF for hours and in this way differ markedly from the corresponding lithium amides which rapidly decompose at this temperature [7–10]. Antiselectivity in aldol reactions can be achieved using the Hauser base 'chloromagnesium diisopropylamide' ($^iPr_2NMgCl$) under thermodynamic conditions in good to high yields, whereas due to the retroaldol reaction the yields are very low in the case of the corresponding lithium derivatives [11]. Magnesiation of indole derivatives with magnesium amides followed by treatment with benzaldehyde or iodine gives the corresponding substituted indoles in excellent yields. The method seems to have potentially wide applications for the functionalization of indoles at the 2-position. It has been shown that the magnesium amide improves the yields of the reductive α-substitution of sulfoxides by promoting the generation of the sulfur stabilizing carbonium ion [12]. Sometimes *o*-lithiations can be complimented by *o*-magnesiations neatly [13].

Structures and properties of the alkylaluminium amides $R_2AlNR'R''$ have been the subject of considerable attention for many years. There has been renewed interest recently due to the application of some of these compounds as precursors to AlN and AlN containing ceramics [14–18]. A variety of electronic, refractory and structural applications exist for AlN systems because of the useful properties such as low dielectric constants, high thermal shock resistance, mechanical toughness and spall resistance [19]. Aluminum compounds are proven catalysts in the ring opening living polymerization of oxiranes [20]. Cationic aluminum reagents are naturally electron-deficient and with the choice of loosely coordinating ligands they may behave as coordinatively unsaturated compounds.

The heterocyclic four-membered ring systems formed by Group II and III metals with one electron alkyl and aryl donors exhibit unusual structural parameters [21]. The study of the relative stereochemical importance of metal–metal interactions, steric effects, dative ligand–metal π bonding, the electron distribution about the bridging atoms and intermolecular forces within the crystal lattice will provide realistic models for the extensive synthetic chemistry involving Group II and III organometallic complexes as intermediates. The dialuminum organomagnesium complexes $Mg[Al(OMe)_2Me_2]_2$ and $Mg(AlMe_4)_2$ are among the best known examples of the mixed metal organoaluminum complexes and are applied as catalysts in the polymerization of ethylene [22]. Although polynuclear aluminum magnesium complexes have been of chemical interest for many years, few papers on this subject exist.

Carbon dioxide is one of the most common carbon resources, but its activation is essential for chemical fixation and utilization because of its inertness under ordinary conditions. In recent years, the reactions of heterocumulenes with various organometallic compounds have been explored extensively as they serve as convenient models for the reactions of CO_2 [23]. Carbon dioxide was initially thought to be a poor ligand but now it has demonstrated surprising versatility by exhibiting a great variety of coordination modes in its metal complexes [24]. The use of carbon dioxide as a raw material for chemical syntheses is an ecologically and economically valuable extension to the carbon sources used at the present time [25]. The insertion of carbon dioxide into a metal–carbon bond is probably the most fascinating subject as it leads to carbon–carbon bond formation and potentially to further chain lengthening processes. Apart from the value of the products from CO_2 fixation like methanol, formate, oxalate other organic acids and methane, the removal of CO_2 from industrial emissions in order to reduce greenhouse effects are the main conditions that prompt research in their area [26].

The CO_2 inserted aluminum–magnesium complexes can provide useful information in understanding the mechanism of the Grignard–CO_2 intermediate (Eq. (1)). These complexes have a strong relevance to the Grignard intermediate and their reactions with CO_2 may proceed through a similar intermediate [27]:

$$\mathrm{RMgX} + \mathrm{CO_2} \rightarrow \underset{\mathrm{X=halide}}{\mathrm{RCO_2MgX}} \xrightarrow{\mathrm{H^+}} \mathrm{RCOOH} \tag{1}$$

The insertion reactions of carbon dioxide and its isoelectronic analogues such as isocyanates, isothiocyanates, carbodiimides and carbondisulfide into M–X (X = C, N, O, H) bonds have been studied extensively [28]. Carbon disulfide has extensive uses both in organic and organometallic chemistry.

Due to excellent bridging character of amides, they can react easily with organoaluminum or magnesium complexes to form organoamides of aluminum and magnesium which are the dimeric, or oligomeric complexes of both homonuclear and heteronuclear species. It has been found that the insertion of heterocumelens into M–N bonds is quite easy in the complexes of polynuclear aluminum and magnesium diamides. Furthermore, the heteropolynuclear diamides are much more reactive towards CO_2 and CS_2 than alkyl magnesium or alkyl aluminum complexes. It would be advantageous to have a better understanding of the chemistry of the organoamides of magnesium, aluminum and the Mg–Al polynuclear diamides in solution and solid state for further improved activity in organic synthesis. In this review article we shall highlight the synthetic approaches to obtain these complexes, their structure–activity relationships, and their reactivity towards the heterocumulenes like carbon dioxide, isocyanates, isothiocyanates, carbodiimides and carbondisulfide. We shall also compare the nature of insertion in this complexes with that in the transition metal complexes which has been better reviewed in recent years.

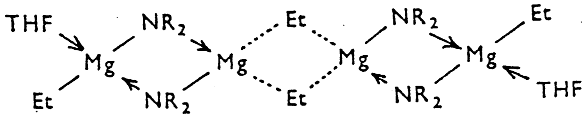
2. Organomagnesium diamides

2.1. Magnesium diamides

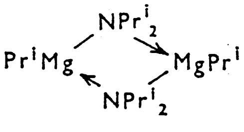
The synthesis, structures and catalytic properties of the magnesium diamides are discussed in this section. There were relatively few structural reports for neutral magnesium amide compounds in the solid state until recently. Most of the structures involve 4-coordinate magnesium centers. A magnesium diamide is generally prepared by following the procedure (Eq. (2)) of Coates and Rigley who reported the reactions of magnesium alkyls with organic functional groups like secondary amines [29]:

$$R_2Mg + R'_2NH \rightarrow RH + (RMgNR'_2) \qquad (2)$$

where R and R′ groups were small, for example $R = Et$, $R' = Me$, insoluble products (apparently polymeric) were obtained. With $R' = Et$, **(1)** $R = {}^iPr_2$, **(2)** products were obtained which contained complexed diethyl ether (used as a solvent) which could not be removed, but was displaced by tetrahydrofuran. Although the amino alkyl dimers described here contain three coordinate magnesiums, it is possible that they associate in the crystalline state despite steric hindrance.



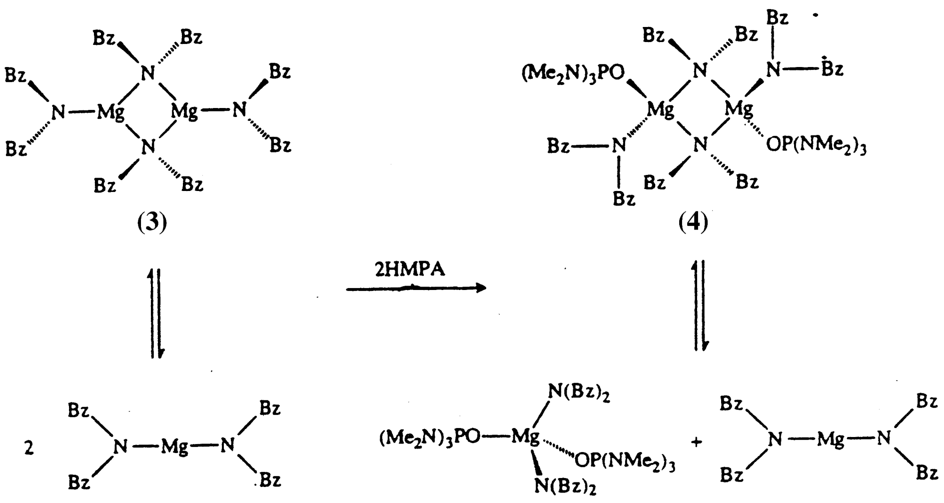
(1)



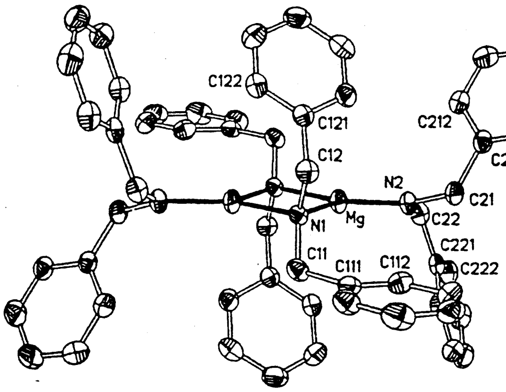
(2)

Mulvey et al. reported the preparation of bis(amido)magnesium complex $[\{\{(PhCH_2)_2N\}_2Mg\}_2]$ (**3**) by the reaction of commercial Bu_2Mg with two molar equivalents of dibenzylamine in toluene [30]. A combination of NMR, X-ray and theoretical data has been used to elucidate the nature of the bis(Dibenzylamido) system. Crystalline compound **3** is dimeric with three coordinate magnesium and the ^1H NMR spectra indicate that this aggregation is retained in arene solution but is in equilibrium with the two coordinate monomer as shown in Scheme 1. Coordinative unsaturation of magnesium in **3** leads to shorter terminal Mg–N bonds.

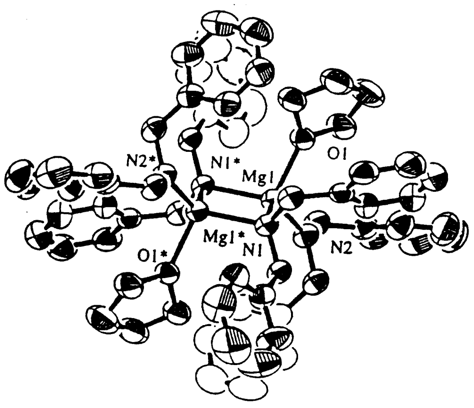
Weak solvation of the metal center by THF or HMPA is possible with the retention of the dimeric framework giving coordination expansion at magnesium which is supported by the relatively long Mg–O(HMPA) bonds and the nearly linear P–O–Mg bond angles. The following six compounds have been isolated and characterized from the systems studied: $\{[[(PhCH_2)_2N]_2Mg]_2\}$ (**3**); $\{[[(PhCH_2)_2N]_2Mg{\cdot}THF]_2\}$ (**5**); $\{[[(PhCH_2)_2N]_2Mg{\cdot}HMPA]_2\}$ (**6**); $\{[(PhCH_2)_2N]_2Mg{\cdot}(HMPA)_2\}$ (**7**); and $\{[(PhCH_2)_2N]_2Mg{\cdot}TMEDA\}$ (**8**).


Bz
N
Mg
(3)
(4)
(Me$_2$N)$_3$PO
OP(NMe$_2$)$_3$
2HMPA
2
N(Bz)$_2$
+

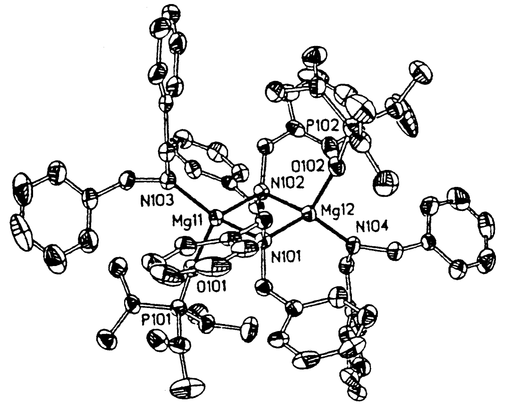
Scheme 1.


C122
C121
C12
C212
C211
N2
C21
C22
N1
Mg
C11
C111
C112
C221
C222

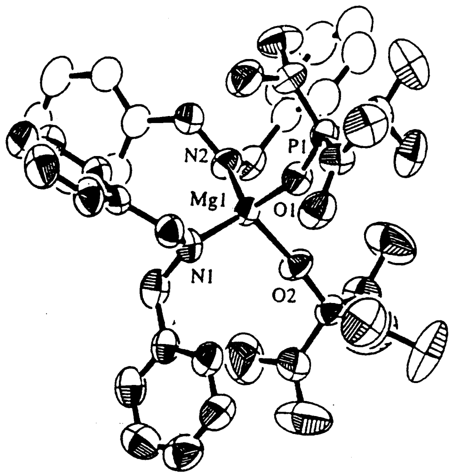
(3)


N2*
N1*
Mg1
O1
O1*
Mg1*
N1
N2

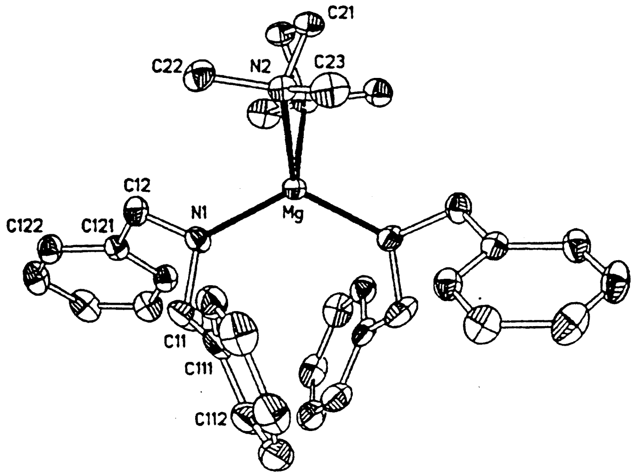
(5)


P102
O102
N102
N103
Mg11
Mg12
N104
N101
O101
P101

(6)


N2
P1
Mg1
O1
N1
O2

(7)

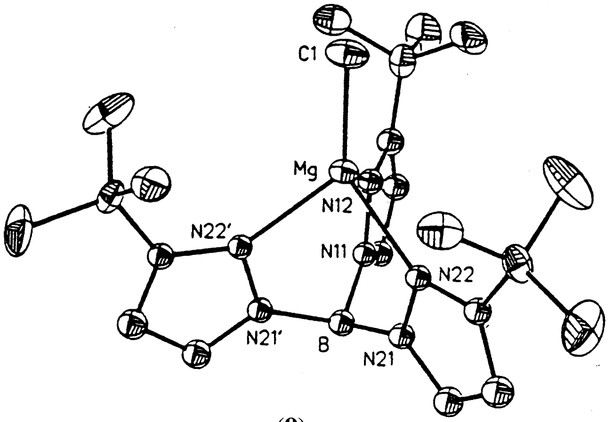

C21
C22
N2
C23
C12
N1
Mg
C122
C121
C11
C111
C112

(8)

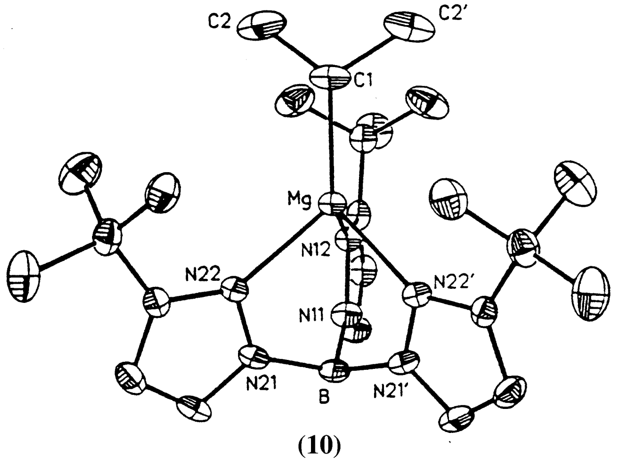
G. Parkin et al. reported [31] the synthesis of monomeric [tris(pyrazolyl)hydroborato] magnesium alkyl derivatives $\{\eta^3\text{-HB(3-}{}^t\text{Bupz)}_3\}\text{MgR}$ and $\{\eta^3\text{-HB(3,5-Me}_2\text{Pz)}_3\}_2\text{MgR}$ ($\text{R} = \text{CH}_3$, CH_2CH_3, $(\text{CH}_2)_3\text{CH}_3$, $\text{CH(CH}_3)_2$, $\text{C(CH}_3)_3$, CH_2SiMe_3, CH=CH_2, C_6H_5) by the metathesis of R_2Mg with $\text{M}\{\text{HB(3,5-R}_2\text{Pz)}_3\}$, ($\text{3,5-R}_2\text{Pz} = \text{3-}{}^t\text{BuPz}$, $\text{3,5-Me}_2\text{Pz}$; M = K, Tl) as shown in Eq. (3):

$$\text{R}_2\text{Mg} + \text{M}\{\text{HB(3,5-R}_2\text{pz)}_3\} \xrightarrow{\text{-[MR], (M = K, Tl)}} \{\eta^3\text{-HB(3,5-R}_2\text{pz)}_3\}\text{MgR} \qquad (3)$$

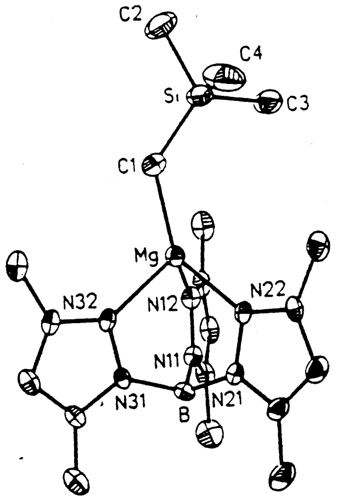
The molecular structures of the complexes $\{\eta^3\text{-HB(3-}{}^t\text{Bupz)}_3\}\text{MgCH}_3$ (**9**) $\{\eta^3\text{-HB(3-}{}^t\text{Bupz)}_3\}\text{MgCH(CH}_3)_2$ (**10**) and $\{\eta^3\text{-HB(3-}{}^t\text{Bupz)}_3\}\text{MgCH}_2\text{Si(CH}_3)_3$ (**11**) have been determined by X-ray diffraction, which shows that in each case the complexes are monomeric with 4-coordinate magnesium centers and η^3-coordinate tris(pyrazolyl)hydroborato ligands.



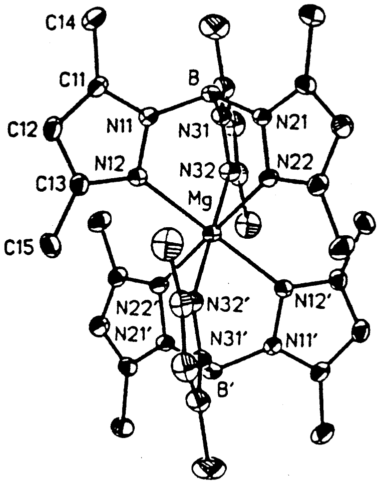
(9)



(10)



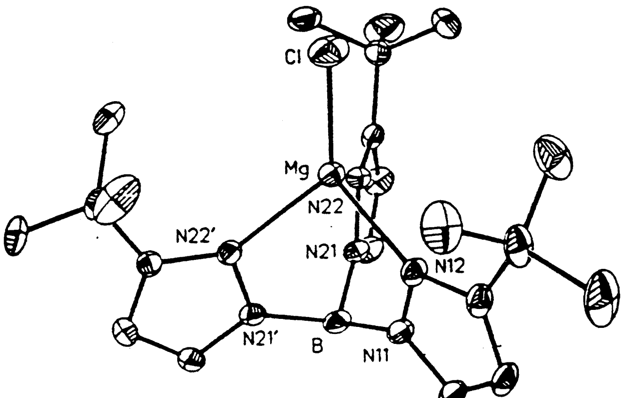
(11)



(12)

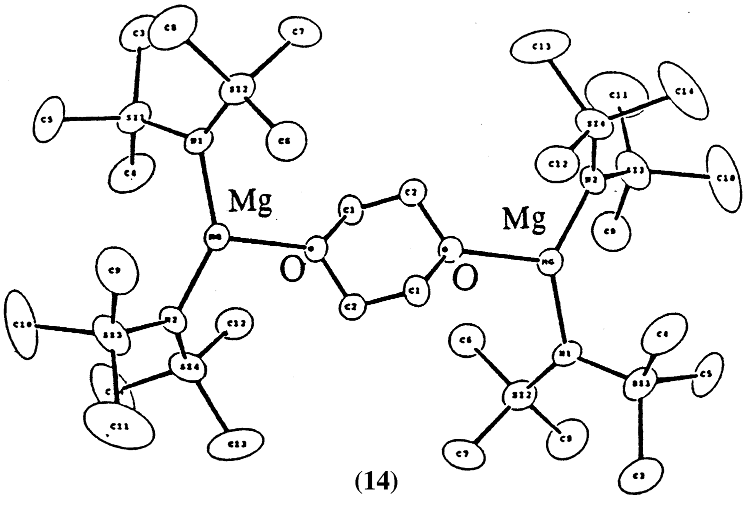
The complexes $\{\eta^3$-HB(3,5-Me$_2$Pz)$_3\}$MgR undergo ligand distribution reactions analogous to the Schlenk equilibrium to give the 6-coordinate sandwich complex $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}_2$Mg (**12**). In contrast, the 4-coordinate magnesium alkyl derivatives supported by the more sterically demanding tris(3-*tert*-butylpyrazolyl)hydroborato ligand, $\{\eta^3$-HB(3-^{t}Bupz)$_3\}$MgR, are stable with respect to the formation of $\{\eta^3$-HB(3-^{t}Bupz)$_3\}_2$Mg. The alkyl complexes $\{\eta^3$-HB(3-^{t}Bupz)$_3\}$MgR are useful precursors for a variety of other 4-coordinate complexes including $\{\eta^3$-HB(3-^{t}Bupz)$_3\}$MgX (X = C$\equiv$CC$_6$H$_5$, C$\equiv$CSiMe$_3$, OEt, O^{i}Pr, O^{t}Bu, OPh, OCH$_2$SiMe$_3$, OSiMe$_3$, OO^{t}Bu, NHPh, SH, SCH$_3$, Cl, Br, I, NCO, NCS) [32]. The reaction of the magnesium (trimethylsilyl)methyl complex $\{\eta^{3-}$HB(3-

^{t}BuPz)$_3$}MgCH$_2$SiMe$_3$ with O$_2$ gives the trimethylsiloxide derivative {η^3-HB(3-^{t}Bupz)$_3$}MgOSiMe$_3$ and formaldehyde as a result of facile cleavage of the Si–C bond upon autooxidation. The molecular structures of {η^3-HB(3,5-Me$_2$Pz)$_3$}$_2$Mg (**12**) and {η^3-HB(3-^{t}Bupz)$_3$}MgCl (**13**) have been determined by X-ray diffraction.



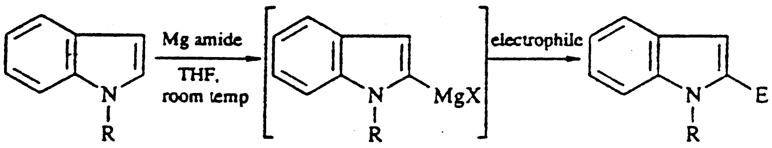
(**13**)

Chang et al. reported the reaction of diethylmagnesium dioxane adduct solution with 1,1,1,3,3,3-hexamethyldisilazane{(CH$_3$)$_3$SiNHSi(CH$_3$)$_3$} for the synthesis of {[(CH$_3$)$_3$ Si]$_2$N}$_2$MgO(CH$_2$CH$_2$)$_2$OMg{N[Si(CH$_3$)$_3$]$_2$}$_2$ (**14**) after sublimation at 100°C [33]. This alkoxomagnesium silylamide in the solid state contains unprecedented three-coordinated magnesium and oxygen atoms in a triangular shape. The molecule belongs to a C_1 symmetry and consists of a pair of {[(CH$_3$)$_3$Si]$_2$N}$_2$Mg subunits associated with a dioxane. The conformation of the dioxane fragment is a chair form with four carbon atoms in a plane, one oxygen atom above and the other below the plane.



(**14**)

Magnesiation of indoles with magnesium amide bases was reported [34] in 1996, wherein 1-substituted indole derivatives are deprotonated with Hauser bases (R_2NMgBr) or magnesium diamide [$(R_2N)_2Mg$] to give magnesioindoles, which are then reacted with electrophiles like benzaldehyde or iodine to give the corresponding substituted indoles in excellent yields as shown in Scheme 2. The phenylsulfonyl group appeared to be a promising protecting and activating group for this magnesiation reaction.

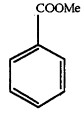
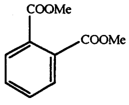
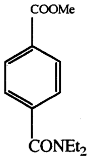
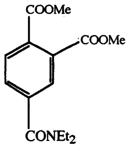
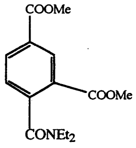
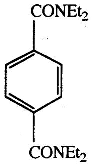
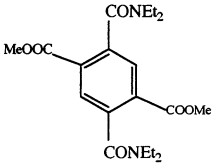
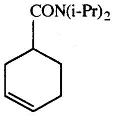
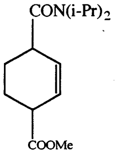
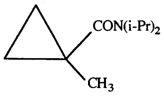
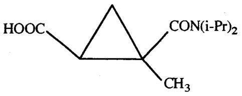
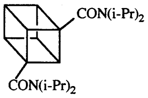
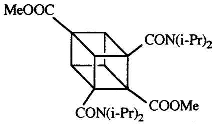
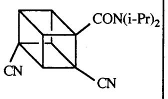
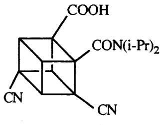


Scheme 2.

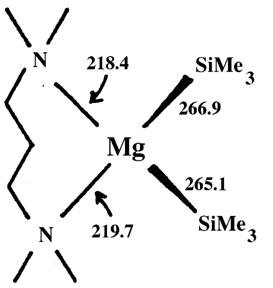
In 1989, Eaton et al. reported [35] the synthesis and uses of bis(2,2,6,6-tetramethylpiperidino)magnesium, $(TMP)_2Mg$ or 2,2,6,6-tetramethylpiperidinomagnesium bromide, TMPMgBr. 2,2,6,6-Tetramethylpiperidine (TMPH) on reaction in refluxing tetrahydrofuran with ethylmagnesium bromide or dibutyl magnesium gave respectively, the clear solutions of TMPMgBr or $(TMP)_2Mg$. Solutions of the corresponding diisopropylamine (DAH) derivatives were obtained similarly. Diisoprpylamido and tetramethyl piperidinomagnesium amide bases so prepared, are stable in refluxing tetrahydrofuran for hours and in this way differ markedly from the corresponding lithium amides which rapidly decompose at this temperature. The ability to employ these magnesium amide bases in refluxing THF is important, particularly in reactions with materials of otherwise low solubility or low reactivity. Many organic transformations are accomplished by Eaton et al. with these reagents which are tabulated in Table 1. The reactions of sulfoxides bearing α-hydrogen(s) ($RSOCHR^1R^2$: R = alkyl or aryl; R^1, R^2 = H, alkyl or aryl with Grignard reagents (R^3MgBr; R^3 = Et, Ph, or vinyl) in the presence of the diisopropylaminomagnesium reagent results in the formation of the corresponding sulfides ($RSCR^1R^2R^3$) including a tertiary alkyl sulfide in moderate to good isolated yields [36].

The results have shown that the magnesium amide improves the yields of the reductive α-substitution of sulfoxides by promoting the generation of the sulfur stabilizing carbonium ion **15** (Scheme 3) which may be possible with only a Grignard reagent, and that the present reaction offers an efficient method for the α-alkylative reduction of sulfoxides to sulfides. Addition of magnesium metal to a solution of $(Me_3Si)_2Hg$ in 1,3-bis(dimethylamino)propane/ether gave [$(Me_3Si)_2Mg(tmpda)$] (**16**) which has a monomeric structure with the Mg atom tetrahedrally coordinated by the silicons of the two anions and the two nitrogens of the chelating tmpda ligand. [37]. Treatment of $HN(SiMe_3)_2$ in heptane with dialkylmagnesium results in the initial formation of $[(Me_3Si)_2NMgCH(CH_3)CH_2CH_3]_2$ (**17**) followed by [$\{(Me_3Si)_2N\}_2Mg$]. The structure of the intermediate is that of a dimer based on

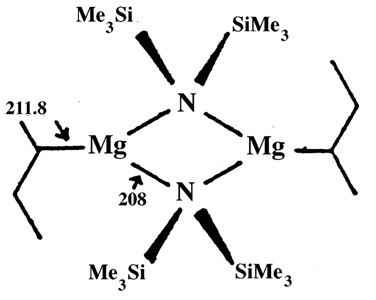
Table 1
Organic transformations reported by Hauser et al. using $(TMP)_2Mg$ or TMPMgBr

Reactant	$\xrightarrow{(TMP)_2Mg,\ CO_2,\ CH_2N_2}$ **Product**
	
	 
	
	
	
	
	(TMPMgBr) 

a planar Mg_2N_2 ring with bridging amido nitrogens and with 222 symmetry; the trigonal coordination of the Mg atom is completed by the *s*-butyl anion.

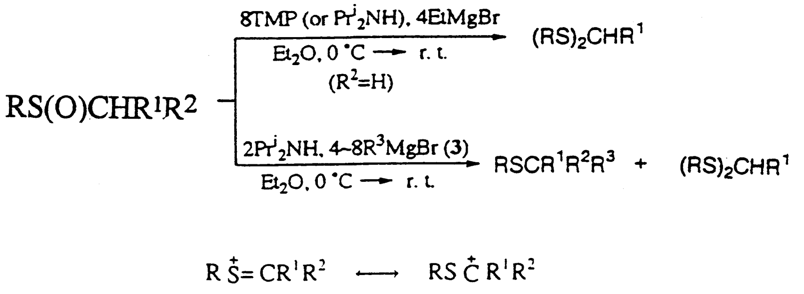


(16)



(17)

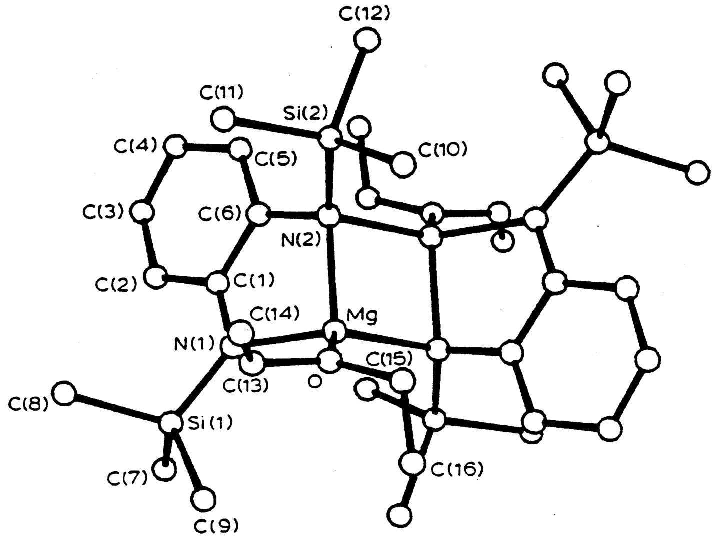
The reaction of the diamine $o\text{-}C_6H_4[N(SiMe_3)H]_2$ with dibutyl magnesium yielded $[Mg\{\mu\text{-}N(SiMe_3)C_6H_4N(SiMe_3)\text{-}o\}(OEt_2)]_2$ (**18**) with two $o\text{-}N(SiMe_3)C_6H_4N(SiMe_3)$ ligands bridging two magnesium atoms and a terminal OEt_2 ligand completing a distorted tetrahedral environment around each Mg atom [38]. Thermally stable and monomeric magnesium amide MgL_2 (L = N(8-quinnolyl)($SiMe_3$) (**19**) has been reported by Raston et al. in 1991, which was prepared



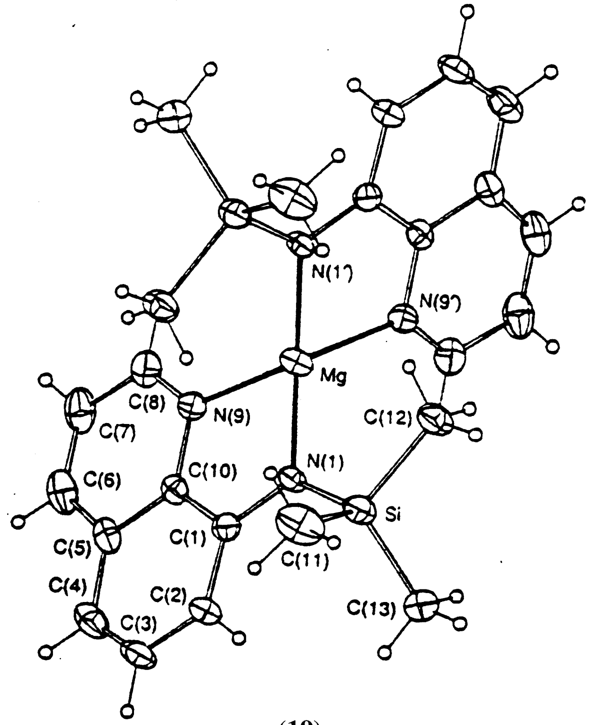
(15)

Scheme 3.

by the reaction of Mg^{n}Bu^{s}Bu with 8-(trimethylsilylamino)quinoline. The magnesium was found to have distorted terahedral geometry. A similar compound, ethyl(1,3,6,8-tetra-*tert*-butylcarbazolyl)magnesium (**20**) was obtained as its monomeric tetrahydrofuran adduct by the reaction of 1,3,6,8-tera-*tert*-butylcarbazole with diethylmagnesium in THF.

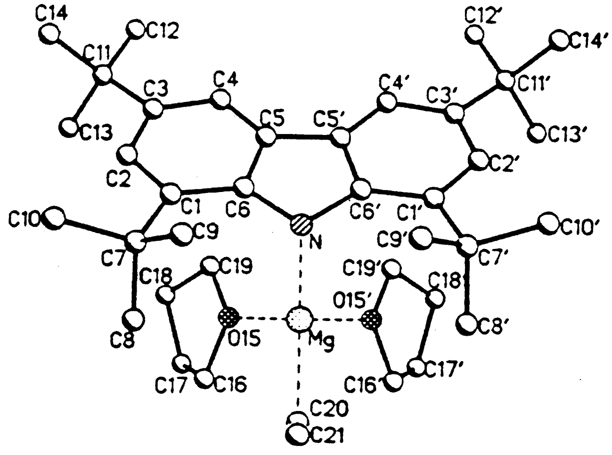


(18)

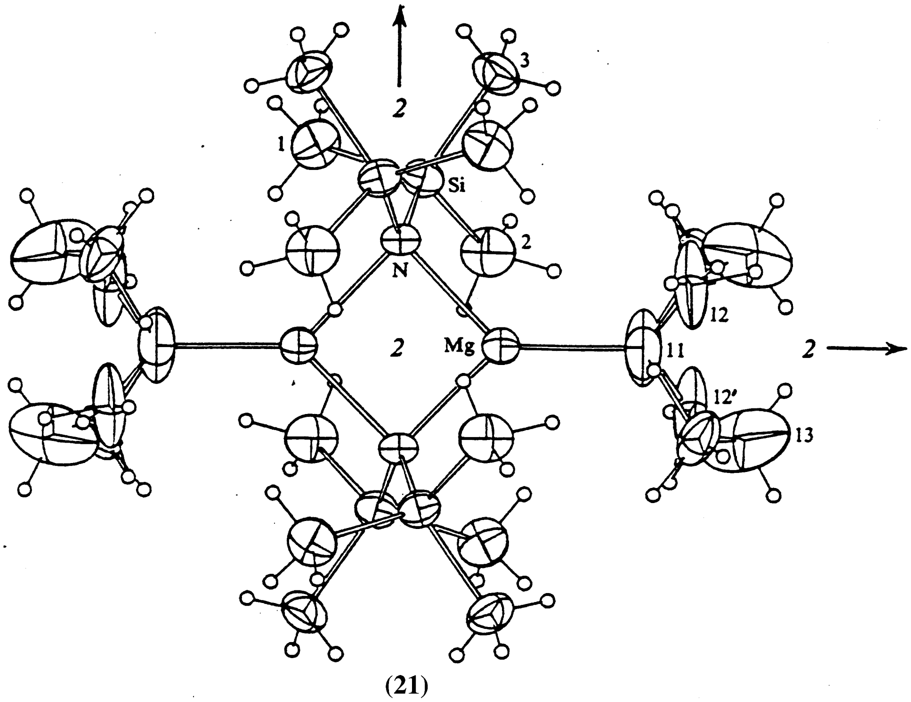


(19)

Treatment of hexamethyldisilaazane with $\mathrm{MgBu^sBu}$ results in the formation of $[\mathrm{Mg^sBu\{\mu\text{-}N(SiMe_3)_2\}}]_2$ (**21**) [39]. The crystal lattice was found to be comprised of discrete molecules with the amido ligands bridging three coordinate metal centers. Of particular novelty is the selective metallation of HN″ using $\mathrm{MgBu^sBu}$ yielding exclusively **21** as the amido-*S*-butyl complex rather than the corresponding *n*-isomer.

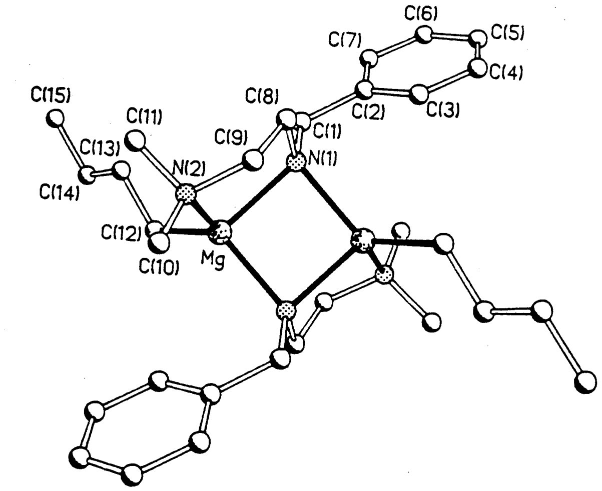


(20)

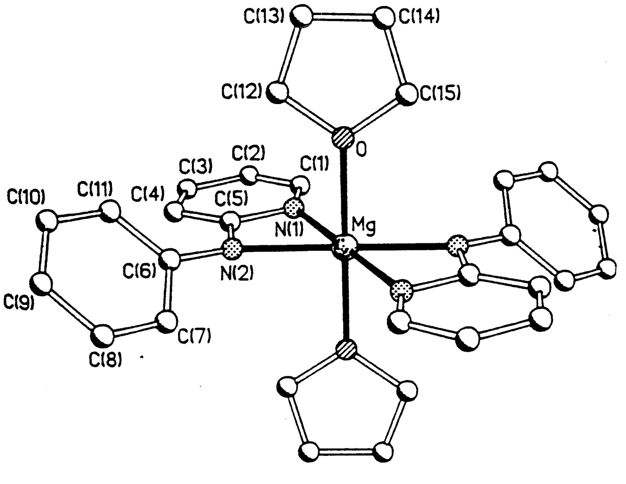


(21)

The mechanism of metallation is presumed to proceed initially by complexation of HN″ to electron-deficient magnesium, as for the metallation of N–H bonds using alkyllithium reagents [40]. However, the *N*-silyl groups render the amine, HN″, a rather weak base that coupled with its steric hindrance may disfavor such complexation and the mechanism involves a concerted process. Chelating alkali metal amides of the secondary amine (PhCH$_2$(Me$_2$NCH$_2$CH$_2$)NH and Ph(2-Pyr)NH react with the Grignard reagent ^{n}BuMgCl to give monoamide [PhCH$_2$(Me$_2$NCH$_2$CH$_2$)NMg^{n}Bu]$_2$ (**22**) and bis(amido){[Ph(2-Pyr)N]$_2$Mg·(THF)$_2$} (**23**), respectively. The structure of **22** shows that it is dimeric with a ring containing (amido-*N*-Mg)$_2$ and tertiary amine nitrogen atoms. The central magnesium atom has pseudo terahedral coordination with the amido and amino nitrogens and the butyl ligands. Compound **23** is monomeric with pseudo octahedral coordination at the magnesium by two bidentate Ph(2-Pyr)N– anions and two THF molecules [41].



(**22**)



(**23**)

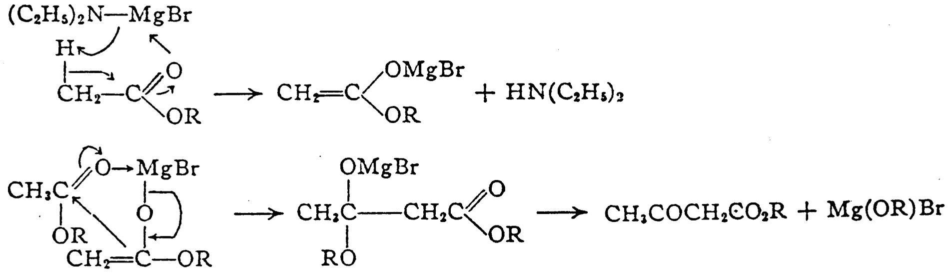
2.2. Alkyl amino magnesium halides

Hauser bases or diethylamino magnesium bromides were first introduced by Hauser et al. in 1947 and are useful for the condensation of certain esters [42]. Diethylaminomagnesium bromide reacts with carboxylic esters either at the α-hydrogen to effect their condensations, or at the carbonyl carbon to produce the corresponding *N*,*N*-diethylamides. These two courses of reaction with alkyl acetates are shown in Eqs. (4) and (5):

$$2CH_3CO_2R + (C_2H_5)_2NMgBr \rightarrow CH_3COCH_2CO_2R + ROH \quad (4)$$

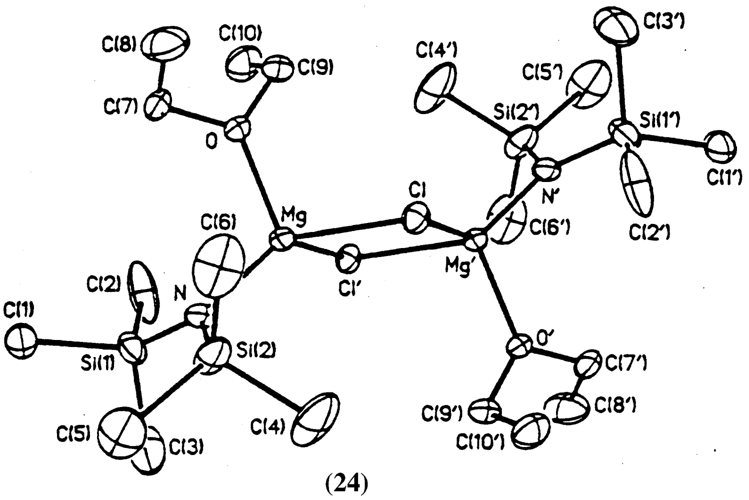
$$CH_3CO_2R + (C_2H_5)_2NMgBr \rightarrow CH_3CON(C_2H_5)_2 + Mg(OR)Br \quad (5)$$

Various esters have been rapidly self condensed to form the corresponding β-keto esters. A cyclic mechanism (Scheme 4) that involves the magnesium enolate intermediate, suggested by Hauser is shown below.

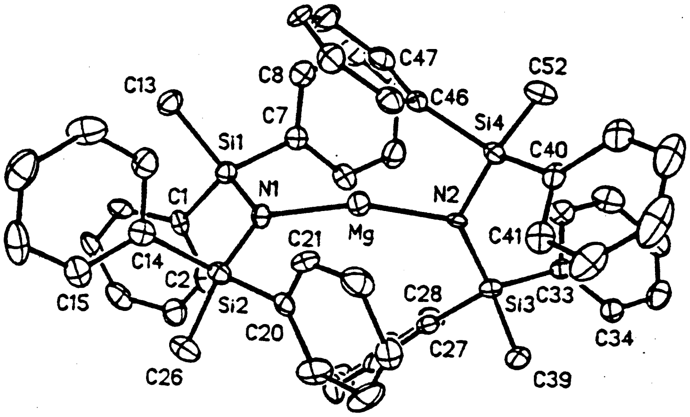


Scheme 4.

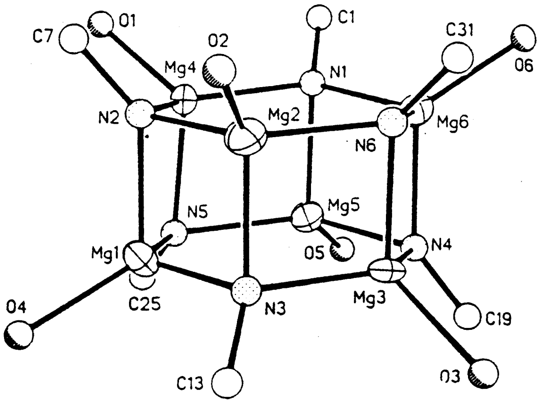
In comparison to the extensive interest in the structures and the degree of association of Grignards in the solid state and solution, relatively little is known about the corresponding amido derivatives of formula R_2NMgX (X = halide) [43]. It is also notable that no simple magnesium amide structures of the general formula $[R_2NMgX]n$ ether (R = alkyl, aryl or related group; X = halide) have been reported. Such an amido halide compound (also called (halmagnesyl)amine or magnesylamine) is derived from the reaction of a secondary amine with a Grignard reagent. The formula corresponds closely to those of ether solvated Grignard reagents themselves, in which the organic amide is replaced by an amide. The structural characterization of the magnesylamine compound $[(Et_2O)Mg(Cl)\{N(SiMe_3)_2\}]_2$ (**24**) and the novel species $Mg\{N(SiMePh_2)_2\}_2$ (**25**) by X-ray crystallography was described in 1994 by Power et al. [44]. The structure of **24** features dimeric molecules with two four-coordinate magnesium centers. Each magnesium is coordinated in a distorted tetrahedral fashion by terminally bound $-N(SiMe_3)_2$ and Et_2O ligands and by two symmetrically bridging chlorides. The structure of **25** is composed of monomeric molecules with the magnesium bonded to two terminal amide groups. The two-fold coordination at the magnesium is found to be distorted from linearity that can be attributed to weak


C(8)
C(10)
C(9)
C(7)
O
C(4')
C(5')
C(3')
Si(2')
Si(1')
C(1')
Cl
N'
C(6)
Mg
C(6')
C(2')
C(2)
Cl'
Mg'
N
C(1)
Si(1)
Si(2)
O'
C(7')
C(5)
C(3)
C(4)
C(9')
C(8')
C(10')

(24)


C47
C52
C13
C8
C46
C7
Si4
Si1
C40
C1
N1
N2
Mg
C21
C41
C14
C2
C28
C33
Si2
Si3
C15
C20
C27
C34
C26
C39

(25)


C7
O1
O2
C1
C31
O6
Mg4
N1
N2
Mg2
Mg6
N6
N5
Mg5
Mg1
O5
N4
C25
N3
Mg3
O4
C19
C13
O3

(26)

Mg–aromatic ring interactions. This structure is the first for a magnesium bis(amide) of formula $Mg(NR_2)_2$ (R = alkyl, aryl or related group) in the solid state.

The disproportionation of phenyl derivative to eliminate MgX_2 to form the cage species $\{(THF)Mg\}_6(NPh)_4X_4$, (**26**) which has an adamantyl Mg_6N_4 core with the nitrogens in the bridgehead positions is reported [45]. The structure of **25** reveals a very rare example of 2-coordination for magnesium.

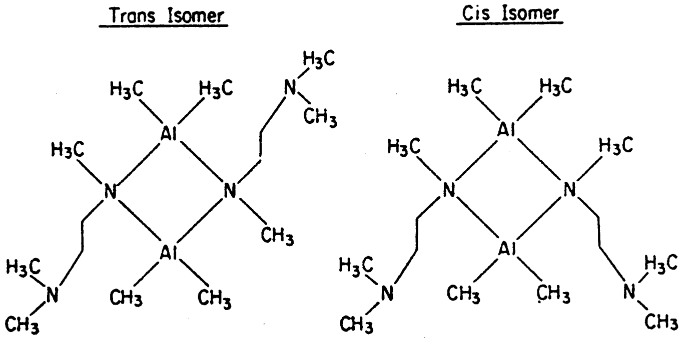
3. Organoaluminum diamides

In contrast to the Mg–N diamides, the chemistry of aluminum–nitrogen compounds provide a wealth of information and many review articles are available [46]. The chemistry of compounds containing Al–N bonds has flourished over the past several years due mainly to current interest in developing optimum AlN precursors. Earlier work on the structures and properties of the alkyl aluminum amides has focused largely on the alkyl and arylamine derivatives $R_2AlNR'R''$ where both R′ and R″ are organic groups or where one of these substituents is hydrogen. Unlike the corresponding boron compounds, the aluminum derivatives show a strong tendency to oligomerize through the formation of Lewis acid–base complexes [47]. Therefore, these compounds are generally found in the form of oligomers of the type $[R_2AlNR'R'']n$ with either four- ($n = 2$) or six-membered ($N = 3$) $(AlN)_n$ rings. The ring size and conformation appear to be intimately dependent on entropy factors (favoring the larger number of molecules, e.g. dimers), ring strain and substituent steric interactions [48]. The various factors affecting the formation and stability of neutral chelated 4-coordinate organoaluminum–nitrogen compounds have been investigated by Beachley and Racette in 1976 [49]. The compounds prepared for this study involved hydrido-, alkyl-, aryl-and chloroaluminum derivatives. In the case of the hydrido and organo derivatives, the appropriate dibasic ligand was reacted with $H_3Al{\cdot}N(CH_3)_3$ or the organoalane according to Eqs. (6) and (7).

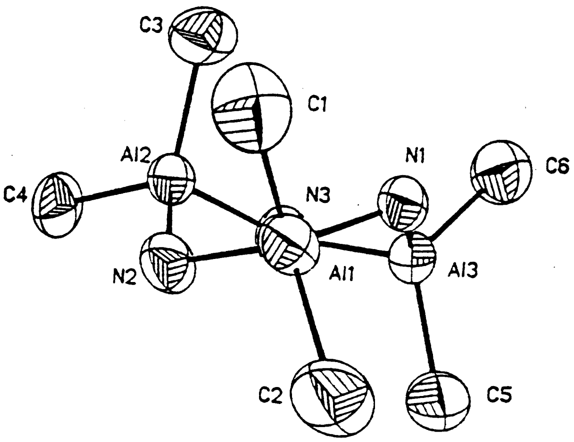
$$H_3AlN(CH_3) + HRNC_2H_4NR_2 \rightarrow [H_2AlN(R)C_2H_4NR_2]_n + H_2 + N(CH_3)_3 \quad (6)$$

$$1/2Al_2(CH_3)_6 + HRNC_2H_4NR_2 \rightarrow [(CH_3)_2AlN(R)C_2H_4NR_2]_n + CH_4 \quad (7)$$

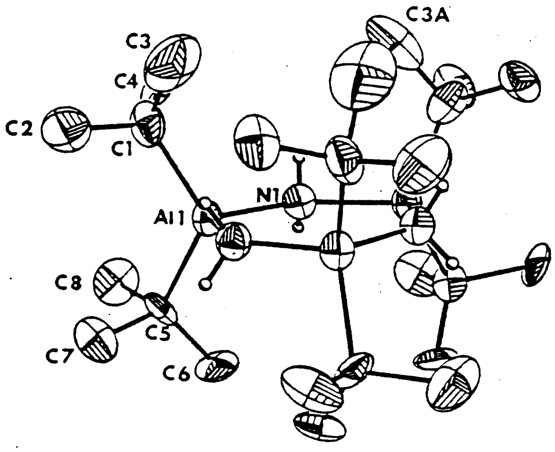
Chelated monomers of the compounds $(CH_3)_2Al(C_2H_5)NC_2H_4N(C_2H_5)_2$, $(C_2H_5)_2Al(CH_3)NC_2H_4N(CH_3)_2$, $(C_6H_5)_2Al(C_2H_5)NC_2H_4N(CH_3)_2$, Cl_2Al (C_2H_5)-$NC_2H_4N(CH_3)_2$ and $(CH_3)_2AlSC_2H_4N(CH_3)_2$ have been prepared and characterized by ^{1}H NMR studies and cryoscopic molecular weight data which suggest that an equilibrium exists between the monomeric chelate and the dimer. Other compounds such as $(CH_3)_2Al(CH_3)NC_2H_4N(CH_3)_2$ (**27**), $(CH_3)_2Al$ $(CH_3)NC_3H_6N(CH_3)_2$ and $(C_2H_5)_2Al(CH_3)NC_3H_6N(CH_3)_2$ show a significant concentration of the dimeric species at room temperature (r.t.). The dimer can exist in *trans* and *cis* conformations as shown below and the latter are preferred in all the cases. The position of the monomer–dimer equilibrium is found to be affected by factors like steric effects



Geometric isomers of (27)



(28)



(29)

of groups bound to aluminum, steric effects of groups bound to potentially bridging and terminal nitrogens of the ligand, ligand base strength and chelate ring size.

3.1. Low coordinate derivatives (C.N. = 3, 4)

In 1989 Interrante et al. reported [47] the reaction of R_3Al ($R = CH_3$, $t\text{-}C_4H_9$) with ammonia in hydrocarbon solvents which gave the adduct $R_3Al{\cdot}NH_3$. The compound was isolated by evaporation of the solvent and subsequent heating gave the compounds **28** and **29** as trimeric species in the solid state. The mass spectra of $[(CH_3)_2AlNH_2]_3$ (**28**) and $[(t\text{-}C_4H_9)_2AlNH_2]_3$ (**29**) are consistent with the retention of the trimeric species in the gas phase.

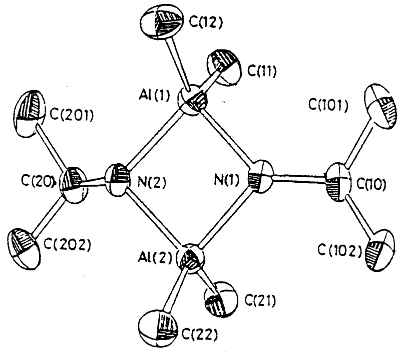
The appreciable electronegativity difference between Al and the bridging atoms (N, O, and halogen) implies a high degree of ionic character in the Al–X bonds which would lead to relaxation in the constraint of sp^3 hybridization and greater flexibility in the bridging angle [47]. The skew boat conformation observed for the $(AlN)_3$ ring in $[(CH_3)_2AlNH_2]_3$ (**28**) could arise from crystal packing interactions. The dominant factor which drives the formation of dimeric units in the case of organoaluminum amides is the 1,2-steric interactions between the Al and N substituents and with less bulky N substituents the trimeric form will generally be favored for dialkylaluminum amides.

The degree of aggregation of isopropylamido-compounds $[\{AlMe(N^iPr)\}_n]$ depends on the preparative route [50]. The hexamer is isolated from the reaction between hexamethyl dialuminum and the hydrido compound $[\{AlH(N^iPr)\}_6]$ but the tetramer is formed from hexamethyl dialuminum and isopropylamine in toluene at 210°C according to Eq. (8):

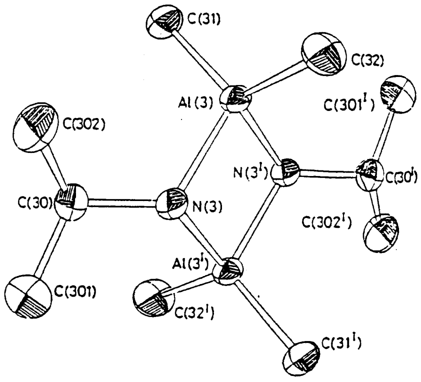
$$4Me_3Al{\cdot}NH2^iPr \rightarrow 2[\{AlMe_2(NH^iPr)\}_2] \rightarrow [\{AlMe(N^iPr)\}_4] \qquad (8)$$

The structure of the imido derivatives depends in part on the structure of the amido precursor. The compound $[\{AlMe_2(NH^iPr)\}_2]$ (**30**) has been made from trimethyl aluminum and isopropylamine. The X-ray structure determination shows that the crystals are triclinic, an asymmetric unit of 1 and 1/2 molecules and the molecules have four-membered $(AlN)_2$ rings with *cis* and *trans* isomers mole ratio of 2:1. The isopropyl groups are *cis* in **30a** and *trans* in **30b**. The compound $[\{AlEt_2(NH^iPr)\}_3]$ has also been characterized. The compounds $[\{AlEt_2(NH^iPr)\}_2]$ and $[\{AlEt_2(NMe_2)_2\}_2]$ are good initiators for the polymerization of methyl methacrylate, acetaldehyde and *n*-butyraldehyde [51].

Amido and imido derivatives of aluminum are characterized by a marked tendency to oligomerize through the formation of strong metal–nitrogen bridges

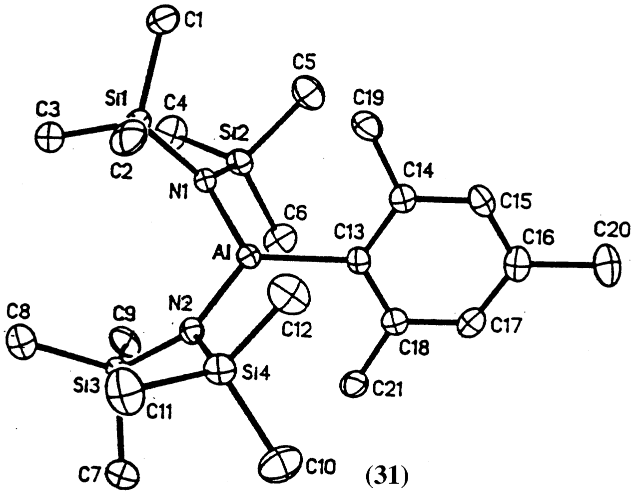


(30 a)

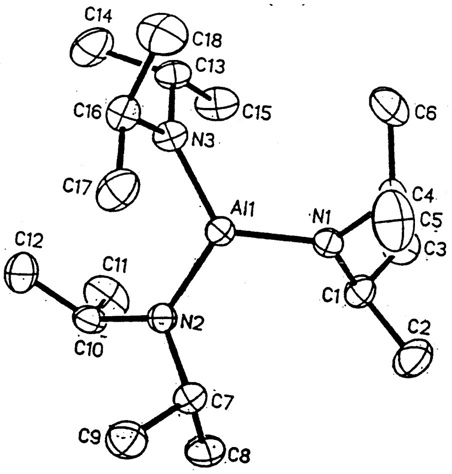


(30 b)

[52]. Under normal conditions unassociated aluminum amides remain quite rare. The monomers are important because the metals are coordinatively unsaturated and the nitrogen centers possess lone pairs that are not involved in σ-bonding. These lone pairs may in principle at least, react with the formally empty π-orbitals on the metal to form π-bonds. The extent of these interactions and their effect on various structural parameters is perhaps the major feature of inherent interest in unassociated, low coordinate amides. For many years the only examples of such compounds were provided by the trisilyl amides $M\{N(SiMe_3)_2\}_3$ (M = Al, ga, In or Tl). The species $Al\{N(^iPr)_2\}_3$ and $Al(NPh_2)_3$ were also reported to be monomeric in benzene solution. The synthesis and spectroscopic and structural characterization of several unassociated amido derivatives of aluminum were described and the possible π-interactions were studied by Power et al. in 1994 [53]. The compounds $MesAl\{N(SiMe_3)_2\}_2$ (**31**) and $Al\{N(^iPr)_2\}_3$ (**32**) along with various gallium compounds were synthesized by simple salt elimination procedures. The structural and the dynamic data suggested that any π-interaction in the M–N bonds is rather weak, 10 kcal mol^{-1}. The structure of $MesAl\{N(SiMe_3)_2\}_2$ (**31**) consists of discrete monomeric molecules. The aluminum coordination is trigonal planar with fairly regular interligand angles (all within ca. 2° of 120°). The Compound $Al\{N(^iPr)_2\}_3$ (**32**) crystallizes with two well-separated identical monomeric molecules in the asymmetric unit and the aluminums and nitrogens have trigonal planar coordination. Significant deviation from the predicted M–N distances is found only in the most severely crowded molecules where presumably steric effects induce some elongation of the M–N bond. Another significant feature is that there appears to be no strong correlation between the bond length and torsion angle and a minor role for Al–N p–pπ bonding. A new family of dimeric aluminum silylamides $[R'_2AlN(H)SiR_3]_2$ ($R' = Me$, $R_3 = Ph_3$, Et_3; $R' = {}^tBu$, $R_3 = Ph_3$, $R_3 = {}^tBu_2H$) were synthesized by Planalp et al. in 1992 from R_3SiNH_2 with R'_3Al in refluxing hexane [53].

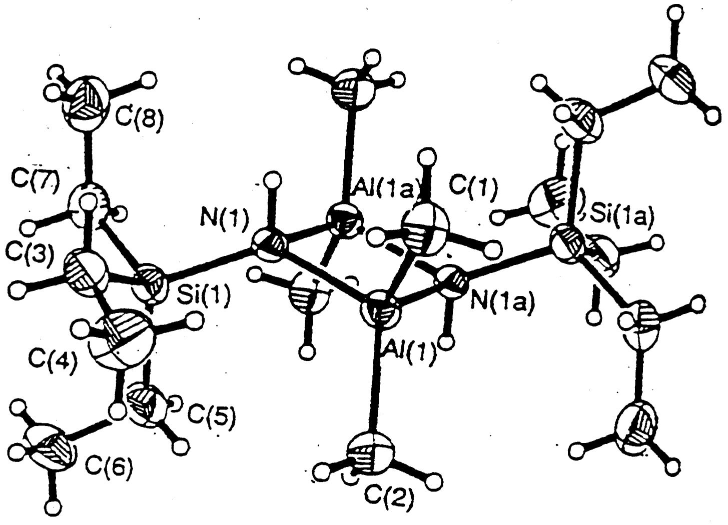


(31)

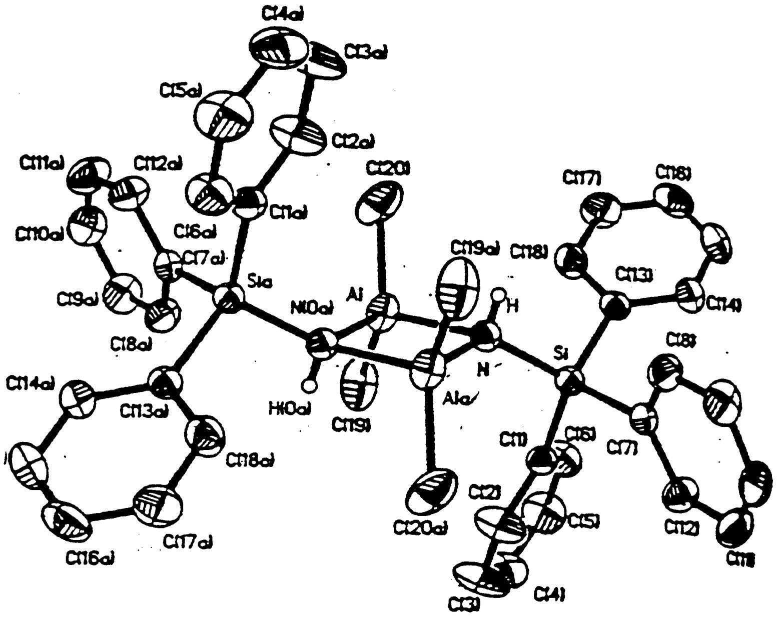


(32)

X-ray crystallography of $[Me_2AlN(H)SiEt_3]_2$ (**33**) and $[Me_2AlN(H)SiPh_3]_2$ (**34**) indicates planar Al_2N_2 ring frameworks with the silyl groups oriented *trans* about the ring, while the N–H bond vector is nearly orthogonal to the Al_2N_2 plane. The degree of distortion depends on the steric bulk of SiR_3. All dimers undergo a *cis–trans* isomerization process in benzene. Isomerization of the methylaluminum compounds is catalyzed by 4-methylpyridine, while hindered pyridines have no effect. Greater amounts of 4-methyl pyridine lead to adduct formation i.e. $(^iBu)_2$(4-Me-py)AlN(H)$SiPh_3$. Preference for the dimer over the Al_3N_3 trimer e.g. in $[^tBu_2AlNH_2]_3$ occurs when the N and Al substituents are bulkier. The mechanism of *cis–trans* isomerization of aluminum amido dimers has been proposed to involve a catalytic Lewis base attack at aluminum, because pyridine accelerates isomerization in $[Me_2AlN(CH_3)(Ph)]_2$.



(33)



(34)

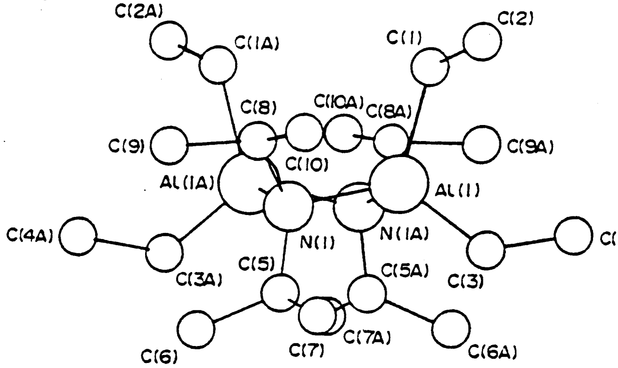
The reactions of organoaluminum compounds with reagents containing one acidic hydrogen may lead to the formation of dimeric or trimeric species. Entropy, ring strain, and steric hindrance are very important on the formation of these dimeric and trimeric molecules and the degree of aggregation depended on the preparation route [54]. The Me_2AlNH_2 trimer is thermodynamically favored in the following equilibrium (Eq. (9)):

$$2(Me_2AlNH_2)_3 \overset{K = 1 \times 10^{-5},\ \Delta H = 38\ kJ,\ T = 40-800°C}{\rightleftharpoons} 3(Me_2AlNH_2)_2 \tag{9}$$

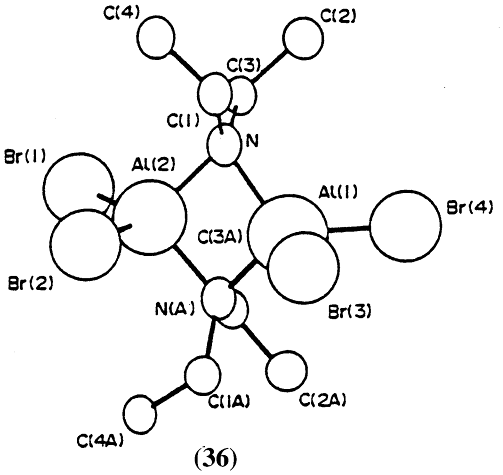
Chang et al. reported [55] the reactions of bis(dialkylamino)magnesium $[Mg(NR_2)_2$; $R = Et$, ${}^{i}Pr]$ with either dialkylaluminum chloride or aluminum bromide which yielded $Me_4Al_2[\mu\text{-}N({}^{i}C_3H_7)_2]_2$, $Et_4Al_2[\mu\text{-}N(Et)_2]_2$, $Et_4Al_2[\mu\text{-}N({}^{i}C_3H_7)_2]_2$ (**35**) and $Br_4Al_2[\mu\text{-}N(Et)_2]_2$ (**36**) according to Eq. (10):

$$2AlX_2Y + Mg(NR_2)_2 \xrightarrow{\text{diethylether}} X_4Al_2(\mu\text{-}NR_2)_2 + MgY_2 \tag{10}$$

The X-ray crystal structures of compounds **35** and **36** were determined. In compound **35**, the central Al_2N_2 moiety is non-planar, with distorted tetrahedral coordination geometry about the aluminum atoms. The relatively short distance between the two aluminum atoms is attributed to dπ–pπ interactions between the aluminum and nitrogen atoms. A comparison of the X-ray structural data of $Al_2(CH_3)_6$, $(CH_3)_5Al_2NPh_2$ and $[(CH_3)_2AlN(CH_3)_2]_2$ reveals that the Al···Al distance as well as the Al–N–Al angle increases as the number of bridging amino groups increase [56]. The stability of these compounds had been studied and it was suggested that an increase in the metal–metal distance across the $(AlX)_2$ or $(AlY)_2$ rings does not necessarily imply that the bridge itself progressively weakens. The propensity of these compounds to dissociate into monomers increases according to the following sequence: $Al_2(CH_3)_6 < Al_2(CH_3)_5(NPh_2) < Al_2(CH_3)_4[N(CH_3)_2]_2$.

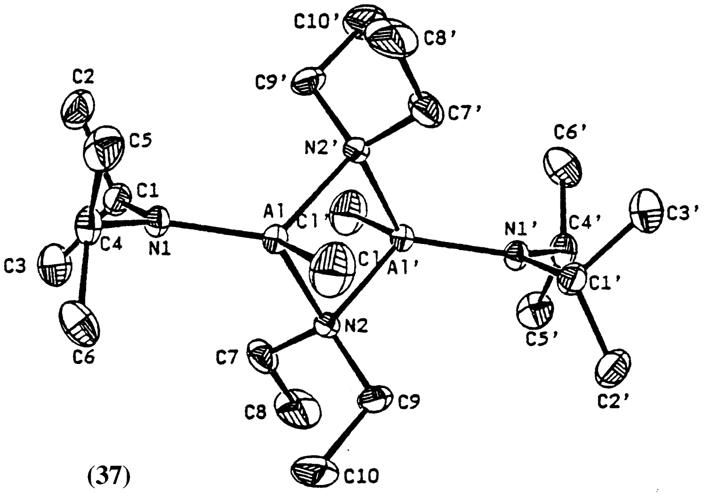


(**35**)

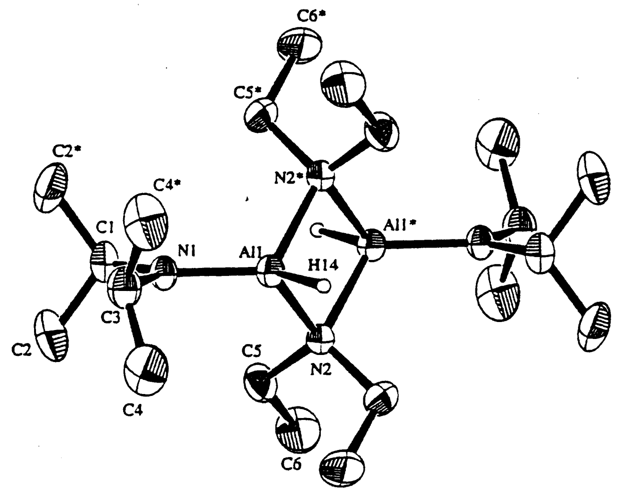


(**36**)

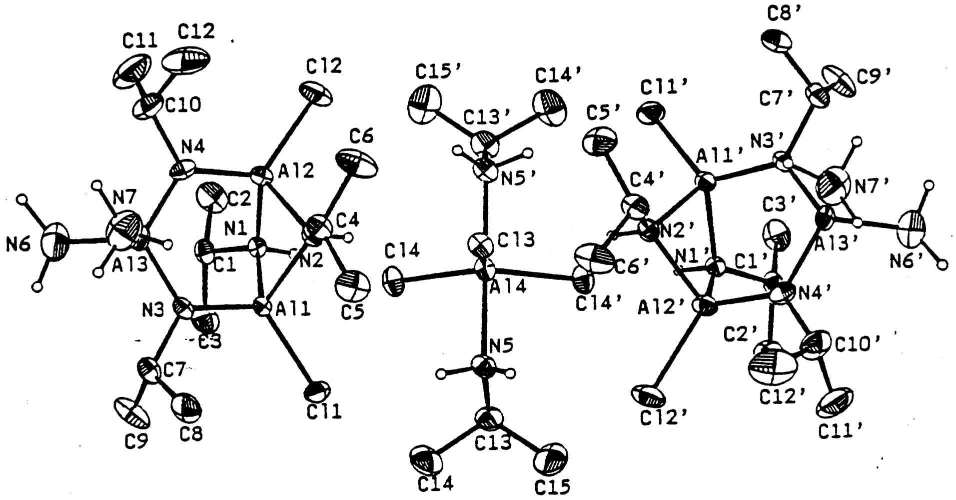
The compound $\{Al(NR'R'')_3\}_n$ was synthesized either by the reaction of aluminum hydride with amine or by treatment of aluminum chloride with amine and lithium amide [57]. The latter reaction can be controlled by stoichiometry. For the main group metals, substitution reactions via lithium amide are common methods to generate Al/NR_2/halide ternary compounds. In order to study the selectivity in substitution and stabilization of the $Al_2(NR_2)_nCl_{6-n}$ complexes, different stoichiometric ratios of aluminum complexes and lithium amides which form the new $Al_2(NR_2)_nCl_{6-n}$ complexes were used. The synthesis, structural characterization and spectroscopic studies on several amido derivatives of 4-coordinated aluminum compounds like $Al_2(NEt_2)_2[N(^iPr_2)]_2Cl_2$, $Al_2[N(^iPr_2)]_4Cl_2$, $Al[N(^iPr_2)]_3$, $\{Al[N(^iPr)H]_3\}_3$, $Al_2(NEt_2)_2[N(^iPr_2)]_2H_2$, and $AlCl_3[N(^iPr)H_2)]_2$-$\{Al(NH_3)(NH_2)[Al\{N(^iPr)H)\}(N^iPr)Cl]_2\}_2$ were reported by Chang et al. in 1997. The structures of $Al_2(\mu\text{-}NEt_2)_2(N^iPr_2)_2Cl_2$ (**37**), $Al_2(NEt_2)_2(N^iPr_2)_2H_2$ (**38**), and $AlCl_3(N^iPrH_2)_2\{Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)\ Cl]_2\}_2$ (**39**) have been determined by single crystal X-ray diffraction. Compound $Al(NEt_2)(N^iPr_2)Cl_2$ (**37**) uses diethylamide as a bridging group to form a dimer, and the dimer sits on an inversion center. The four atoms Al, N(2), Al′ and N(2′) form a coplanar four-membered ring. Compound **38** exists as a dimer with a center of inversion and both compounds **37** and **38** possess identical frameworks. The Al_2N_2 four-membered ring skeleton is nearly square–planar. The X-ray data suggest that there is a distorted tetrahedral geometry around the aluminum atom.



(37)

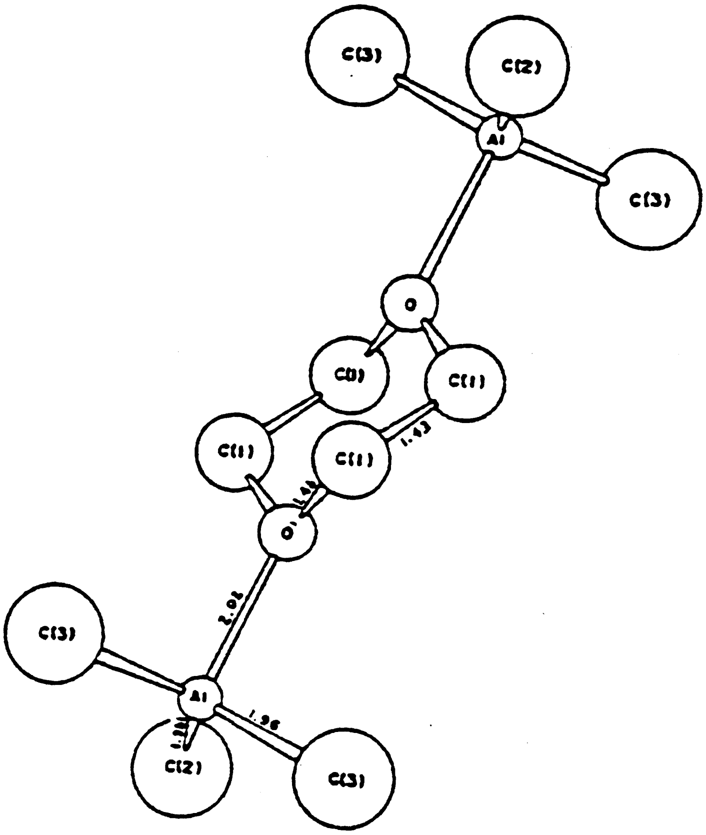

C6*
C5*
C2*
C4*
N2*
C1
N1
Al1
Al1*
H14
C3
C2
C5
N2
C4
C6

(38)


C11
C12
C10
C12
C15'
C14'
C13'
C11'
C5'
C8'
C7'
C9'
C6
N4
Al2
N5'
Al1'
N3'
N7
C2
C4
C4'
N7'
C3'
N1
N2'
N6
Al3
C1
N2
C14
C13
C6'
N1'
C1'
Al3'
N6'
N3
Al1
C5
Al4
C14'
Al2'
N4'
C3
N5
C2'
C10'
C7
C11
C12'
C12'
C11'
C9
C8
C13
C14
C15

(39)

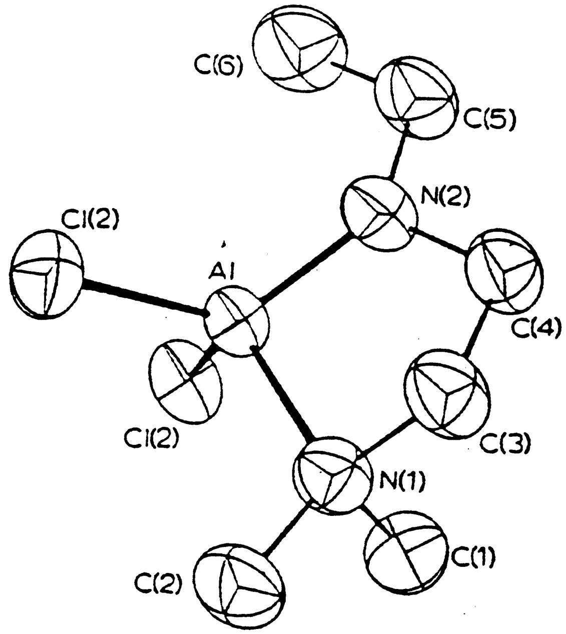
The molecule **39** is composed of two parts of $\{Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl]_2\}_2$ (**39a**) and $AlCl_3(N^iPrH_2)_2$ (**39b**) coordinated to seven aluminum atoms are ammonia, amide, imide and free amine as shown in **39a**. The organoaluminum amides of the general molecular formula $R_2AlNR'R''$ where $NR'R''$ is a simple monofunctional amide group occur as cyclic or oligomeric species with either four- or six-membered $(AlN)_n$ rings. In these structures both N and Al are typically 4-coordinate in a distorted tetrahedral geometry analogous to that found in crystalline AlN. On the other hand, with multidentate amines, more complicated structures are formed in which the coordination number of Al is 4, 5 or 6.



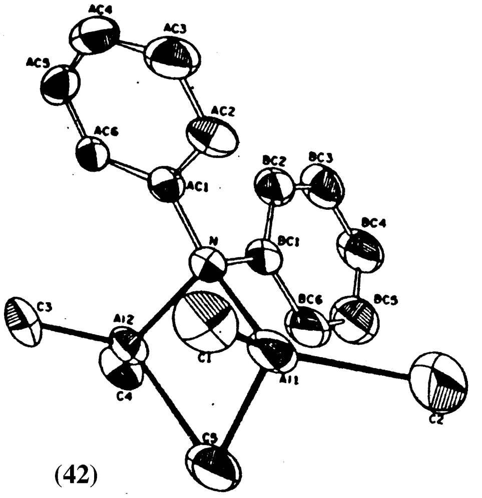
(40)

The crystal and molecular structure of $[Al(CH_3)_3]_2 \cdot C_4H_8O_2$ (**40**) was determined by J.L. Atwood et al. in 1967 [58]. The molecule has $2/m$ symmetry consisting of two $Al(CH_3)_3$ groups bonded one each to the oxygen atoms in the dioxane ring in the chair form. The aluminum atoms appear to be more nearly trigonal than tetrahedral.

In aromatic solvents the compound $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ has been characterized as a monomeric chelate, whereas in aliphatic solvents there is an equilibrium between the monomeric chelate and a dimeric species. A similar substance, $Cl_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ (**41**) was reported by J.L. Atwood et al. in 1980 [59].



(**41**)

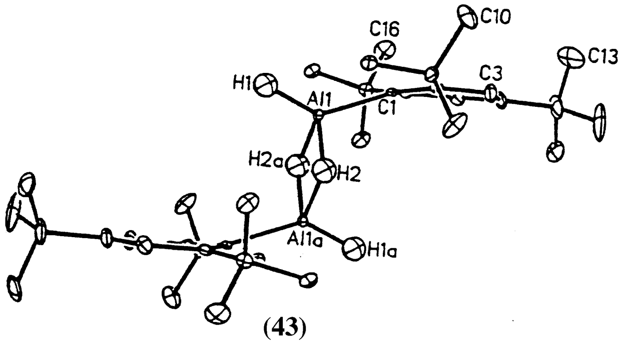


(**42**)

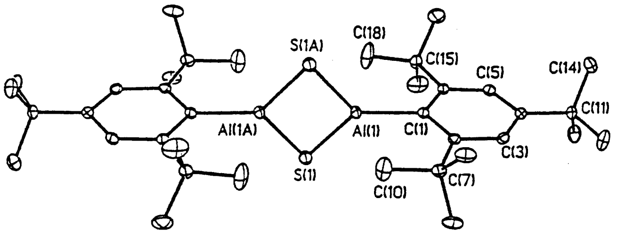
During studies of the reactivity of the system, $(CH_3)_3Al$ with $(C_6H_5)_2NH$, the mixed electron deficient–nonelectron-deficient compound $(CH_3)_5Al_2N(C_6H_5)_2$ (**42**) was isolated. The molecular structure of this compound has been determined in 1969 by Stucky et al. [60] which explains the stereochemistry and bridging within the four-membered heterocyclic ring system. The basic structural feature of this complex is the four-membered heterocyclic ring system composed of two Al atoms, one C atom and one N atom and the ring atoms Al(1)–C(5)–Al(2)–N being non-coplanar. Neutral aluminum hydride compounds that are free of donor ligands are rare [61]. Synthesis and characterization of $[Mes^*AlH_2]_2$ (**43**) which is dimeric in the solid and solution phases was reported by Power et al. in 1994 [62]. The compound was prepared by the reaction of $[Mes^*AlH_3Li(THF)_2]_2$ with two equivalents of MeI according to Eq. (11):

$$[Mes^*AlH_3Li(THF)_2]_2 + 2MeI \xrightarrow{PhMe,\ 25°C} [Mes^*AlH_2]_2 + 2LiI + 2CH_4 + 4THF \tag{11}$$

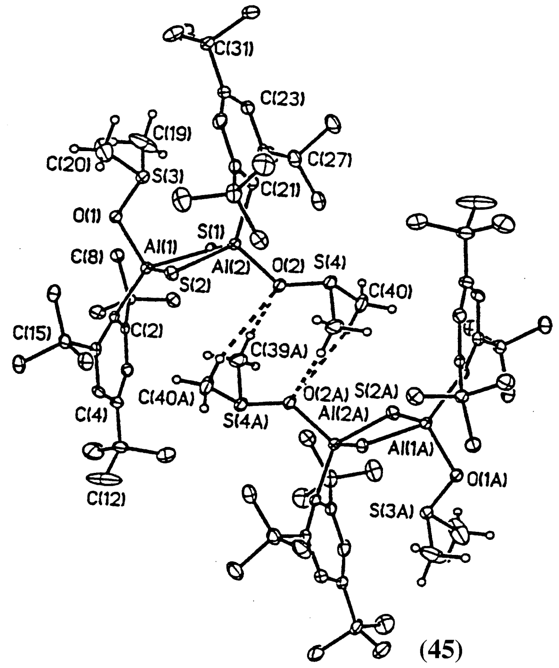
$(Mes^*AlS)_2$ (**44**) ($Mes^* = –C_6H_2^tBu3$-2,4,6) was synthesized by refluxing $(Mes^*AlH_2)_2$ with two equivalents of $S(SiMe_3)_2$ in either toluene or *n*-octane and its dimethyl sulfoxide adduct $[Mes^*AlS(OSMe_2)]_2$ (**45**) can be prepared by the addition



(43)



(44)

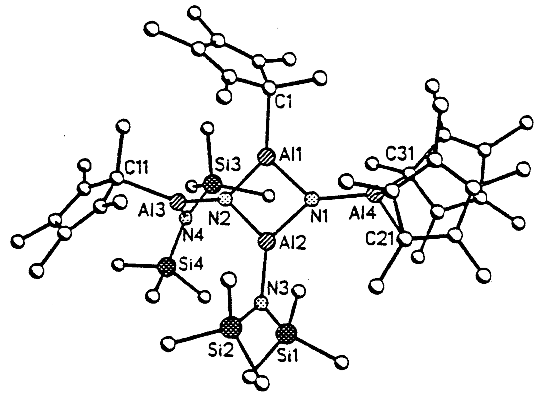


(45)

of two equivalents of Me_2SO to **44** in benzene [63]. The crystal structure of **44** shows a dimeric structure and it was noticed that the dimeric configuration is retained in **45** which also shows weak intermolecular interactions between neighboring dimers

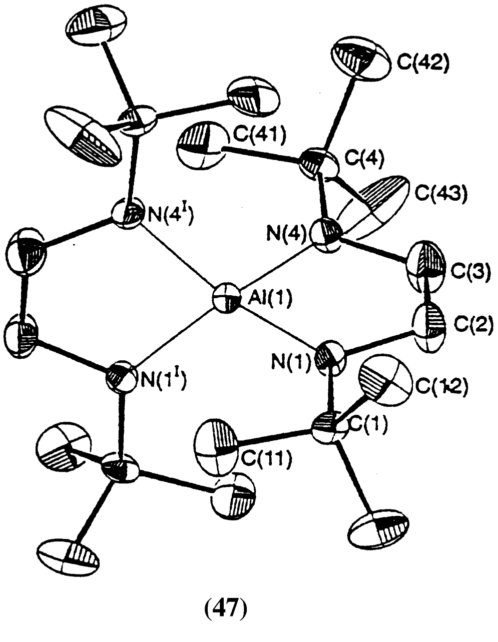
Iminoalanes can be prepared by oxidative addition [64]. The driving force of this reaction is the desire of the aluminum centers to reach the oxidation state (III). By applying sterically demanding substitiuents on the nitrogen atoms it is possible to prepare dimeric iminoalanes containing Al_2N_2 ring. The first dimeric iminoalane $[Cp^*Al\{\mu\text{-}NH(C_6H_2\text{-}4,6\text{-}Me_2\text{-}2\text{-}CH_2)\}]_2$ (**46**) was prepared by the reaction of $(Cp^*Al)_4$ with $MesN_3$ ($Mes + Me_3C_6H_2$) in a molar ratio of 1:4. The X-ray crystal structure determination of **46** verified the presence of a dimeric iminoalane. The central core was found to be a four-membered almost ideally planar Al_2N_2 ring.

In 1996, Raston et al. reported [65] on the metallation and hydrometallation of various secondary amines and imines by some aluminum and gallium hydride sources which was found to proceed through the formation of the unstable secondary amine-stabilized amidoalane $[AlH_2({}^tBuNCH_2CH_2N{}^tBuH)]$. This compound reacted

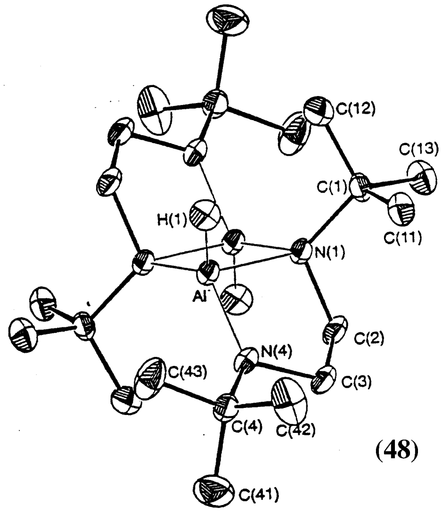


(46)

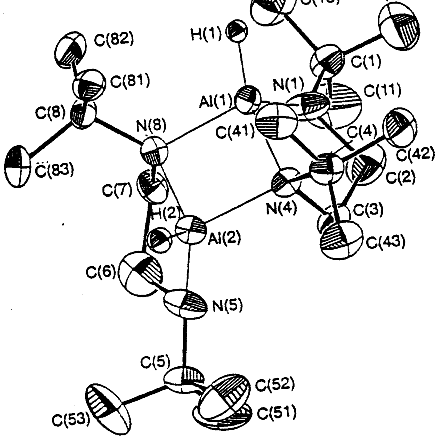
with an additional equivalent of $\mathrm{AlH_3{\cdot}NMe_3}$ to yield the di-bridging amidoalane complex [(AlH2)2{μ-N(^{t}Bu)$\mathrm{CH_2CH_2}$N(^{t}Bu)}] or a molecule of diamine to give the triamido aluminum species [Al(^{t}BuN$\mathrm{CH_2CH_2}$N^{t}Bu)(^{t}BuN$\mathrm{CH_2CH_2}$N^{t}BuH)] (**47**). In the absence of an excess of $\mathrm{AlH_3{\cdot}NMe_3}$ or *N*,*N*′-di-*tert*-butylethylenediamine, [$\mathrm{AlH_2}$(^{t}BuN$\mathrm{CH_2CH_2}$*n*^{t}BuH)] eliminates molecular hydrogen to give the *trans* isomer of the dimeric diamidoalane complex *trans*-[{AlH[μ-N(^{t}Bu)$\mathrm{CH_2CH_2}$N^{t}Bu]}$_2$] (**48**) which is stable toward reaction with either of the reactants. A stable analogue of the intermediate [$\mathrm{AlH_2}$(^{t}BuN$\mathrm{CH_2CH_2}$N^{t}BuH)] was made by replacing a hydride by a chloride, with $\mathrm{AlH_2Cl{\cdot}NMe_3}$ as the metallating agent. The *cis* isomer of the dimeric diamidoalane *cis*-[AlH{[μ-N(^{t}Bu) $\mathrm{CH_2CH_2}$N^{t}Bu]}$_2$ (**49**) was prepared from the unstable lithium diamido aluminum hydride species [{Li[N(^{t}Bu)$\mathrm{CH_2CH_2}$N^{t}Bu]-$\mathrm{AlH_2}$}$_n$] via elimination of lithium hydride. The aluminum triamide and the *cis* and *trans* isomers of the dimeric aluminum diamide have been structurally authenticated.



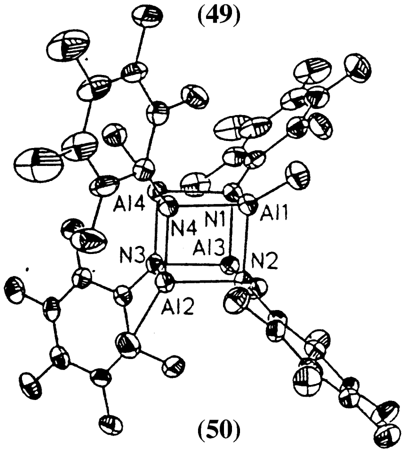
(47)


C(12)
C(13)
C(1)
C(11)
H(1)
N(1)
Al
C(2)
N(4)
C(43)
C(3)
C(4)
C(42)
C(41)

(48)


C(13)
C(12)
H(1)
C(82)
C(1)
C(81)
N(1)
C(11)
Al(1)
C(8)
N(8)
C(41)
C(4)
C(42)
C(83)
C(2)
C(7)
N(4)
C(3)
H(2)
Al(2)
C(43)
C(6)
N(5)
C(5)
C(52)
C(53)
C(51)

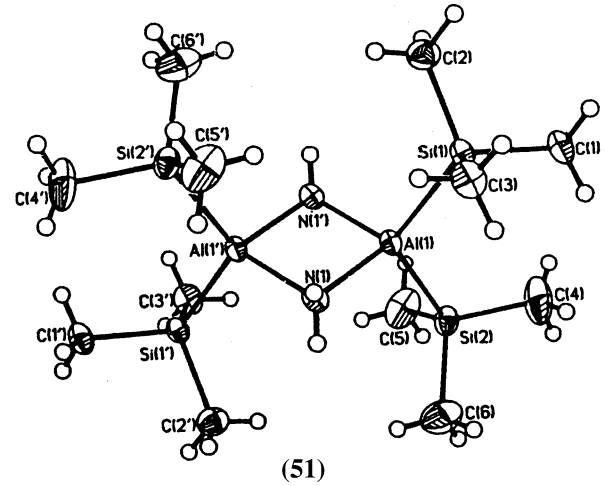
(49)


Al4
N1
Al1
N4
Al3
N3
N2
Al2

(50)

In 1994 Roesky et al. reported [64] the synthesis of tetrameric iminoalane $(MeAlNC_6F_5)_4$ (**50**) and the aminometallane $Mes_2AlNHC_6F_5$. Compound **50** was isolated from the reaction of $AlMe_3$ with pentafluoroaniline and the low temperature X-ray diffraction studies of **50** shows that there are two independent molecules of $(MeAlNC_6F_5)_4$ heterocubanes and a single *n*-hexane molecule present in the asymmetric unit. The nitrogen atoms bond the three adjAcent aluminum atoms through π-orbitals. Electron releasing substituents at the nitrogen atom like silyl groups increase electron density on nitrogen resulting in higher N···N repulsions. Electron withdrawing substituents like the C_6F_5 group lower the electron density and N···N repulsion is less pronounced.

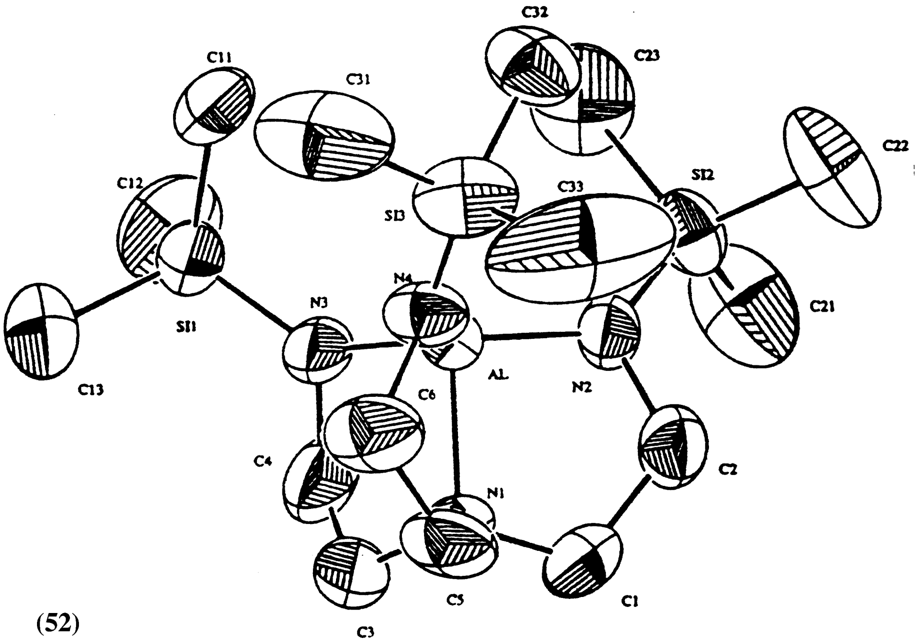
The coordination chemistry of alanes and tertiary amines has been studied extensively and a large number of simple, stable acid–base complexes $X_3Al{\cdot}NR_3$ have been isolated. Although the alanes and NH_3, primary or secondary amines also form such types of adducts, the products tend to undergo elimination–condensation reactions which produce amino- and imino-substituted alanes. The elimination reactions appear to be dependent upon aluminum-substituent group bond strengths showing an increase in the ease of elimination from the aluminum fragment in the following order: Al–Cl < Al–R < Al–H. The reaction chemistry of $(Me_3Si)_3Al$ with a variety of inorganic and organometallic reagents has been examined and it was reasoned that the weaker Si–Al bond compared to the C–Al bond in aluminum alkyls, and the bulky steric environment in $(Me_3Si)_3Al$ might provide a more useful aluminum precursor for the synthesis of AlN and other aluminum bearing solid state materials. In 1987 Paine et al. reported [66] the reaction of NH_3 and $(Me_3Si)_3Al{\cdot}Et_2O$. X-ray crystal structure determination for an intermediate product, $[(Me_3Si)_2AlNH_2]_2$ (**51**) formed by molecular elimination–condensation was reported and the pyrolysis chemistry of the dimer or a polymeric species resulted in solid solutions of AlN and SiC.



(51)

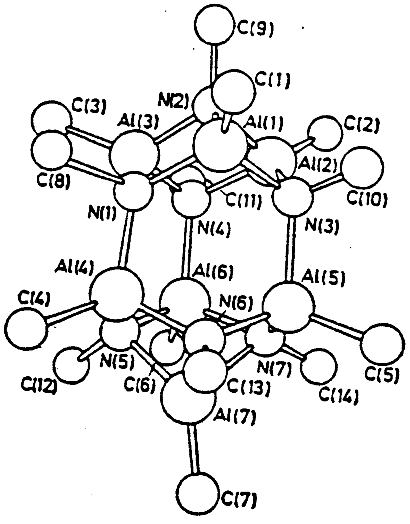
In 1993 Verkade et al. reported [67] the synthesis and characterization of aluminum azatranes which exhibit monomeric or dimeric behavior depending on the nature of the central aluminum atom and on the bulkiness of the pseudoequatorial substituents rendering the Al center in the monomers or dimers 4- or 5-coordinate, respectively.

Because of the volatility of these azatranes, they are attractive to evaluate as MOCVD precursors for nitride films. The monomeric azaaluminatrane Al(^{t}BuMe$_2$SiNCH$_2$CH$_2$)$_3$N was reported [68] in 1994 by the reaction of [Al(NMe$_2$)$_3$]$_2$ and (^{t}BuMe$_2$SiNHCH$_2$CH$_2$)$_3$N. Its analogue Al(Me$_3$SiNCH$_2$CH$_2$)$_3$N (**52**) was structurally characterized and shown to contain a trigonal monopyramidal aluminum center.



(52)

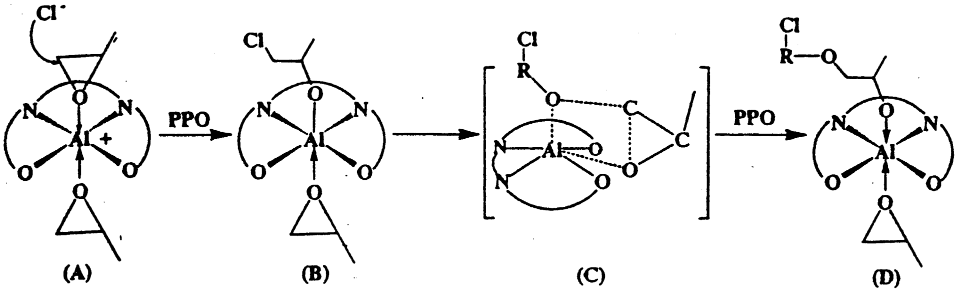
In 1976, Smith et al. solved [69] the crystal structure of (MeAlNMe)$_7$ (**53**). This was found to have a cage structure with C_{3v} symmetry in which each aluminum and each nitrogen atom in 4-coordinate are bound to one methyl group and three atoms within a cage.



(53)

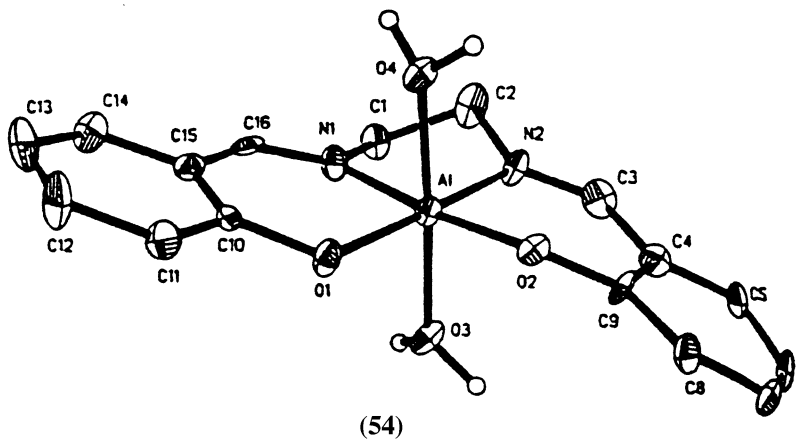
3.2. High coordinate derivatives (C.N. = 5, 6)

D.A. Atwood et al. reported [70] the syntheses and characterization of the cationic aluminum complexes of the formula LAlR (where R = Cl and L = Salen, SalenCl, Acen and where R = Me and L = Salen SalenCl, Acen; Salen = *N*,*N*′-ethylenebis(2-hydroxyphenyl)methylimine), SalenCl = *N*,*N*′-ethylenebis((2-hydroxy-5-chlorophenyl)methylimine), Acen = *N*,*N*′-ethylenebis((2-hydroxyphenyl)-1-ethylimine)). The LAlCl derivatives dissolve in water and MeOH to yield the cationic complexes $[LAl(H_2O)_2]^+Cl^-$ (L = Salen (**54**), salenCl, Acen) and $[LAl(MeOH)_2]^+Cl^-$ (L = Salen, SalenCl, Acen), respectively. An alternative preparation of the cationic species involves the reaction of the LAlCl derivative with $NaBPh_4$. This leads to complexes of formula $[LAl(MeOH)_2]^+BPh_4^-$ (L = Salen (**55**), SalenCl, Acen (**56**)). Al(Salen)R or Al(Acen)R complexes can be reacted with either MeOH or 4-chloro-3,5-dimethyl phenol (Ph′) to form complexes of general formula LAlOR (R = Me, L = Salen, SalenCl, Acen (**57**); R = Ph′, L = Salen, SalenCl, Acen). X-ray crystallographic study of $[SalenAl(H_2O)_2]^+Cl^-$ (**54**) indicates that the H_2O groups occupy the axial positions of an octahedral coordination environment around Al with an O–Al–O′ angle of 176.0(3)°. Complexes **55** and **56** also confirm a 6-coordinate geometry for Al centers. They adopt a distorted octahedral geometry and both are of same morphology as **54** thus, the coordinated solvents occupy axial positions while the ligand occupies the equatorial sites. As determined by X-ray crystallography, **57** adopts a methoxy bridged dimeric structure. There are two independent identical dimers in the unit cell and the Al_2O_2 four-membered ring is found to be planar. (Salen)AlCl or (Acen)AlCl complexes were found to be useful for the polymerization of propylene oxide where as the compounds LAlMe did not polymerize PPO monomer under the identical conditions. The results indicate that the MeOH bound cations polymerize propylene oxide while the H_2O bound cations do not. The catalytically active species is the aluminum cation and the polymerization of propylene oxide can be envisioned as shown in Scheme 5. One of the two coordinated substrates is activated by the counter anion (A) which reacts with PPO

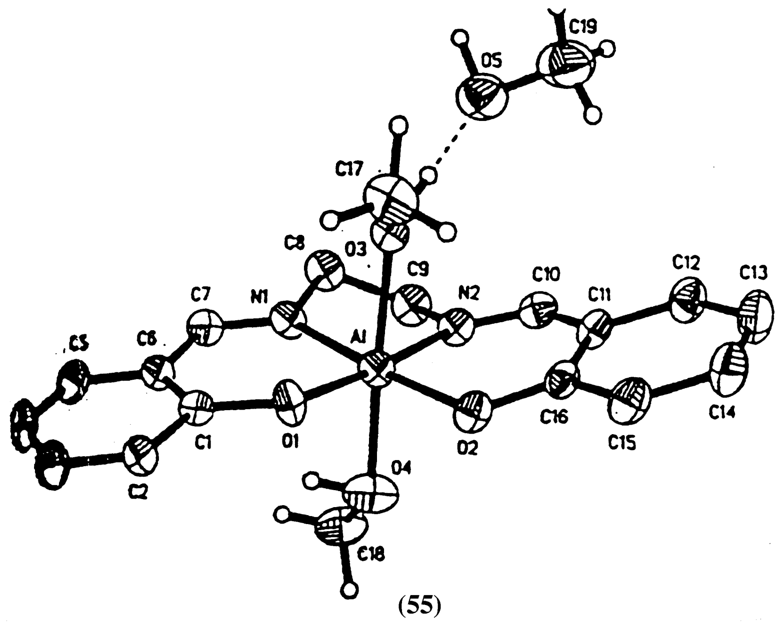


Scheme 5. Proposed mechanism of propylene oxide oligomerization.

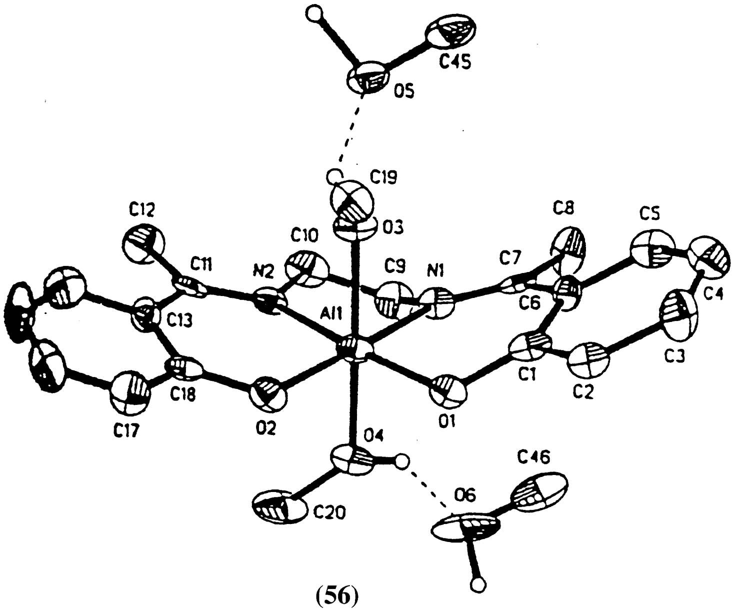
to give 1-chloro propanol (B) after hydrolysis. Subsequently each additional PPO group is added to the Al–O bond through a four centered intermediate (3C) resulting in the lengthening of the polyether (3D).



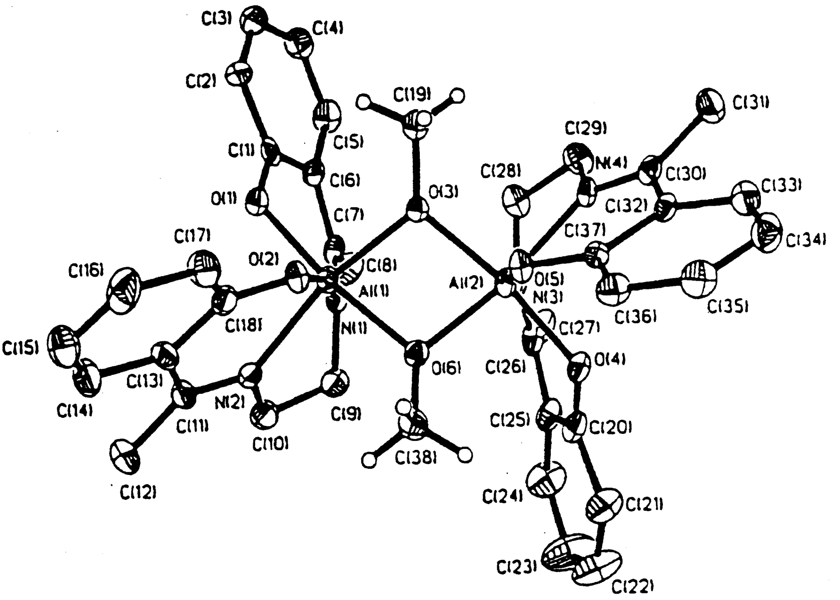
(54)



(55)



(56)

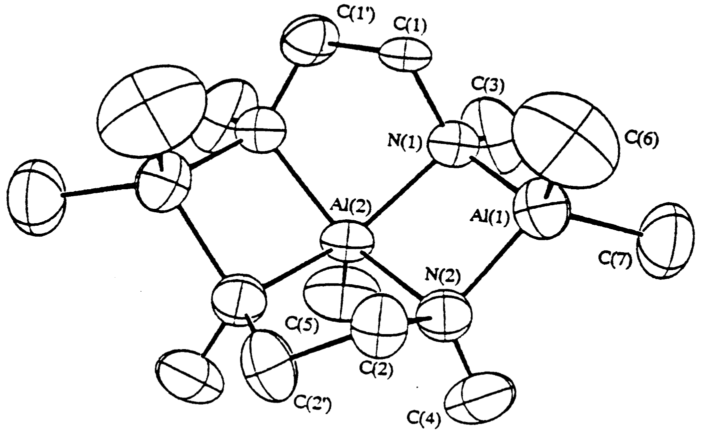


(57)

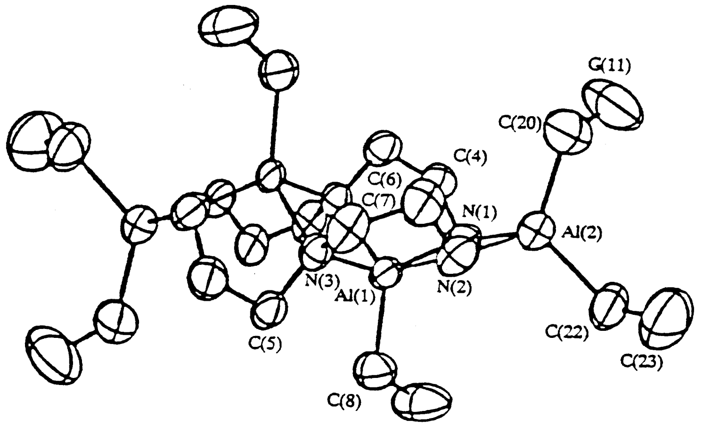
Reactions of $Al_2R'_4[N(C_2H_5)_2]_2$ ($R' = CH_3$, C_2H_5) with ethylene diamine or *N*,*N*′-dimethylethylenediamine yield air sensitive trialuminum products $[AlR'_2]_2[RNCH_2CH_2NR]_2[AlR']$ ($R' = CH_3$, $R = H$; **5**; $R' = CH_3$ (**58**); $R = CH_3$; $R' = C_2H_5$, $R = H$; $R' = C_2H_5$, $R = CH_3$) as shown in Eq. (12) [71]. Reactions of $Al_2R'_4[N(C_2H_5)_2]_2$ with diethylene triamine, $[(NH_2CH_2CH_2)_2NH]$, yield air sensitive tetraaluminum products, $(AlR'_2)_2[(HNCH_2CH_2)_2N]_2(AlR')_2$ ($R' = CH_3$; $R' = C_2H_5$) (**59**) as shown in Eq. (13):

$$3Al_2(NEt_2)R'_4 + 4RHNCH_2CH_2HNR$$
$$\rightarrow 2[AlR'_2]_2(NHCH_2CH_2NR)_2[AlR'] + 6Et_2NH + 2R'H \qquad (12)$$
$$2Al_2(NEt_2)_2R'_4 + 2(H_2NCH_2CH_2)_2NH$$
$$\rightarrow Al_4R'_6[(HNCH_2CH_2)_2N]_2 + 4Et_2NH + 2R'H \qquad (13)$$

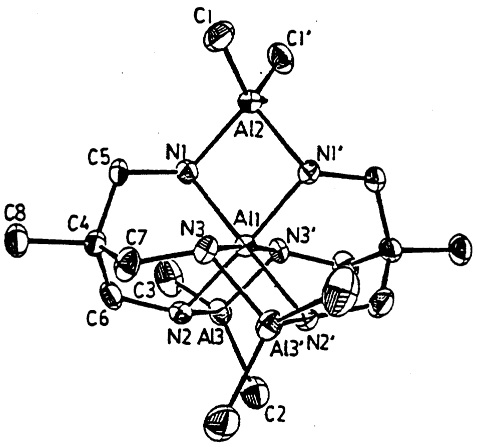
Complex **58** displays two different environments for the aluminum atoms and the ethylene diamines are bridged to three organoaluminum groups such that two Al_2N_2 cores are linked by the central aluminum atom. The coordination environments of the two outer aluminum atoms are in the usual tetrahedral coordination and the central aluminum atom is obviously in a square–pyramidal configuration. The complex $(AlEt_2)_2[(HNCH_2CH_2)_2N]_2(AlEt)_2$ (**59**) consists of two different environments for the aluminum atoms and the diethylenetriamine bridge four organoaluminum groups revealing three Al_2N_2 cores connected consecutively by two central aluminum atoms. The two outermost aluminum atoms are in the usual tetrahedral coordination and the two inner aluminum atoms are in a square–pyramidal configuration.



(58)



(59)

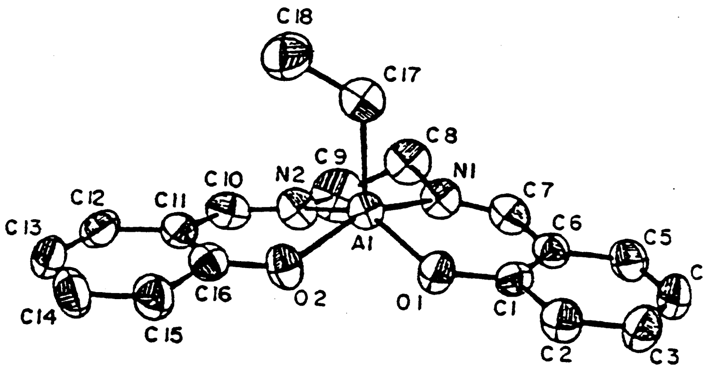


(60)

In 1994 Chang et al. reported [72] a novel organo aluminum amide $[Al(CH_3)_2]_3Al[CH_3C(CH_2NH)_3]_2$ (**60**) the first example involving a tripodal ligand of an organo aluminum compound. The compound was synthesized by reacting $[Al_2(NEt_2)_2Me_4]$ with excess 1,1,1-ethylidynetris(methanamine). Both 4- and 6-coordinated Al atoms were observed with the tripodal NH groups serving both as chelating and bridging ligands. The four aluminum atoms of the complex lie in a plane with three aluminum atoms forming an equilateral triangle around the fourth central aluminum atom. The central AlN_6 unit of the complex has an octahedral symmetry and the other three Al atoms are in a tetrahedral environment. The exact molecular symmetry is C_2 with the crystallographic two-fold axis passing through Al(1) and Al(2). There are two tripodal ligands coordinated to the four aluminum atoms. Aluminum alkyls are used extensively in bimolecular industrial catalytic processes, functioning primarily as reducing agents for the transition metal centers [73].

Aluminum alkyls are also known to form adducts with Lewis bases resulting in decreasing reactivity at the aluminum carbon bond. The coordination chemistry of alkyl aluminum species with classical type ligands however has received less attention. This is probably a consequence of the hydrolysis that occurs in aqueous solution and the apparent difficulty in finding suitable Al^{3+} starting reagents. Aluminum chelate complexes have been largely ignored compared to the transition metal complexes of Schiff base ligands because synthetic difficulties were perceived and possibly because the inert gas neon configuration provides no interesting electronic spectra in contrast to the rich and informative spectra obtained from transition metal compounds [74]. The oxophilicity of aluminum and the tendency for hydrolysis precludes the synthesis of aluminum nitrogen bonded complexes by conventional ligand exchange reactions. The properties of aluminum chelate complexes once isolated are expected to be similar to those of first row transition metals on the basis of considerations of size and charge. The ionic radius of aluminum is comparable to those of high valent first row transition metals and thus, aluminum should have a good fit into the centers of the chelating rings.

The Schiff base aluminum alkyl complexes can be synthesized by the addition of trialkylaluminum to the tetradentate bases having two replaceable protons. The reactions are exothermic; ethane and aluminum alkyl ligand complex are produced immediately on mixing. The ligands used include the 2:1 condensation products of salicylaldehyde with ethylenediamine, *o*-phenylenediamine and propylenediamine (Salen, Salophen and Salpn, respectively) and of acetylacetone with ethylene diamine (Acen). The susceptibility of these complexes to moisture in solution is dependent to a remarkable degree on the flexibility of the ligand. Goedken et al. proposed [74] that the remarkable resistance to hydrolysis as compared with nonchelated aluminum alkyl species is related to the high energy state of the square–planar 4-coordinate Al^{3+} species remaining on loss of the alkyl group. The X-ray crystal structure of $Al(Salen)C_2H_5$ (**61**) reveals a five coordinate square–pyramidal aluminum complex strongly bound to both the oxygen and nitrogen ligand atoms. The Salen moiety adopts the usual inverted umbrella structure observed for monomeric transition metal species. The ethyl bridge is rigid, one methylene carbon above and one below the plane of the nitrogen and oxygen donor atoms. The ethyl group is staggered with respect to the N and O of a salicylidene moiety and away from the methylene carbon.

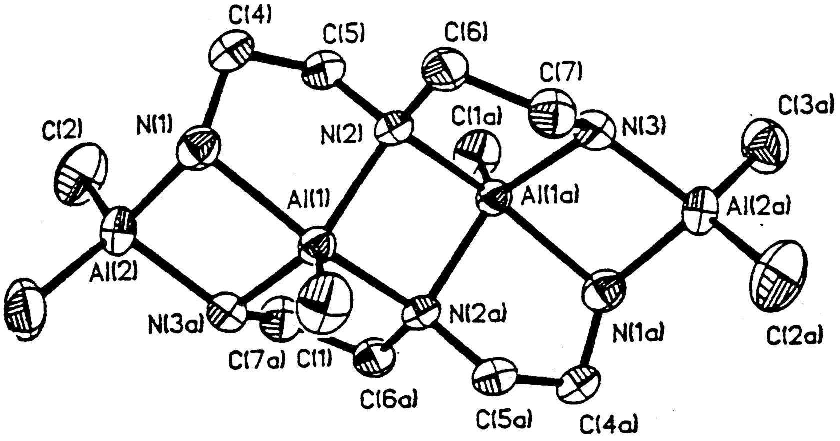


(61)

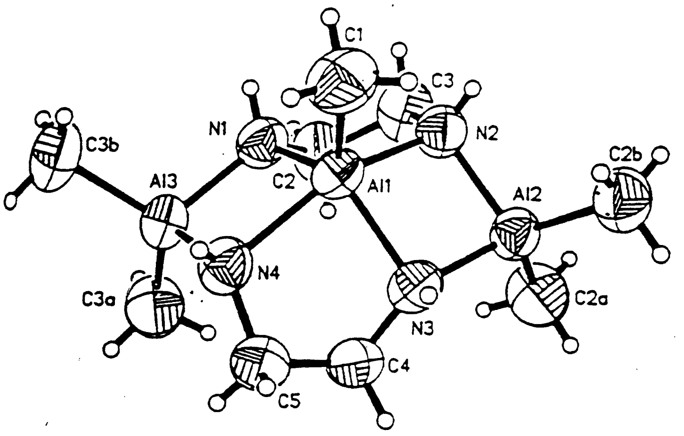
$[Al(CH_3)]_2[C_8H_{20}N_6][Al(CH_3)_2]_2$ (**62**) was prepared by the reaction of an excess of trimethyl aluminum with diethylene triamine as shown in Eq. (14) [75]. This represents the first report of an organometallic complex containing aluminum atoms in square–pyramidal environment:

$$2(H_2NCH_2CH_2)_2NH + 4Al(CH_3)_3 \rightarrow [Al(CH_3)]_2[C_8H_{20}N_6][Al(CH_3)_2]_2 + 6CH_4 \qquad (14)$$

Smith and coworkers reported that the reaction temperature played a pivotal role in determining the nature of the reaction products when aluminum alkyls react with amines [76]. It was further noted that primary and secondary amines react with aluminum alkyls at low temperatures forming 1:1 addition compounds $((H_3N)AlR_3)$. However at significantly higher temperatures alkane was released due to cleavage of N–H and Al–R bonds resulting in reaction products possessing Al_2N_2 fragments.

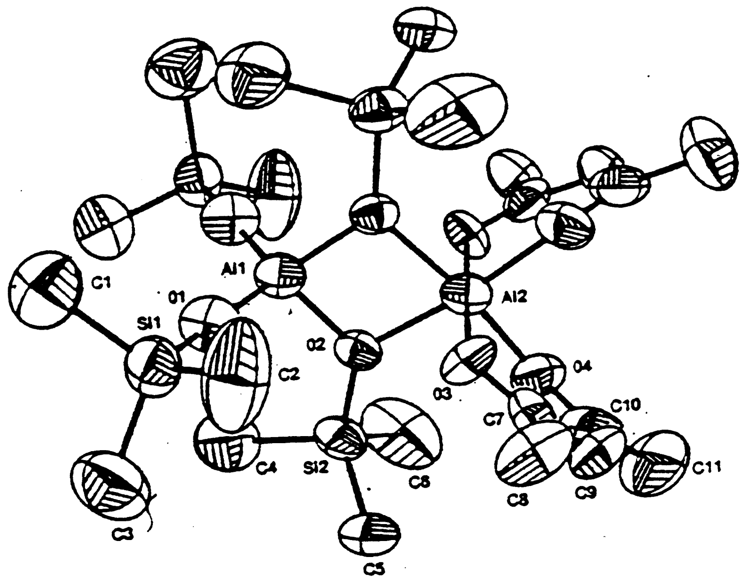


(62)

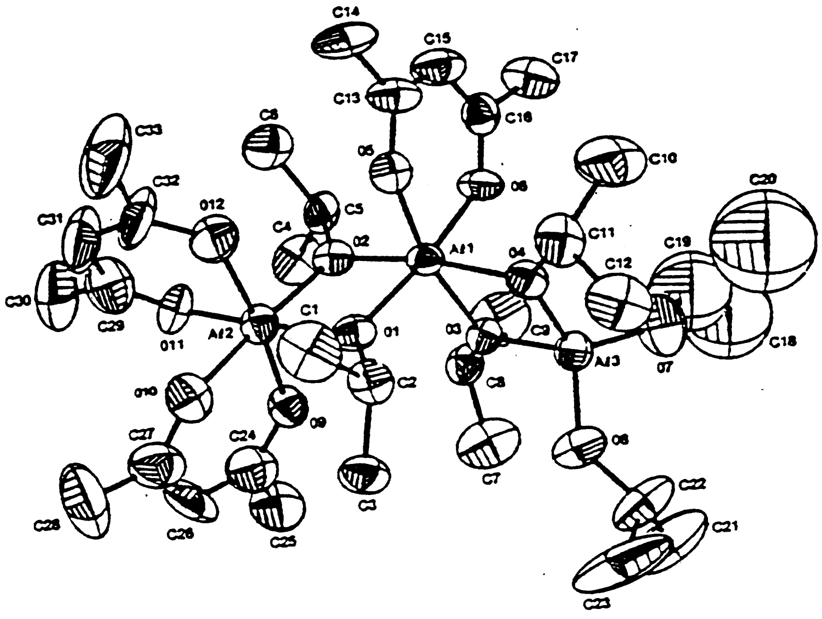


(63)

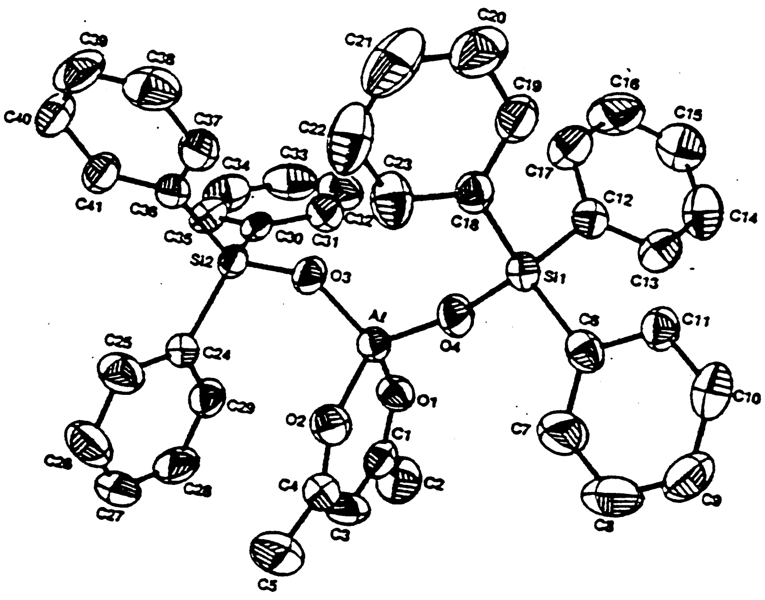
In order to obtain precursors with the appropriate physical and chemical properties for use in the generation of the aluminum nitride, in particular final forms (e.g. powder, monolith, fiber, thin film), as well as to control the purity and microstructure of these products, a better basic understanding of the dependence of the physical properties and pyrolysis reactions of organoaluminum nitrogen compounds on molecular structure is needed. In 1991, Interrante et al. reported [77] the details of the studies of the reactions of ethylenediamine with triethylaluminum or trimethylaluminum in a 2:3 ratio which resulted in the formation of $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$ (**63**) and $EtAl[Al(HN(CH_2)_2NH)AlEt_2]_2$. The crystal structure of **63** shows that Al atoms were found to have both tetra and penta coordinations. An insoluble, presumably polymeric solid was also obtained by the pyrolysis of **63** at 180°C. Synthesis and characterization of several Al alkoxide and


C1
Al1
O1
Si1
O2
C2
Al2
O4
O3
C7
C10
C4
Si2
C6
C8
C9
C11
C3
C5

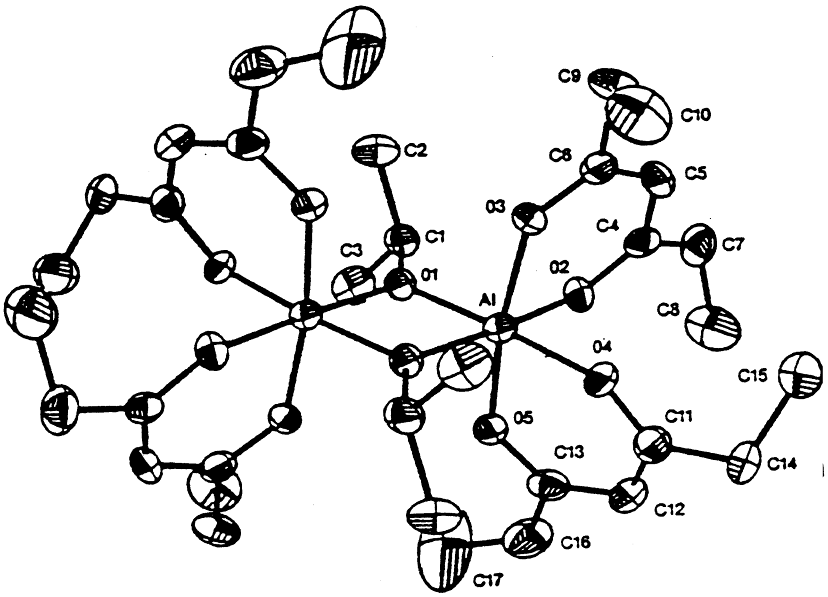
(64)


C14
C15
C17
C13
C16
C6
C33
O5
O6
C10
C32
O12
C20
C31
C5
C4
O2
Al1
O4
C11
C19
C12
C30
C29
O11
Al2
C1
O1
O3
C9
Al3
O7
C18
C2
C8
O10
O9
O8
C27
C24
C7
C22
C3
C28
C26
C25
C21
C23

(65)

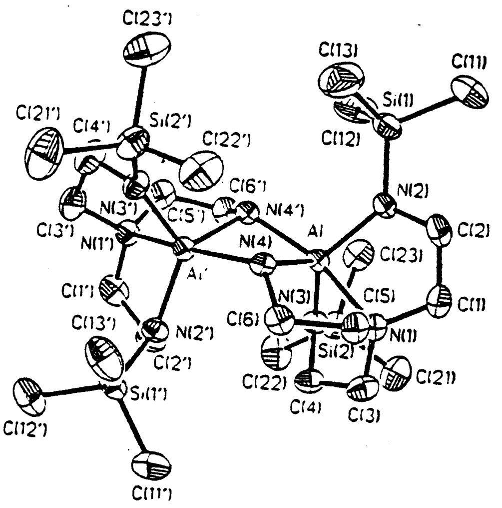


(66)



(67)

siloxide β-diketonate complexes including aluminum compounds of the general formula $[Al(OR)_2(acac)]_n$ (acac = acetylacetone; $n = 1$ for $R = SiPh_3$; $n = 2$ for $R = SiMe_3$, ^iPr and ^tBu; $n = 3$ $R = {}^iPr$) and $[Al(OR)(\beta\text{-diketonate})_2]_2$ (for $R = {}^iPr$,

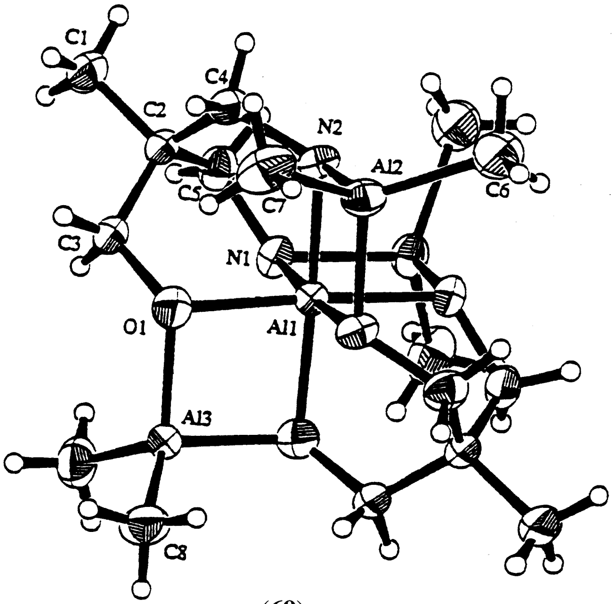


(68)

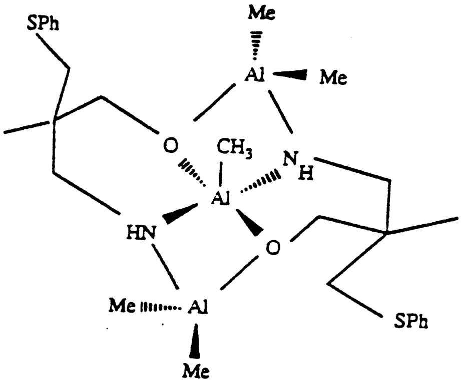
β-diketonate = acetylacetone, 3,5-heptanedione and ethyl acetoacetate for R = Me, β-diketone = ethylacetoacetate) were reported by Wengrovius et al. in 1986 [78]. These compounds have unprecedented structures and reactivity and pose some interesting considerations as to their activity as catalyst and ceramic precursors. The X-ray crystal structures of $[Al(OSiMe_3)_2(acac)]_2$ (**64**) and $[Al(O\text{-}^iPr)_2(acac)]_3$ (**65**), $Al(OSiPh_3)_2(acac)$ (**66**), and $[Al(O\text{-}^iPr)(Et_2)(acac)_2]_2$ (**67**) are reported. The compounds of the type $[Al(OR)_2(acac)]_n$ contain tetrahedral and octahedral aluminum sites and n is dependent on the size of the alkoxide or siloxide ligand. The $[Al(OR)(\beta\text{-diketonate})_2]_2$ complexes are dimers containing two octahedral aluminum centers bridged by alkoxide groups. These compounds are thermally unstable in solution and decompose via ligand disproportionation to $Al(\beta\text{-diketonate})_3$ and $[Al(OR)_2(\beta\text{-diketonate})]_n$. Dynamic ^1H NMR spectra of $[Al(O\text{-}^iPr)(acac)_2]_2$ show isomerism between meso and D,L isomers and restricted rotation of the bridging isopropoxide groups at low temperatures.

The dimeric azaaluminatrane $[Al(Me_3SiNCH_2CH_2)_2(HNCH_2CH_2)N]_2$ (**68**) possesses an unusual *cis* configuration of the central four-membered ring and the aluminum atoms display a distorted trigonal bipyramidal coordination sphere [68].

Organoaluminum compounds have received much attention due to their importance in synthetic applications. Among these complexes, coordination of polydentates towards an aluminum center is an interesting topic which provides much information about the properties of organoaluminum compounds. The polydentates commonly seen are tripodal ligands. The reactions of $[Me_2Al(\mu\text{-}NEt_2)_2]$ with mixed donor tripodal ligands were reported [79] by Chang et al. in 1998. 2,2-Bis(aminomethyl)-1-propanol yielded a tetranuclear $[AlMe_2]_3Al[CH_3C(CH_2NH)_2\text{-}(CH_2O)]_2$ (**69**) whereas the reaction of the aluminum dimer with 2-aminomethyl, 2-(thiophenylmethyl)-1-propanol, $CH_3C(CH_2NH_2)(CH_2OH)(CH_2SPh)$ yielded a trinuclear compound $(AlMe_2)_2AlMe[CH_3C(CH_2NH)(CH_2O)(CH_2SPh)]$ (**70**), respec-



(69)



(70)

tively. The central aluminum atom is surrounded by two tripodal ligands in an octahedral geometry, whereas the other three aluminum atoms act to bridge the two ligands. From the ^{1}H, ^{13}C NMR data, IR, mass and elemental analytical data, it was observed that compound **70** has a pentacoordinated aluminum center surrounded by two tripodal ligands and one methyl group. The sulfur atoms on the tripodal ligand were not coordinated to the central aluminum atom.

4. Organo aluminum–magnesium diamides

Complexes between Mg alkyls and Al alkyls have been known since 1957. Ziegler and Holzkamp prepared and characterized highly soluble complexes of the type $RMg(AlR_4)$ and $Mg(AlR_4)_2$ ($R =$ methyl or ethyl) from R_3Al and Grignard reagents [80]. More attention was directed to the dialuminum magnesium complexes owing to their catalytic role in polymerization. The reactions of nucleophiles with aluminum magnesium complexes were found to give interesting results due to the rich coordination chemistry and the partially positive magnesium centers. Oligomers are preferred in the solid state instead of monomers. A well established feature of the organometallic chemistry of Mg–Al is the tendency of their alkyl aryl derivatives, amino-groups and alkoxides to adopt a structure with three center or even four center electron pair bonds with multiple Al centers. However, there are only limited reports on the chemistry of the mixed metal organometallic compounds.

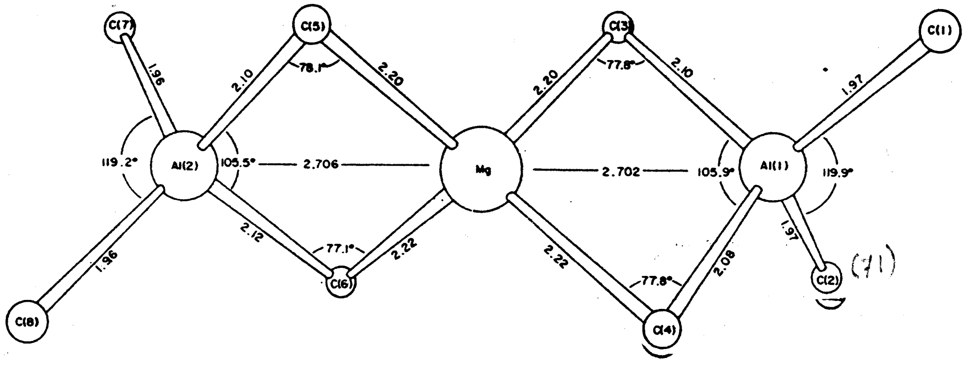
Organoaluminium magnesium complexes can be generally prepared as described in Eq. (15). In 1975 Malpass et al. reported that in $(R_2Mg)\cdot(R'_3Al)$ alkyl group exchange occurs between the organoaluminium and organomagnesium compounds and that the state of association increases as the Mg/Al ratio in the complex increases [81]:

$$2RX + 2Mg \rightarrow R_2Mg + MgX_2 \xrightarrow{\overset{R'_3\ Al}{\text{hydrocarbon}}} (R_2Mg)(R'_3Al) \tag{15}$$

The heterocyclic four-membered ring systems formed by Group II and III metals with one electron alkyl and aryl donors are characterized by metal–metal distances approximately equal to their single bond metallic diameters and relatively small metal–carbon metal bridge angles ranging from 66 to 78°. In order to learn more about the relative stereochemical importance of metal–metal interactions, steric effects of groups external to the heterocyclic ring, steric effects across the ring between bridging atoms, dative ligand–metal π-bonding, the electron distribution about the bridging atom in isoelectronic series of the type R_3C–, R_2N–, RO– and F– and intermolecular forces within the crystal lattice a systematic investigation of a number of polynuclear systems is required. Such a study will provide realistic models for the extensive synthetic chemistry involving Group II and III organometallic complexes as intermediates. The structural features of $(CH_3)_8MgAl_2$ and the NMR spectra of $(CH_3)_2$–Mg–Al$(CH_3)_3$ were reported by G.D. Stucky et al. in 1963.

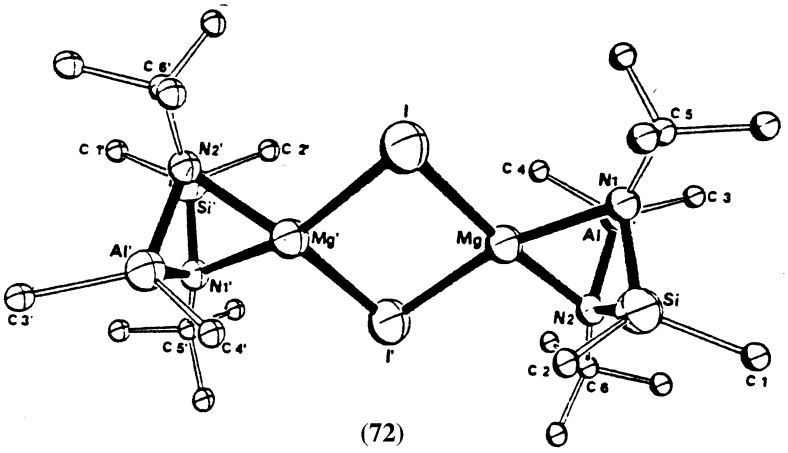
Dimethylmagnesium dissolves in trimethylaluminum to give two crystalline compounds and the crystal structure of the lower melting electron deficient product octamethyldialuminum monomagnesium, $Mg[Al(CH_3)_4]_2$ (**71**) has been determined by X-ray diffraction. Solution studies of $Mg[Al(CH_3)_4]_2$ are complicated by the existence of the equilibrium.

$$2Mg[Al(CH_3)_4]_2 \Leftrightarrow [MgAl(CH_3)_5]_2 + 2Al(CH_3)_3$$



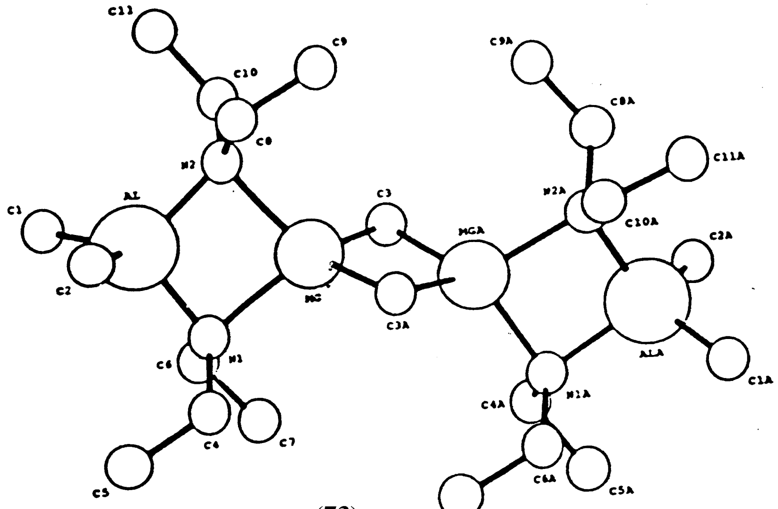
(71)

In 1987, Veith et al. reported the crystal structure of an interesting $[AlMg]_2$ complex $\{Me_2Si[N(^tBu)]_2(AlMe_2)(MgI)]_2$ (**72**). The geometry around both the metal centers are distorted tetrahedral with I^- bridging ligands [82]. In 1992 Chang et al. reported the synthesis and spectral characterization of Mg/Al multinuclear bridged complexes $Al_2X_6Mg[N(C_2H_5)_2]_2$ ($X = Cl$, Br), $Al_2X_4(NR_2)_2$ ($R = C_2H_5$, $^iC_3H_7$, $X =$ Cl, Br), $AlX_3HNR_2(R = {}^iC_3H_7)$ by the reaction of $AlCl_3$ with $Mg(NR_2)_2$ ($R = Et$, $^iPr_2$) [83].

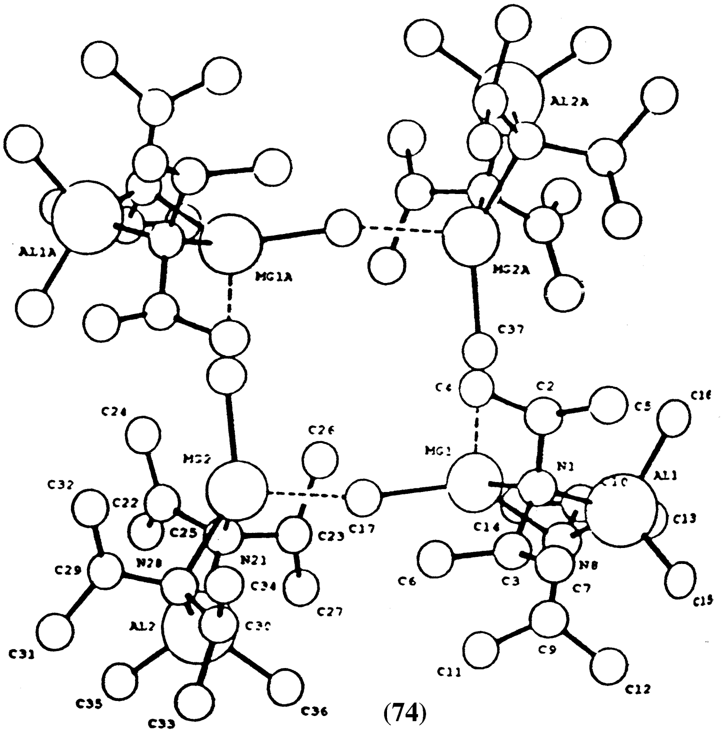


(72)

Crystal structures of the two aluminum complexes $Al_2Cl_4[N(C_2H_5)_2]_2$ and $AlCl_3HN(^iC_3H_7)_2$ show that the Al atoms are in tetrahedral bonding geometry and the four-membered ring of Al_2N_2 in $Al_2Cl_4[N(C_2H_5)_2]_2$ is almost planar. The

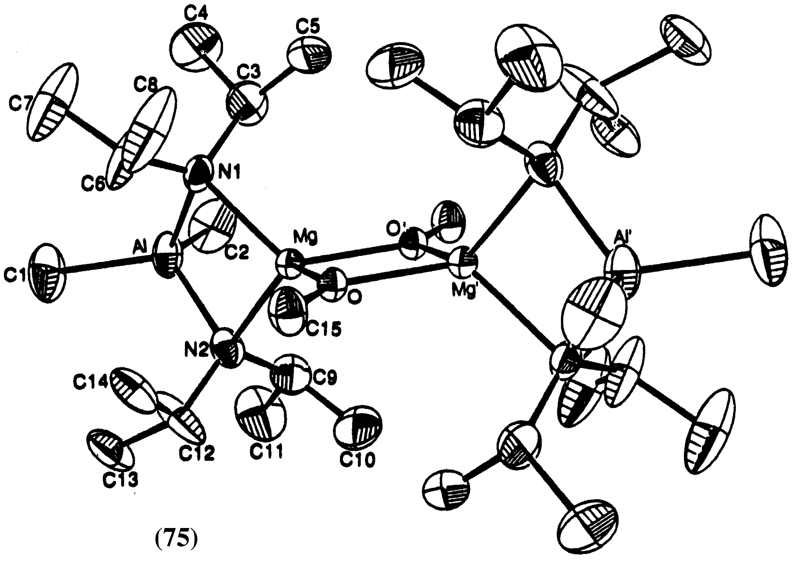

C11
C9
C10
C8
N2
AL
C1
C2
MG
C3
C3A
C6
N1
C4
C7
C5
C9A
C8A
C11A
N2A
C10A
MGA
C2A
ALA
C1A
C4A
N1A
C6A
C5A
C7A

(73)


AL2A
AL1A
MG1A
MG2A
C37
C4
C2
C5
C16
C24
C26
MG2
MG1
N1
AL1
C32
C22
C25
C23
C17
C14
C13
N21
C29
N28
C34
C27
C6
C3
N8
C7
C15
AL2
C30
C31
C9
C11
C12
C35
C33
C36

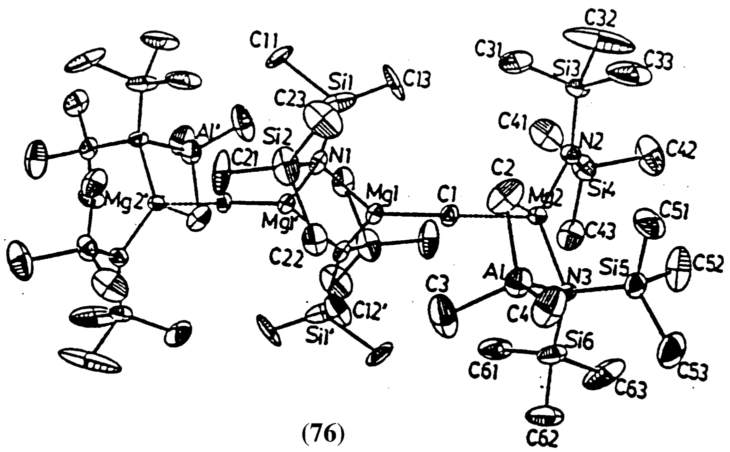
(74)

reaction of $AlMe_3$ with $Mg(NEt_2)_2$ or $Mg[N(^iPr_2)_2]_2$ gives $\{Me_2Al(\mu\text{-}NEt_2)_2MgMe_2\}_2$ (**73**) or $\{Me_2Al[\mu\text{-}N(^iPr_2)]_2MgMe\}_4$ (**74**), respectively [84]. Four molecules of $Me_2Al[\mu\text{-}N[^iPr_2)]_2MgMe$ associate weakly as a tetramer **74** in the solid state through the interactions of tricoordinate magnesiums with carbons and or hydrogens yielding the first example of the Mg···Me–Mg unsymmetrical interactions such as in $(LiR)_n$. Compound **74** formed the magnesium–aluminium alkoxide derivative $\{Me_2Al(\mu\text{-}N^iPr_2)_2Mg(\mu\text{-}OMe)\}_2$, (**75**) on oxidation which has been structurally characterized. Pyrolysis of the Al–Mg complexes resulted in the formation of Al dimers

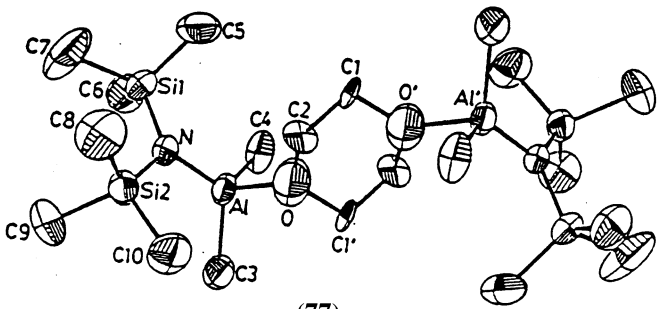


(75)

Two molecules of $Me_2Al[\mu\text{-}NEt_2]_2MgMe$ associate as a dimer through the interactions of 4-coordinate magnesiums with carbons in the case of **73**. In this molecule, Al, N(1), Mg and N(2) form a coplanar heterocyclic four-membered ring and the two Mg atoms are linked by the methyl group and the Mg···Mg contact is less than the sum of van der Waals radius. In the case of **74**, Al(1), N(1), Mg(1) and N(8) form a non-coplanar heterocyclic four-membered ring. Bulky $N(SiMe_3)_2$ and different alkyl groups can be used to stabilize the monomer. Reaction of bis(dialkylamido)magnesium with trialkylaluminum yielded dimeric complexes and a tetrameric aluminum–magnesium complex. The syntheses, characterization and structures of the compounds $[\{R_2N)Mg(Me)\}_2\{Mg(NR_2)(NR_2)AlMe_3)\}_2]$ (**76**) and $\{Me_2Al[NR_2]\}_2$ (1,4-dioxane) (**77**) ($R = SiMe_3$) were studied by Chang et al. in 1994 [85]. The novel dimer $[\{R_2N)Mg(Me)\}_2\{Mg(NR_2AlMe_3)\}_2]$ ($R = SiMe_3$) contains unusual linear metal···methyl-metal bridge interaction and agostic Mg···C–Al interaction. The structure of compound **76** contains two monomeric $Me_3Al\{\mu\text{-}N(SiMe_3)_2\}Mg\{N(SiMe_3)_2\}$ molecules bound through Mg atoms to the methyl groups of $MeMg\{\mu\text{-}N(SiMe_3)_2MgMe$ with a center of inversion related to the two equivalent fragments. The coordination geometries about the Mg(2), Mg(1) and Al atoms are linear (quasi-two-coordinate), triangular, and distorted tetrahedral, respectively.

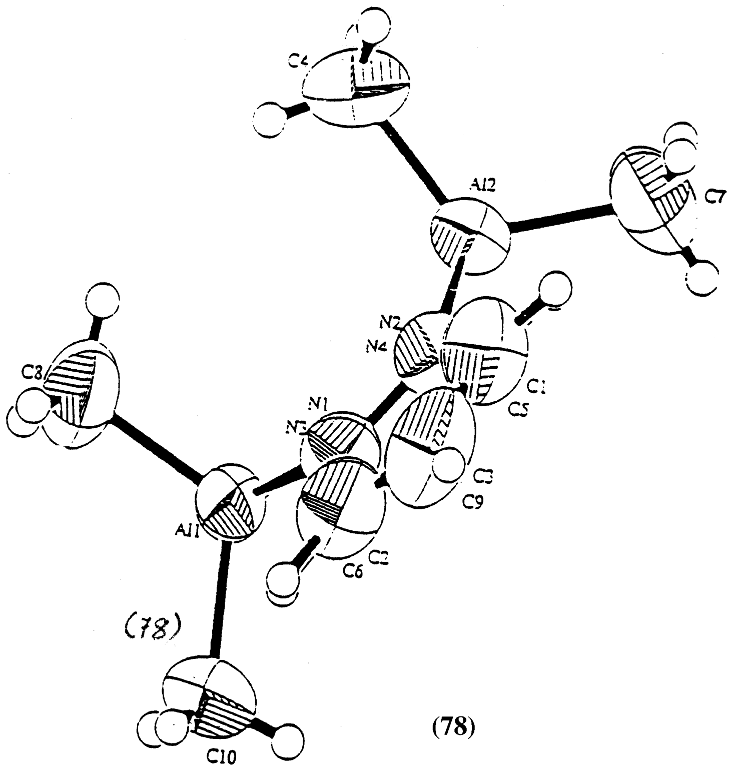


(76)



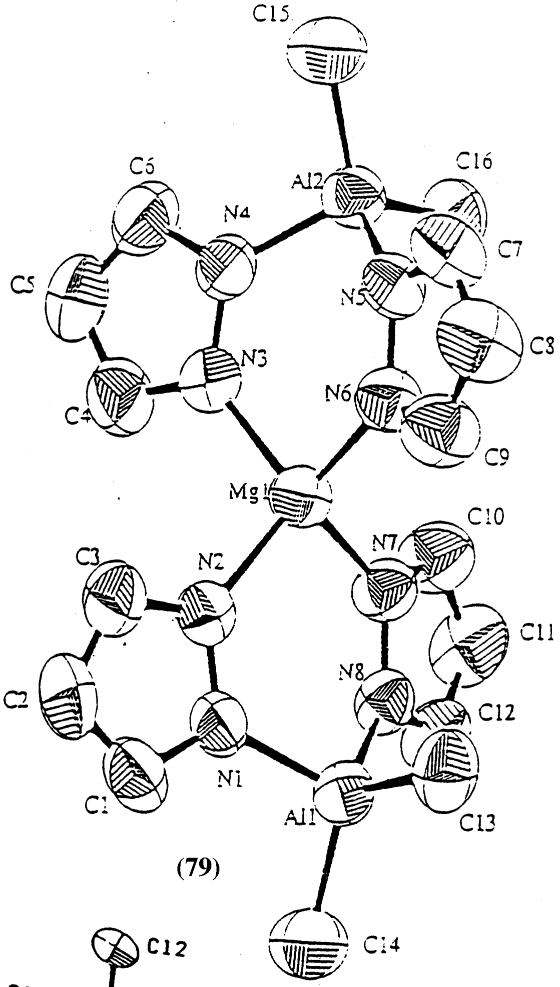
(77)

Compound **77** consists of a pair of $Me_2\{(Me_3Si)_2N\}Al$ moieties linked by a common dioxane molecule with an inversion center located at the center of the dioxane molecule. The dioxane moiety is in the chair conformation with the aluminum atoms in the distorted tetrahedral environments. Chemical reactions of $\{AlMg\}_2$ with nucleophiles in varied stoichiometry were reported by Chang et al. in 1994 [86]. $[Me_2Al(\mu\text{-}N^iPr_2)_2MgMe]_4$ reacted with chloroform to give $[Me_2Al(\mu\text{-}N^iPr_2)_2MgCl]_2$ in high yield which underwent metathesis with LiR ($R = t\text{-}C_4H_9$, C_6H_5) to give $[Me_2Al(\mu\text{-}N^iPr_2)_2MgR]_n$ ($n = 1, 2$). Reaction with pyrazole (pz) in a molar ratio 1:1 gave $[Me_2Al(\mu\text{-}N^iPr_2)_2Mg(Pz)]_2$ and in a molar ratio 1:3 to gave $[Me_2Al(\mu\text{-}Pz)_2AlMe_2]_4$ (**78**) and $[Me_2Al(\mu\text{-}Pz)_2Mg(\mu\text{-}Pz)_2AlMe_2]$ (**79**). The compound $[Me_2Al(\mu\text{-}N^iPr_2)_2MgCl]_2$ reacted with $AlMe_3$ to give $[Me_2Al(\mu\text{-}N\text{-}^iPr_2)(\mu\text{-}Me)Mg(\mu\text{-}N^iPr_2)(\mu\text{-}Me)AlMe_2]$ (**80**) which was also obtained from reaction with $Mg(N^iPr_2)_2$ in a molar ratio 3:1. The crystal structures of compounds **78** and **79** show that both have either Al_2Mg or Al_2 frameworks with pyrazolides replacing amides as bridging ligands. The pyrazolides serve as bridges between the two metals and the six-membered ring consisting of N_4 on pyrazolides and Al_2 was found to have boat shaped conformation. The aluminum atoms exist in distorted tetrahedral environment. In compound **80** both the amido and methyl groups act as bridging ligands between aluminum and magnesium atoms. Al(1), N(1), Mg, C(1) and Al(2), N(2), Mg, (C(2) make up two non-planar heterocyclic four-membered rings, respectively, in a spiro form.

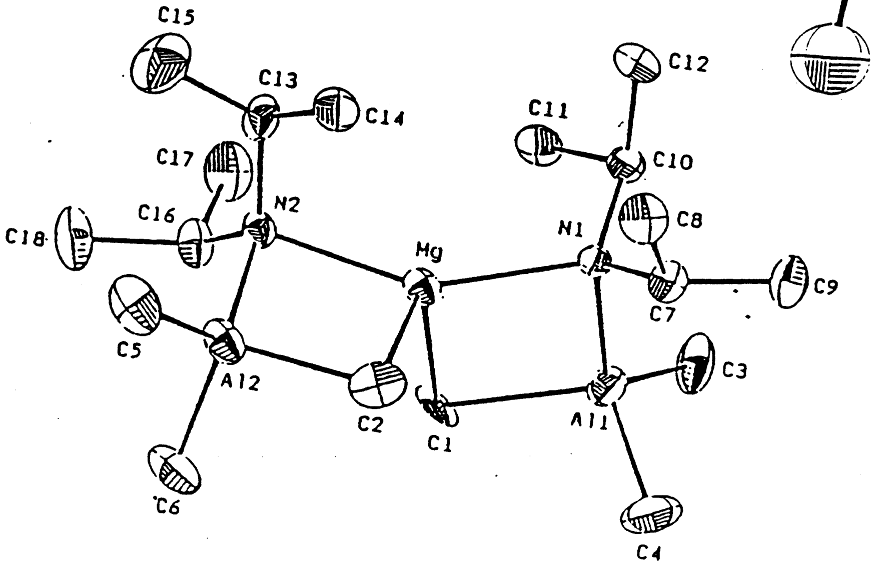


(78)

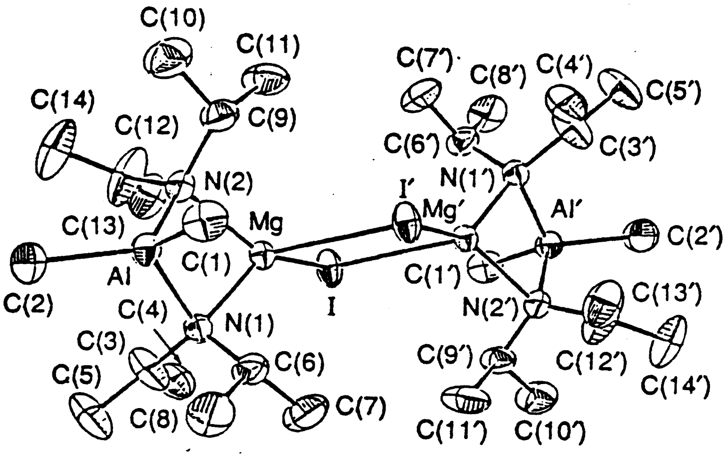
The nucleophilic attack of alcohols, amines and iodine on the magnesium atoms of the complex $[Me_2Al(\mu\text{-}N^iPr_2)_2MgMe]_4$ (**74**) and $[Me_2Al(\mu\text{-}NEt_2)_2MgMe]_2$ (**73**) has also been investigated [87]. Compound **74** undergoes metathesis with amines (Et_2NH and $^iPr_2NH$) and I_2 to give $[Me_2Al(\mu\text{-}N^iPr_2)_2Mg(\mu\text{-}NR_2)]$ ($R = Et$ or ^iPr) and $[Me_2Al(\mu\text{-}N^iPr_2)Mg(\mu\text{-}I)]_2$ (**81**), respectively. Partial degradation of **74** with MeOH or ethanol gives $Me_2Al(\mu\text{-}N^iPr_2)(\mu\text{-}OMe)Mg(\mu\text{-}N^iPr_2)(\mu\text{-}OMe)AlMe_2$ and $[Me_2Al(\mu\text{-}N^iPr_2)(\mu\text{-}OEt)Mg(\mu\text{-}N^iPr_2)(\mu\text{-}OEt)AlMe_2$ (**82**), respectively. Whereas, partial degradation of **74** with ^tBuOH gives $Me_2Al(\mu\text{-}O^tBu)_2Mg(\mu\text{-}O^tBu)_2AlMe_2$ (**83**) and $[Me_2Al(\mu\text{-}O^tBu)_2Mg(\mu\text{-}O^tBu)]_2AlMe_2$ (**84**). Compound **73** underwent metathesis with ^tBuOH also to give **83** and **84**. Degradation products were also obtained on heating due to the thermal instability of $\{AlMg\}_2$ systems. $[AlMg]_2$ could not be isolated due to its instability and in the presence of excess $\{AlR_3\}$, transformed to $\{Al_2Mg\}$ and $\{Al_2\}$ species which were stable enough to be isolated and characterized.


C15
Al2
C16
C6
N4
C7
C5
N5
C8
N3
N6
C4
C9
Mg1
C10
N7
C3
N2
C11
C2
N8
C12
N1
C1
Al1
C13
C14

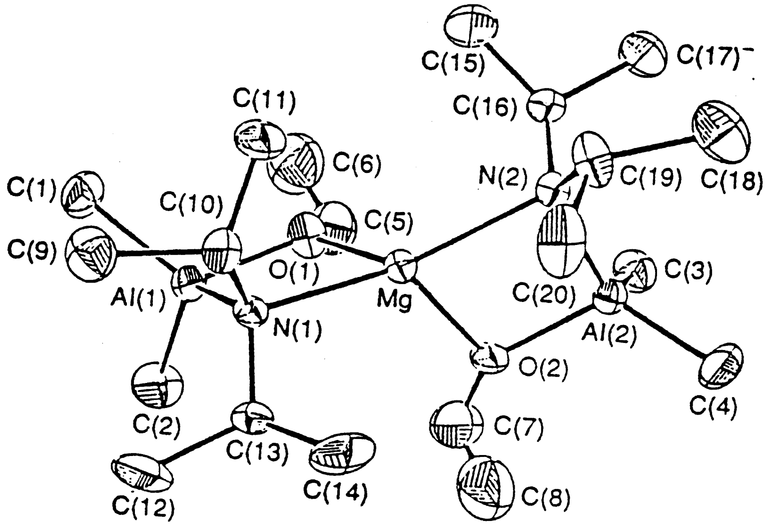
(79)


C15
C13
C14
C12
C11
C17
C10
C16
N2
C8
C18
Mg
N1
C9
C7
C5
C3
Al2
C2
C1
Al1
C6
C4

(80)

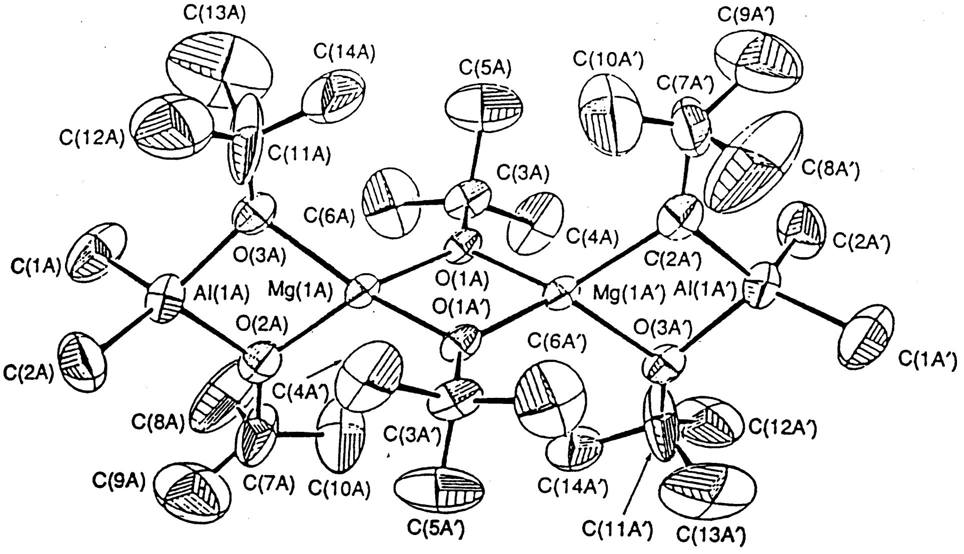


(81)

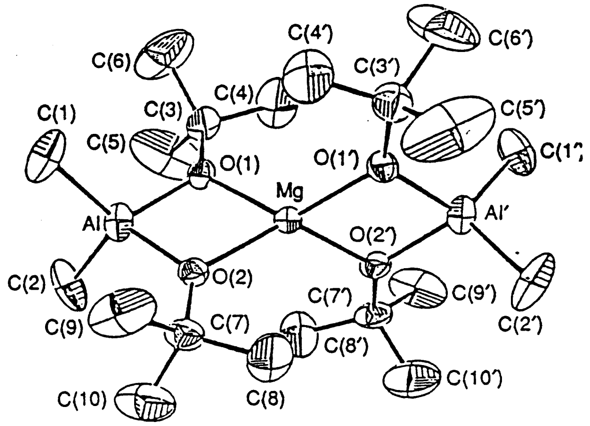


(82)

Compound **81** exists as a dimer with an inversion center in the middle of the molecule. The Al and the Mg atoms are in distorted tetrahedral environment and the Mg, I, Mg′, I′ atoms form an asymmetric coplanar four-membered ring in a spiro structure. The Al, N(1), Mg and N(2) atoms form a non-coplanar four-membered ring. In compound **82**, Al(1), N(1), O(1), Mg and Al(2), N(2), O(2), Mg atoms form two coplanar four-membered rings with spiro structure. Owing to the different bridging ligands the Al(1)–Mg–Al(2) angle of 150° denotes strong bending when compared with the other structures. The magnesium atoms are in highly

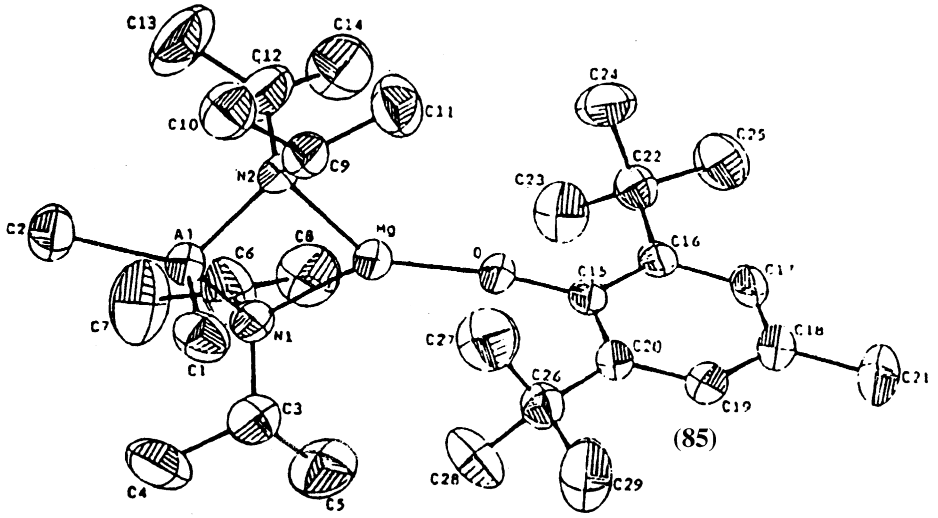


(83)

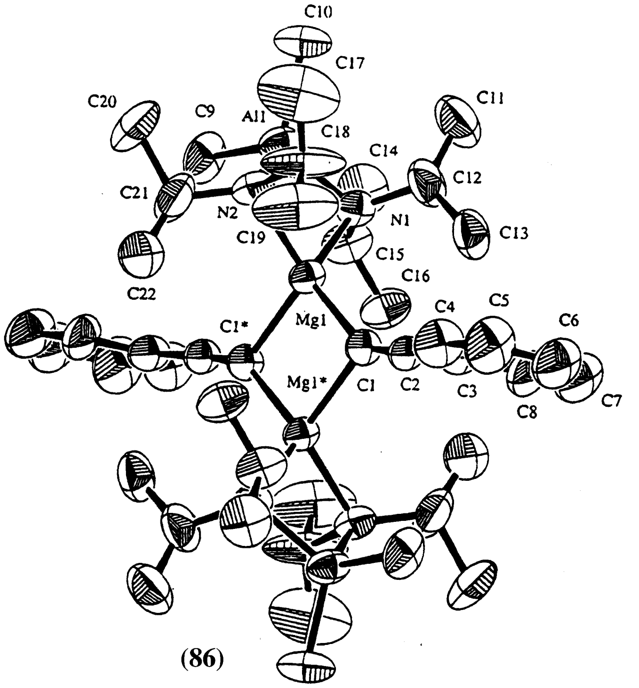


(84)

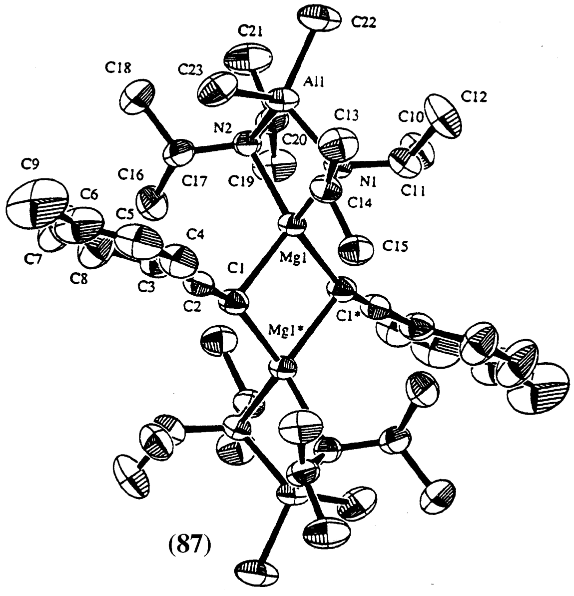
distorted tetrahedral environment. Compound **84** also has a spiro structure consisting of two planes formed by the AlO(1)–O(2)Mg atoms and that the Al and Mg atoms also exist in a distorted tetrahedral environment. Compound **83** is characterized by three orthogonal metal-(μ-O)-metal planes. The Al and Mg atoms exist in a distorted tetrahedral environment and an overlap between the metal and bridging ligand orbitals, i.e. dπ–pπ interactions between Al and O atoms and pπ–pπ interactions between Mg and O atoms are also observed. In 1995 Chang et al. also reported an example for the monomeric aluminum–magnesium complex {Me_2Al-[μ-$N(^iC_3H_7)_2]_2Mg[O$-2,6-$(^tC_4H_9)_2$-4-MeC_6H_2]} (**85**) which can be prepared by the reaction of tetrameric {Me_2Al[μ-$N(^iC_3H_7)_2]_2MgCH_3\}_4$ with 2,6-di-*tert*-butyl-4-methylphenol in a 1:4 ratio [88]. The compound was found to be sterically hindered due to the bulkiness of the phenol. The magnesium is triply coordinated and the aluminum is 4-coordinated and the four-membered ring of Al, N(1), Mg and N(2) does not exhibit the coplanar feature.



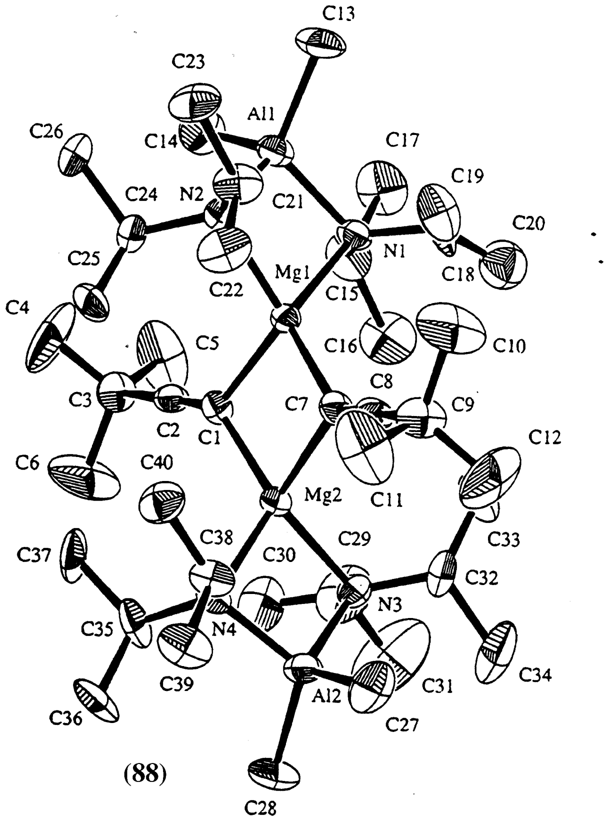
(85)



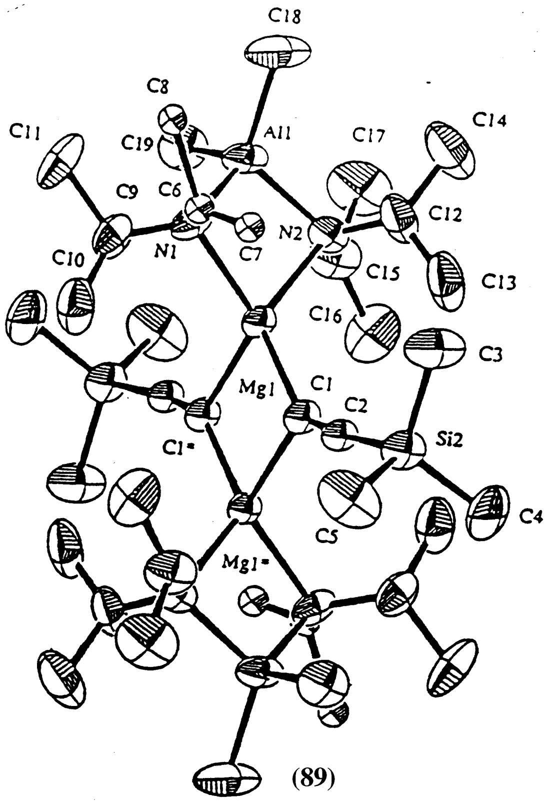
(86)


C22
C21
C23
Al1
C18
C12
C13
C10
N2
C20
C9
C16
C17
C19
N1
C11
C6
C14
C5
C4
Mg1
C15
C7
C1
C8
C3
C2
Mg1*
C1*

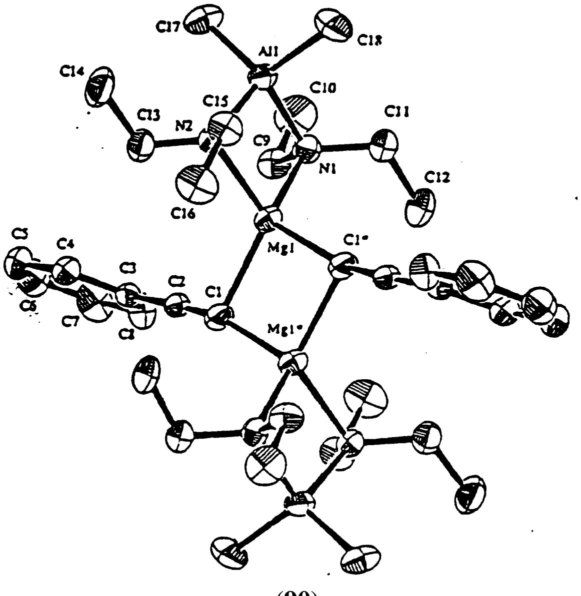
(87)


C13
C23
Al1
C26
C14
C17
C19
C24
N2
C21
C20
C25
N1
C18
C4
C22
Mg1
C15
C5
C16
C10
C8
C3
C7
C9
C2
C1
C12
C6
C40
Mg2
C11
C33
C38
C30
C29
C37
C32
N3
C35
N4
C39
C31
C34
Al2
C27
C36
C28

(88)


C18
C8
C11
C19
Al1
C17
C14
C9
C6
C12
N1
C7
N2
C10
C15
C13
C16
C3
Mg1
C1
C2
C1*
Si2
C4
C5
Mg1*

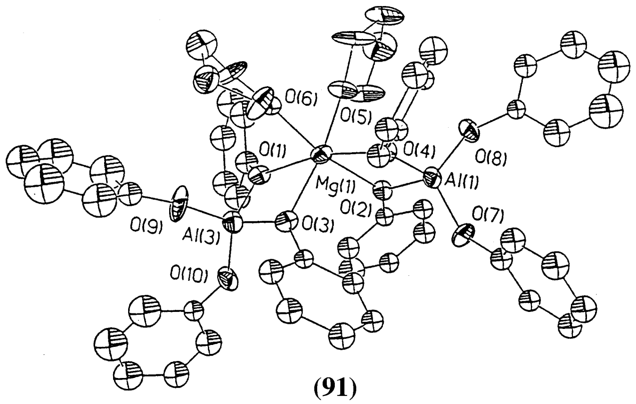
(89)


C17
Al1
C18
C14
C10
C15
C11
C13
N2
C9
N1
C12
C16
C5
C4
C3
C2
C1
Mg1
C1*
C6
C7
C8
Mg1*

(90)

A series of ethynyl bridged polynuclear aluminum–magnesium complexes $[Me_2Al(\mu\text{-}R'N)_2Mg(\mu\text{-}C{\equiv}CR)]_2$ ($R = C_6H_5$, (**86**), $C_6H_4\text{-}p\text{-}CH_3$, (**87**); ^{t}Bu, (**88**), $SiMe_3$, (**89**); $R = C_6H_5$, (**90**); $R' = {}^iPr$ or Et) were prepared by reaction of the aluminum–magnesium tetramer, $[Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg(\mu\text{-}Me)]_4$ (**74**) and the dimer $[Me_2Al(\mu\text{-}Et_2N)_2Mg(\mu\text{-}Me)]_{2,}$ (**73**) with various substituted acetylenes [89]. Ethynyl bridged complexes consists of three four-membered rings made of two tetrahedrally coordinated Al and Mg atoms with two bridging amido groups. The ethynyl bridging groups are almost perpendicular to the Mg–Mg vector. No substantial π-interactions between the magnesium and the ethynyl groups were observed. The central ring is defined by two magnesium and two a carbon atoms of the ethynyl groups. Complexes **86**, **87**, **89**, **90** contain inversion centers and therefore the central rings are planar. Complex **88** also has a planar Mg_2C_2 ring but without an inversion center. These complexes can be viewed as the first group of examples of dimeric ethynyl magnesium complexes.

Gilkje et al. reported the synthesis and structural characterization of $(THF)_2Mg[(\mu\text{-}OPh)_2Al(OPh)_2]_2$ (**91**) from the reaction of a mixture of Mg metal, HOPh and $[Al(OPh)_3]_n$ in refluxing THF motivated by a need for chemical vapor deposition (cvd) precursors to $MgAl_2O_4$ thin films [90]. The crystal structure shows that two independent molecules of $(THF)_2Mg[(\mu\text{-}OPh)_2Al(OPh)_2]_2$ occur within each asymmetric unit of the non-centric unit cell. The magnesium ion is coordinated by two THF molecules and by two $Al(OPh)_4$ ligands which chelate through double OPh bridges.

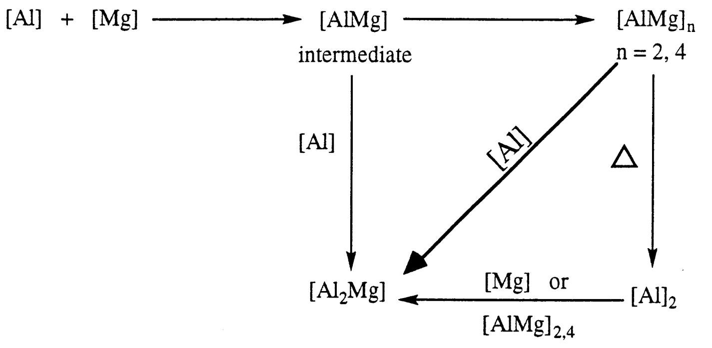


(91)

Aluminum alkyls, which are largely dimeric, interact with polymeric magnesium alkyls through complex formation, reducing the latter to smaller oligomeric units which are soluble in hydrocarbons. It was also reported by Malpass et al. [81] that on increasing the Mg/Al ratio of the reaction mixture polymers are obtained. Chang et al. also concluded [86] that an increase in the Mg/Al ratio of the reaction mixture results in viscous materials which are difficult to be characterized and when the Al/Mg ratio is increased from 1:1 to 3:1, an intermediate of formula $\{AlMg\}_2$

was observed. This could not be isolated due to its instability and in the presence of excess of {AlR$_3$}, transformed to {Al$_2$Mg} and {Al$_2$} species which were stable enough to be isolated and characterized. {AlMg}2 or 4 are thermally unstable and give {Al}. All of the above results can be rationalized as shown in Scheme 6.

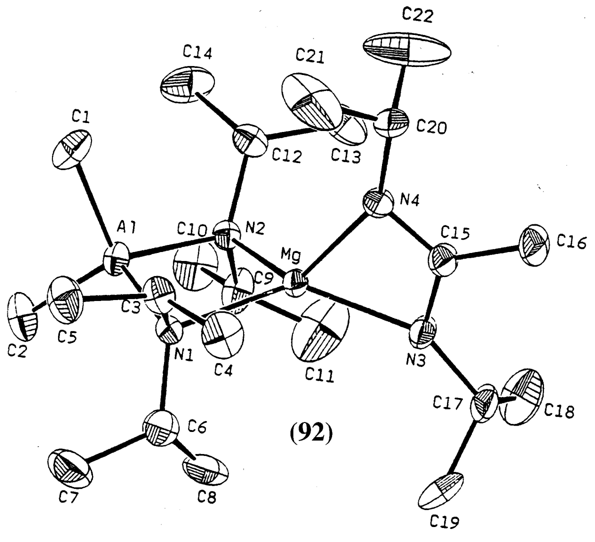
^{1}H NMR studies indicated that the reaction of {AlMg}$_2$ with a 1:1 ratio of AlMe$_3$ produced a thermally unstable geometrical isomer of {Al$_2$Mg}. Hence, it should be noted that the nature of the product formed in Mg–Al systems depends largely on the proportion of reactants.



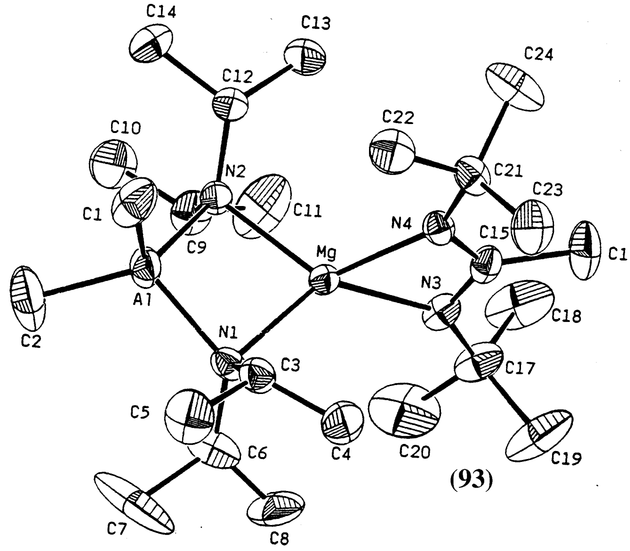
Scheme 6.

5. Heterocumulene insertions

The compounds of the class $[\mathrm{R_2Al(\mu\text{-}R'_2N)_2Mg(\mu\text{-}R)}]_n$ (R = Me, Et; R′ = Et, ^{i}Pr) ($n = 2$, 4) react with carbodiimides (RNCNR) to give a series of amidino bridged aluminum–magnesium complexes, $\{[\mathrm{R_2Al(\mu\text{-}R'_2N)_2Mg[(R'')NC(R)\ N(R'')]}]\}$ [91]. The structures of $\{[\mathrm{Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg[({}^iPr)NC(Me)N({}^iPr)]}]\}$ (**92**) and $\{[\mathrm{Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg[({}^tBu)NC(Me)N({}^tBu)]}]\}$ (**93**) have been determined which show that the bonding of the two nitrogens of the carbodiimide to the magnesium atom is (σ,σ) symmetric and indicate a weak interaction between Mg and C(15). Pyrolysis at 130°C of the amidine bridged complexes result in the dialuminum amido complex and some unisolated species due to the thermal decomposition. The unisolated species was assumed to be the polymer of MeMg(Et$_2$N). Both compounds **92** and **93** possess similar structural features except for the substituents of the [(R″)NC(Me)N(R″)] groups. Both exist as monomers possessing two coplanar heterocyclic four-membered rings AlN(1)N(2)Mg and MgN(4)C(15)N(3). The Mg–N distance of the AlN$_2$Mg moiety is longer than that of the MgCN$_2$ moiety which suggests that the chelating amidino ligand is more nucleophilic than the bridging amido ligand.



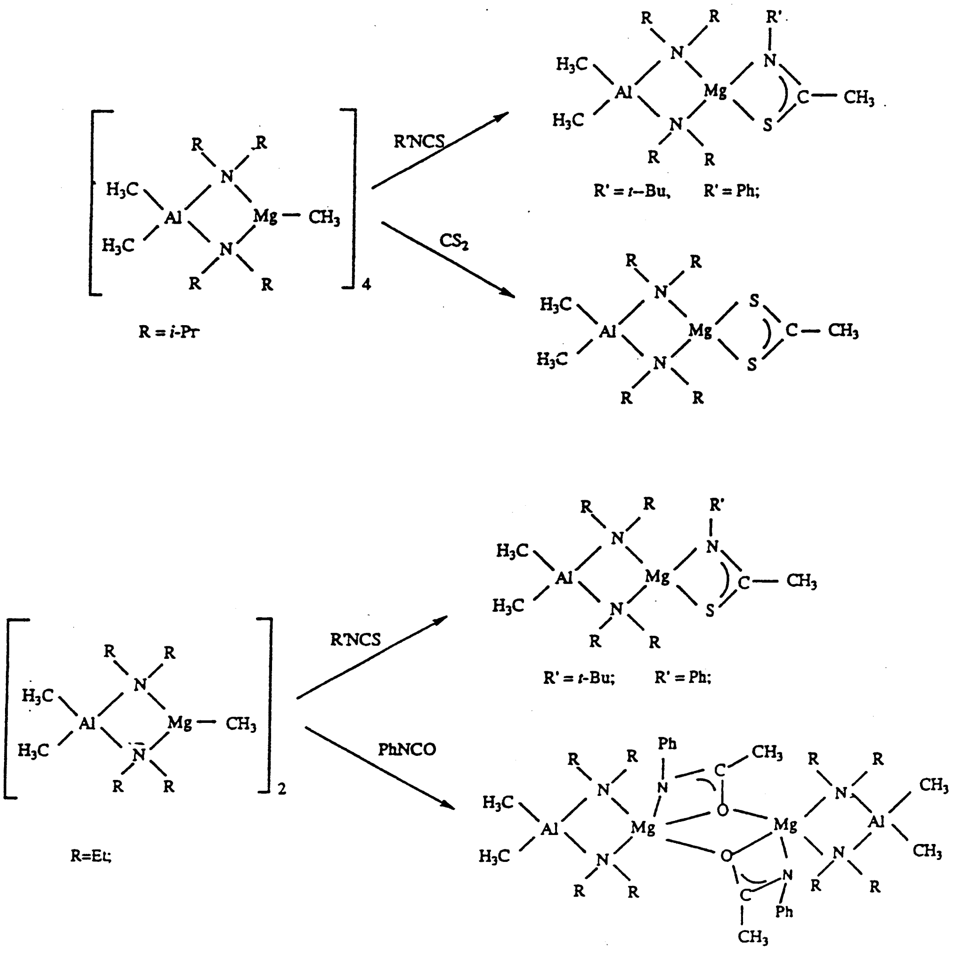
(92)



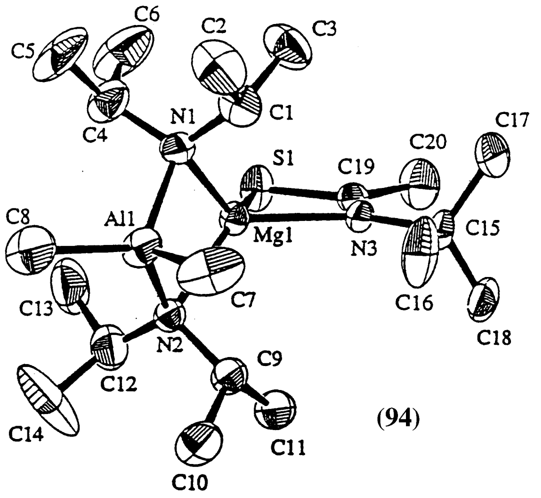
(93)

A number of insertion products, viz. $Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg[({}^tBu)NC(CH_3)S]$ (**94**), $Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg[(Ph)NC(CH_3)S)]$, $Me_2Al(\mu\text{-}Et_2N)_2Mg[({}^tBu)NC(CH_3)S]$, $Me_2Al(\mu\text{-}Et_2N)_2Mg[(Ph)NC(CH_3)S]$, $\{Me_2Al(\mu\text{-}Et_2N)_2Mg[(Ph)NC(CH_3)\ O]\}_2$ (**95**), and $Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg[SC(CH_3)S]$ have been synthesized by the straightforward reaction between the reagents *t*-butyl, and phenyl isothiocyanate, phenyl isocyanate, and carbon disulfide with the respective polynuclear aluminum–magnesium precursor compounds as shown in Scheme 7 [92]. Compound **94** possesses an interlinked bicyclic structure one of the rings being formed by Al, Mg and the amide nitrogen atoms of the two $({}^iPr_2)N$ ligands while the other is formed by a Mg atom, and carbon, sulfur and nitrogen atoms of the methyl-migrated *t*-butyl isothiocyanate moiety. These two rings are connected through the magnesium atom. Each of the rings are nearly coplanar and approximately perpendicular to each other.

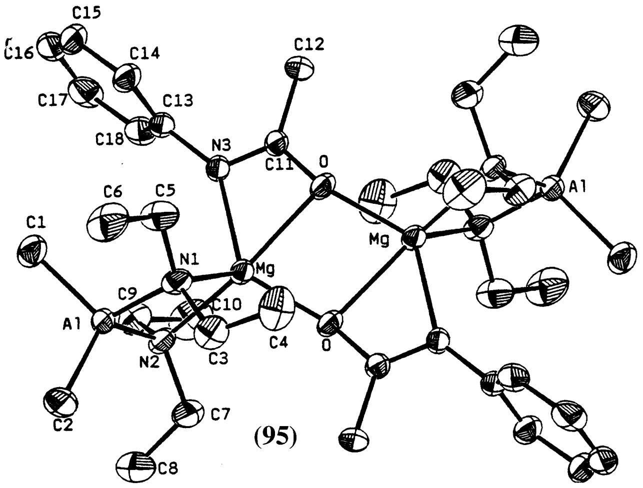
Compound **95** consists of an interlinked tricyclic structure similar to that of its parent compound and it possesses crystallographic inversion center symmetry at the center of the Mg_2O_2 ring. The two symmetrically related terminal rings are formed by Al, Mg, and amide nitrogen atoms of the (Et_2N) groups. The middle ring is defined by two sets of symmetrically related Mg and oxygen atoms, and is planar. In the case of compound **94**, since the *t*-butyl group is disposed away from the Mg center, a similar tetranuclear arrangement as in **95** could not be expected. We assume that the considerably longer Mg–S distance and larger bite-angle of the ^{t}BuNC(CH_3)S ligand, preclude such a tetranuclear arrangement.



Scheme 7.



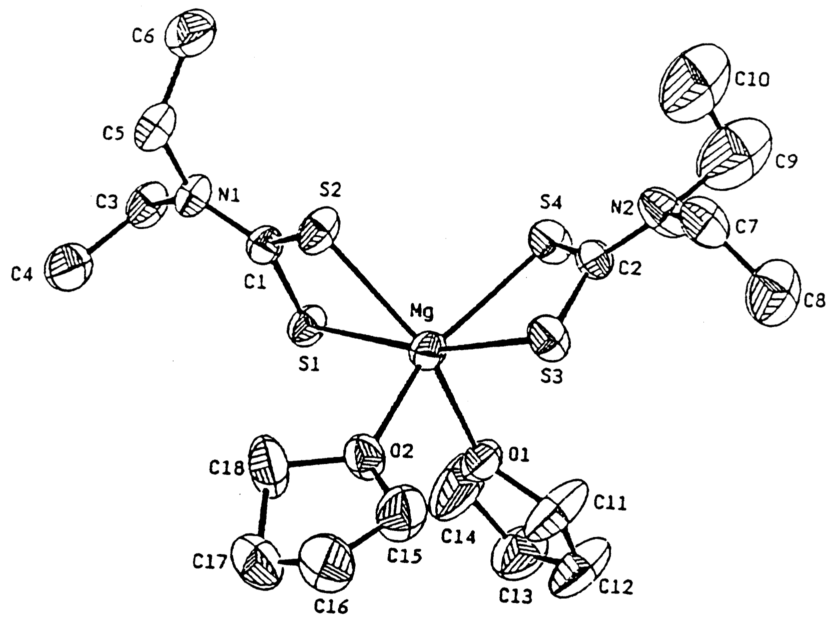
(94)



(95)

CS_2 reacts exothermally with $Mg(NEt_2)_2$ in THF solvent at r.t. to form the monomeric $(THF)_2Mg(SC(NEt_2)S)_2$ (**96**). The insertion takes place at the Mg–N bond and the Mg center is characterized by trigonal prismatic geometry. The two CS_2 molecules are bonded to the Mg center forming four-membered spiro structures [96].

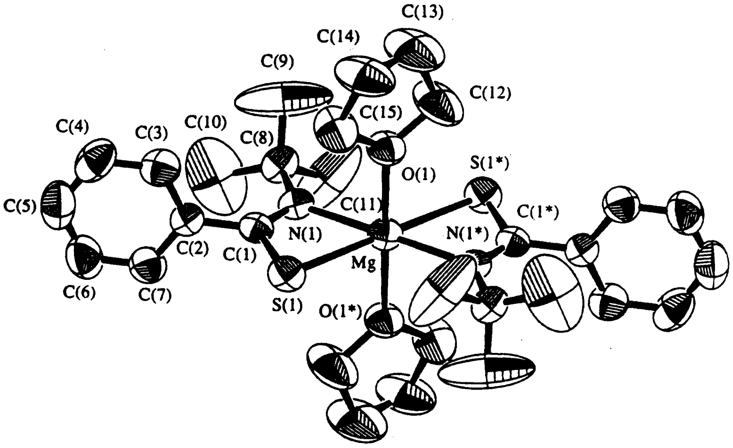
A series of magnesium–isothiocyanate and carbodiimide insertion products, $[(^tBu)NC(C_6H_5)S]_2Mg(THF)_2$ (**97**), $[(C_6H_5)NC(C_6H_5)S]_2$ $Mg(THF)_2$, $[(^iPr)NC(C_6H_5)N(^iPr)]_2Mg(THF)_2$ (**98**), $[(^iPr)NC(C_2H_5)N$ $(^iPr)]_2Mg(THF)_2$, $[(^iPr)NC(^iPr)N(^iPr)]_2Mg(THF)_2$ and $[(^tBu)NC$ $(C_2H_5)N(^tBu)]_2Mg(THF)_2$ have been prepared by the stoichiometric reactions between $MgR_2(R = C_6H_5, C_2H_5, {}^iC_3H_7)$ and various isothiocyanates and carbodiimides in THF [93]. The insertion is also coupled with the migration of aryl group onto the carbon of isothiocyanate or carbodiimide.



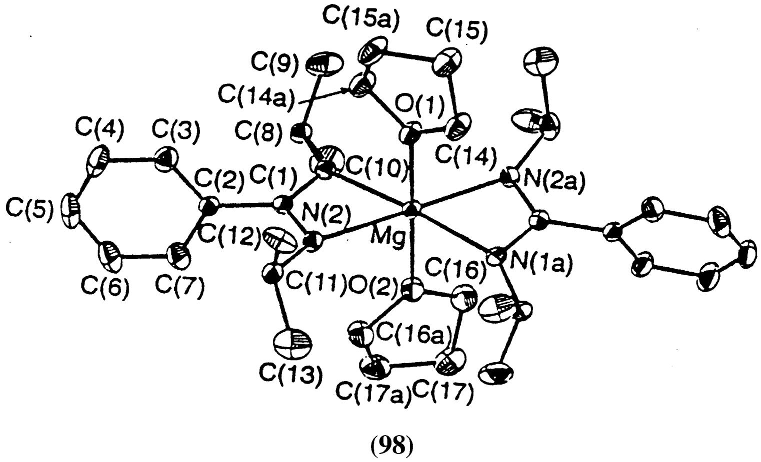
(96)

The reaction between bis(diisopropylamido)magnesium and 1,3-diisopropyl carbodiimide gives a dinuclear complex $[(^{i}Pr)NC(^{i}Pr_2N)N(^{i}Pr)]_2Mg_2(\mu\text{-}^{i}Pr_2N)_2$ when reacted in 1:1 stoichiometric ratio and a mononuclear complex $[(^{i}Pr)NC(^{i}Pr_2N)N(^{i}Pr)]_2Mg{\cdot}THF$ (**99**) when the stoichiometry is 1:2. The mononuclear complexes $[(C_6H_5)NC(^{i}Pr_2N)S]_2Mg(THF)_2$ (**100**) and $[(C_6H_5)NC(Et_2N)S]_2Mg(THF)_2$ were obtained using phenylisothiocyanate and bis(diethylamido) magnesium or bis(diisopropylamido)magnesium in 1:1 stoichiometric ratio. Reaction between RMgX ($R = C_2H_5$, $X = Br$) and phenylisothiocyanate in diethylether solvent in 1:1 molar ratio gave the dinuclear complex $\{[(C_6H_5)NC(C_2H_5)S]_2Mg(O\text{-}Et_2)\}_2$ (**101**). The reactive species was the R_2Mg which was formed as a result of the famous Schlenk equilibrium viz. $2RMgX \Leftrightarrow R_2Mg + MgX_2$. The reaction of complex **97** with excess phenylisocyanate resulted in the cyclotrimerization of phenylisocyanate to give $(PhNCO)_3{\cdot}THF$. The molecule **97** possesses an inversion center and distorted octahedral geometry around the magnesium atom bonded through both sulfur and nitrogen atoms of the RNCS ligand. There are two molecules of THF at the apical positions. The four-membered ring constituted by Mg(1)–S(1)–C(1)–N(1) linkages is planar. The two RNCS ligands are *trans* to each other forming almost coplanar framework due to steric interactions. The amidino magnesium complex **98** structurally similar to complex **97**, also possesses octahedral geometry around the magnesium center with a two-fold axis passing through the O(1)–Mg–O(2) axis. Complex **99** possesses a square bipyramidal geometry around magnesium. The diisopropyl carbodiimide ligands act as bidentate chelate forming the basal plane and the solvent THF occupying the axial position.

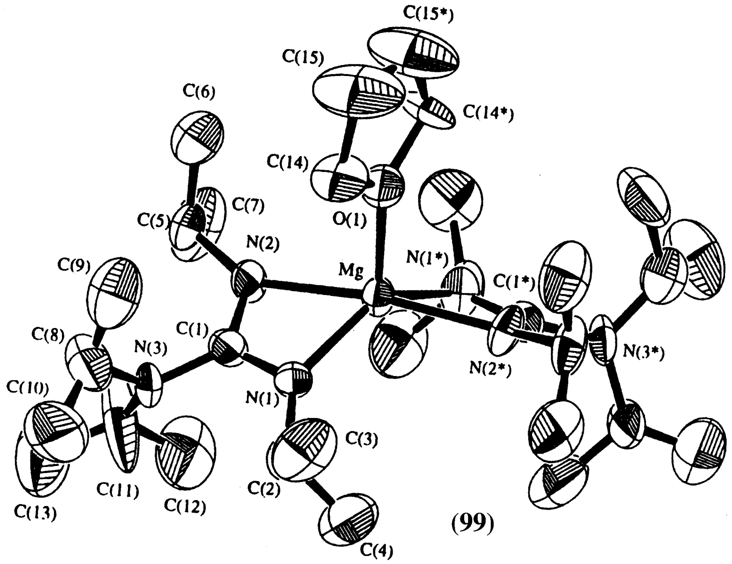
The structure of complex **100** consists of monomeric $[(C_6H_5)NC(^iPr_2N)S]_2Mg(THF)_2$ molecules with axially compressed rhombic geometry around magnesium centers. The equatorial donor atoms are planar and form a rhombic plane in which also lies the magnesium atom. The structure of complex **101** consists of discrete dimeric $MgL(\mu\text{-}L)\cdot OEt_2$ molecules (where $L = (C_6H_5)NC(C_2H_5)S)$. The bidentate PhNCS ligand binds the metal center in two different modes. In one mode, the sulfur and nitrogen atoms of the ligand occupy the equatorial positions, and in the second mode, the nitrogen and sulfur atoms of the ligand occupy equatorial and axial positions, respectively. The geometry of the six-coordinate magnesium center is distorted octahedral and the four equatorial and the central magnesium atoms are not planar. The dimeric structure of this complex seems to be the result of the two modes of coordination exhibited by the ligand. A comparison of the structural features of the structures **100** and **101** suggests that a similar dimeric structure for the former complex will be sterically disfavored due to the presence of the bulky diisopropyl amido substitution on the carbonyl carbon atom.



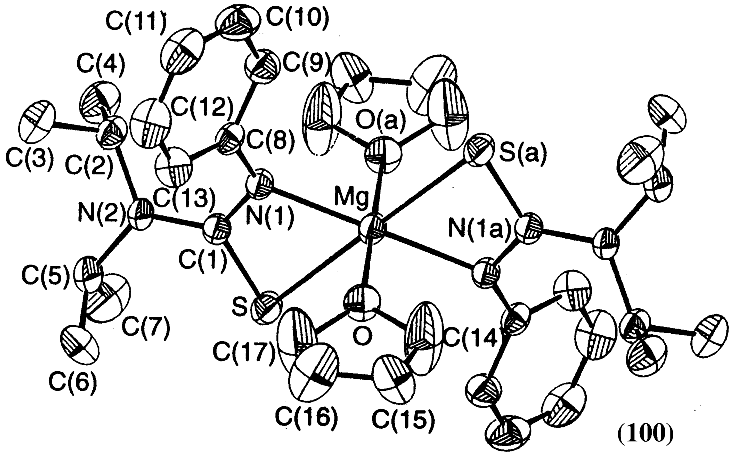
(97)



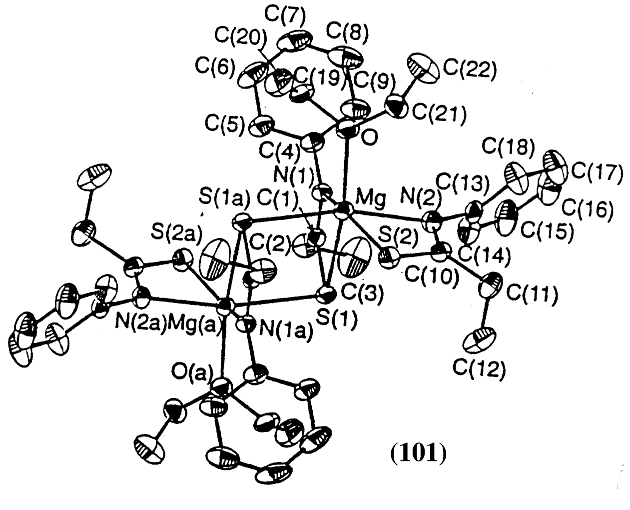
(98)


C(15*)
C(15)
C(14*)
C(6)
C(14)
C(7)
C(5)
O(1)
N(2)
Mg
N(1*)
C(1*)
C(9)
C(1)
C(8)
N(3)
N(2*)
N(3*)
N(1)
C(10)
C(3)
C(11)
C(12)
C(2)
C(13)
C(4)

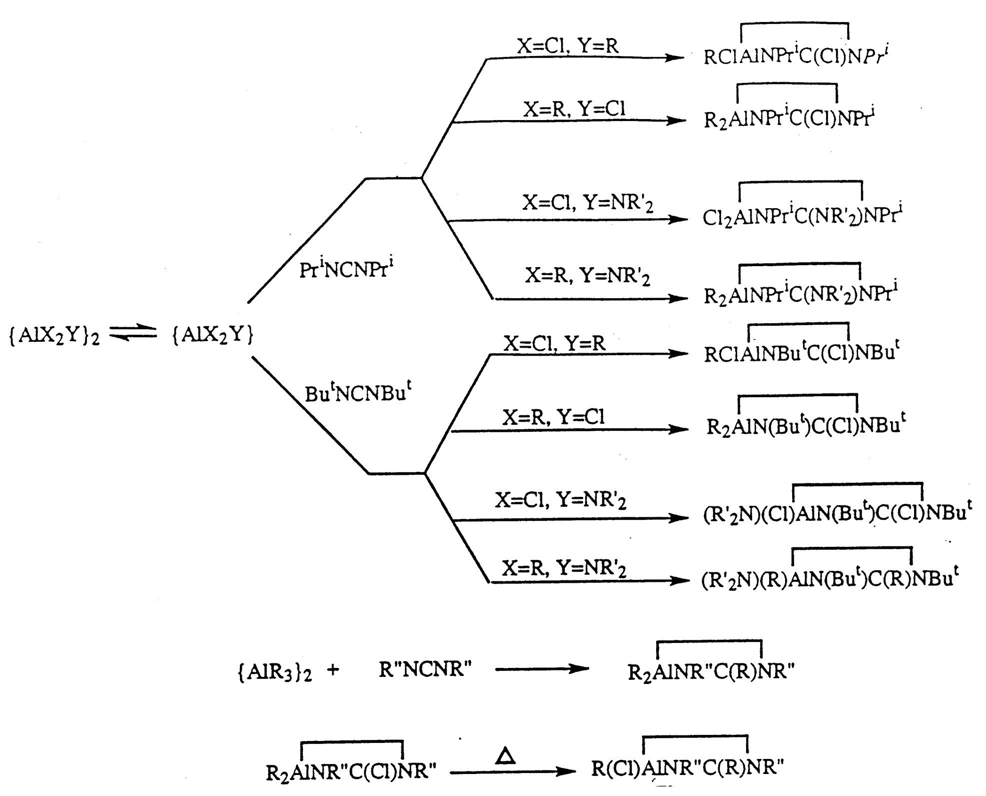
(99)


C(11)
C(10)
C(4)
C(9)
C(12)
C(8)
O(a)
S(a)
C(3)
C(2)
C(13)
Mg
N(2)
N(1)
N(1a)
C(1)
C(5)
S
O
C(14)
C(7)
C(17)
C(6)
C(16)
C(15)

(100)


C(7)
C(20)
C(8)
C(6)
C(19)
C(9)
C(22)
C(21)
C(5)
O
C(4)
C(18)
N(1)
C(17)
S(1a)
C(1)
Mg
N(2)
C(13)
C(16)
S(2a)
C(2)
S(2)
C(15)
C(14)
C(10)
C(3)
C(11)
N(2a)
Mg(a)
N(1a)
S(1)
O(a)
C(12)

(101)

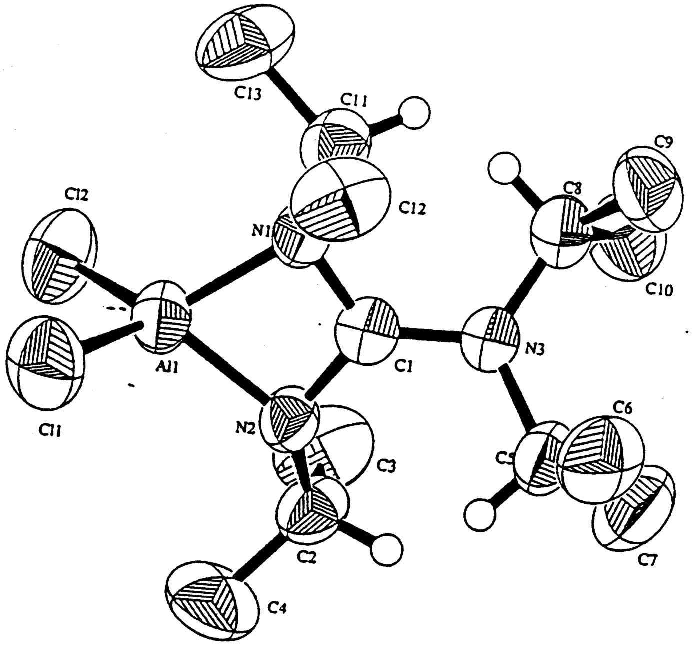


Scheme 8.

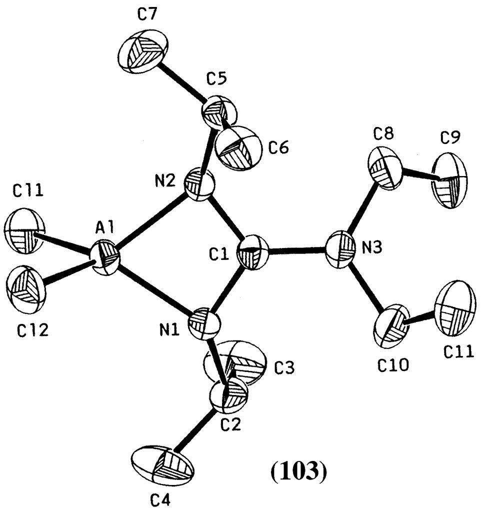
Various compounds of the general composition $XY\overline{ALNR''C(X')N}R''$ (X = migrating group) (X = Cl, R; Y = Cl, NR'_2) were prepared by Chang et al. from the reaction of the aluminum complexes AlX_2Y and AlR_3 with 1,3-dialkyl carbodiimides as shown in Scheme 8 [94]. The crystal structures of $Cl_2\overline{AlN^iPrC(N^iPr_2)N}{}^iPr$ (**102**) and $Cl_2\overline{AlN^iPrC(NEt_2)N}{}^iPr$ (**103**) show that the migration of diisopropylamido or diethylamido anion from $Al(^iPr_2N)Cl_2$ or $Al(Et_2N)Cl_2$ to the sp carbon of the carbodiimide has occurred during the reaction. The aluminum center is in distorted terahedral geometry and coordinated to two nitrogen atoms of the anionic ligand species, and to two chloride ligands with a twisted four-membered chelate ring. The reaction of 1,3-diisopropyl carbodiimide with Me_2AlCl, which apparently contained the oxidized impurity MeAl(OMe)Cl, yielded a dinuclear aluminum compound $(Me_2Al)_2\{\mu\text{-}OMe)(\mu\text{-}^iPrNC(Me)N^iPr)\}$ (**104**).

The crystal structure of **104** revealed a cyclic structure wherein the migration of a methyl anion to the sp-carbon of the carbodiimide was observed. The terahedrally distorted aluminum centers also are bridged by a methoxy group, resulting in the formation of a 6-membered cyclic core. The migrating abilities of various groups have been investigated under different experimental conditions and it was observed

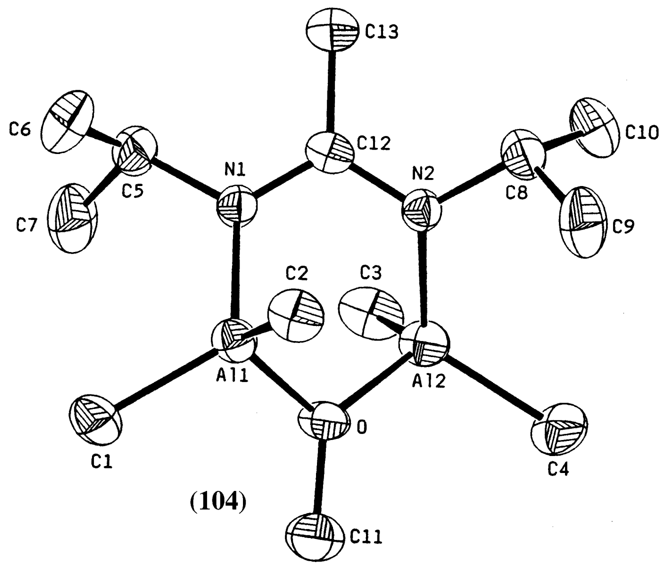
that with 1,3-diisopropyl carbodiimide the migration order is $NR'_2 > Cl > R$ whereas in reactions using 1,3-di-*tert*-butyl carbodiimide the migration order in this set of complexes is $Cl > R > NR'_2$. The compound $Et_2\overline{AlN(^tBu)C(Cl)N}{}^tBu$, when heated or distilled, isomerized to the thermodynamically favored product $EtCl\overline{AlN(^tBu)C(Et)N}{}^tBu$. Similar isomerization is also observed in the reaction of Et_2AlCl with 1,3-diisopropyl carbodiimide that resulted in two products, $Et_2\overline{AlN(^iPr)C(Cl)N}{}^iPr$ and $EtCl\overline{AlN(^iPr)C(Et)N}{}^iPr$ at r.t. and upon distillation, respectively.



(102)

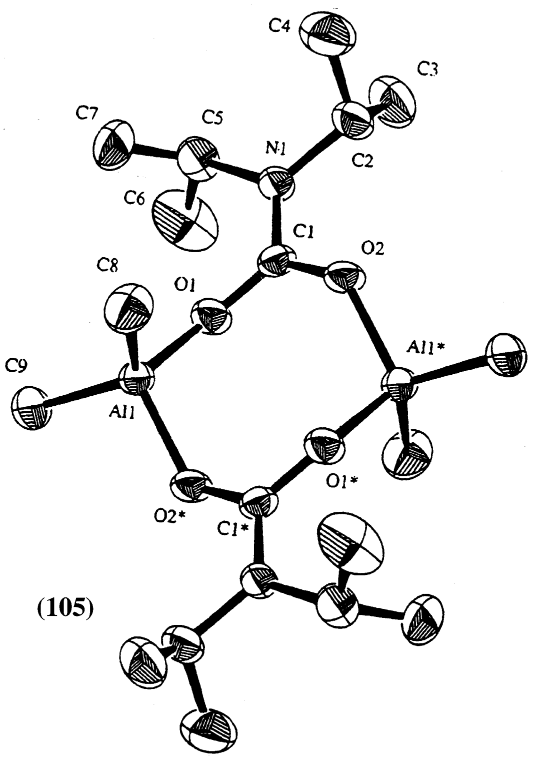


(103)

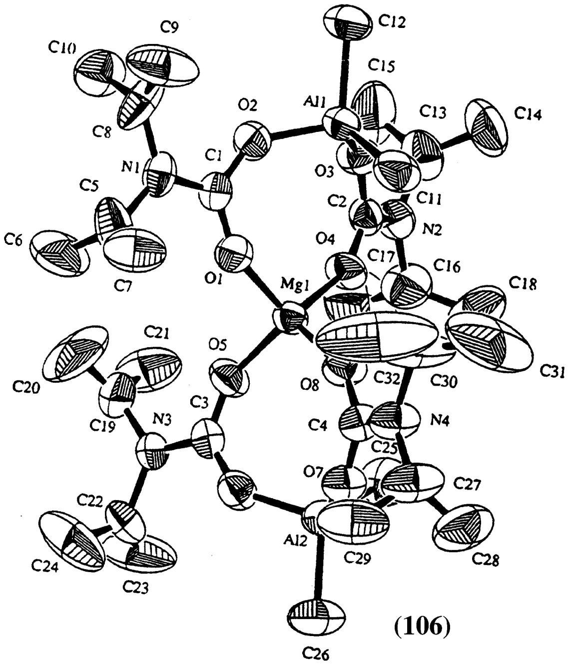


(104)

Chemical fixation of carbon dioxide is of great interest in connection with resource utilization and in relation to biochemical photosynthesis. Reaction of compound $[Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg(\mu\text{-}Me)]_4$ (**74**) with CO_2 in diethyl ether gives two different insertion products, $\{(Me_2Al)_2[\mu\text{-}OOC({}^iPr_2N)]_2\}$ (**105**), a dialuminum carbamato complex and $\{(Me_2Al)_2[(\mu\text{-}OOC({}^iPr_2N))_2]_2\}Mg$ (**106**), a mixed metal aluminum–magnesium carbamato complex [95]. Reaction of compound $[Me_2Al(\mu\text{-}NEt_2)_2Mg(\mu\text{-}Me)]_2$ with CO_2 gives $\{(Me_2Al)_2[(\mu\text{-}OOC(Et_2N))_2]_2Mg\}$ and sublimation of this compound results in $\{(Me_2Al)_2[\mu\text{-}OOC(Et_2N)]_2\}$. The dialuminum and aluminum–magnesium mixed metal carbamato complexes **105** and **106** were formed the insertion of CO_2 into the Metal–N bond at the bridging amido ligands. The dialuminum CO_2 insertion product, $\{(Me_2Al)_2[\mu\text{–}OOC({}^iPr_2N)]_2\}$ (**105**) possesses an inversion center with the two Al centers bridged by two $\mu\text{-}OOC({}^iPr_2N)$ groups. The less volatile fraction, $\{(Me_2Al)_2[(\mu\text{-}OOC({}^iPr_2N))_2]_2Mg\}$ (**106**) was obtained as a second product during the sublimation process and this possesses a linear Al–Mg–Al trinuclear unit in which the central Mg atom is surrounded by four $\mu\text{-}OOC({}^iPr_2N)$ units. The geometry of the Al and Mg atoms are nearly tetrahedral. The two-eight-membered chelate rings around the Mg atoms are approximately perpendicular to each other. The diisopropyl amido groups symmetrically bridge the aluminum and magnesium atoms, while the bidentate carbamato ligands are bonded slightly asymmetrically.

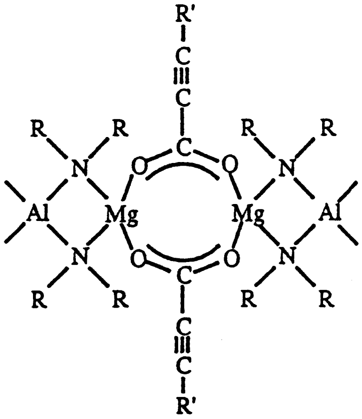

C4
C3
C7
C5
N1
C2
C6
C1
O2
C8
O1
Al1*
C9
Al1
O1*
O2*
C1*

(105)


C12
C9
C10
C15
Al1
C13
C14
O2
C8
C1
N1
O3
C5
C2
C11
N2
C6
O4
C17
C16
C18
C7
O1
Mg1
C21
O5
C20
O8
C32
C30
C31
N3
C3
C19
C4
N4
C25
O7
C27
C22
Al2
C29
C28
C24
C23
C26

(106)

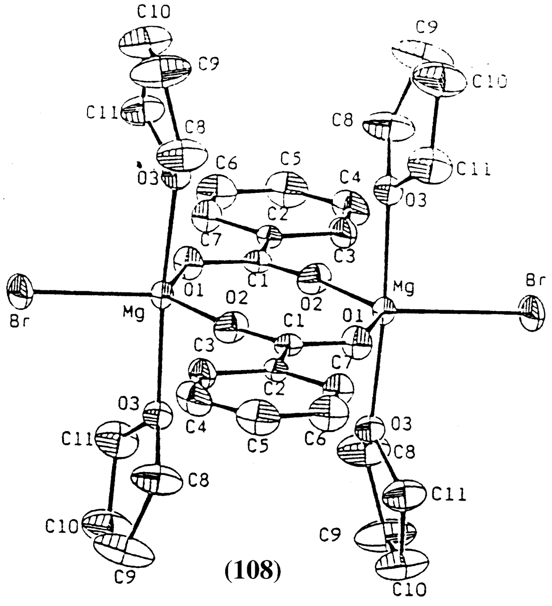
Reactions of **85** and **86** with CO_2 give selective insertion products viz $\{[Me_2Al(\mu\text{-}^iPr_2N)_2Mg[\mu\text{-}OOC(C{\equiv}CR)]\}_2$ (**107**) $R = C_6H_5$ or C_6H_4-*p*-CH_3 and the spectral data show that the insertion occurs at the Mg–C bond [94]. The reaction of the Grignard reagent PhMgBr with CO_2 in THF solvent results in the formation of $(THF)_2BrMg[OC(Ph)O]_2MgBr(THF)_2$ (**108**) [96]. X-ray structure of **108** shows that the molecule possesses an inversion center and the CO_2 molecules bridge the two Mg centers forming an eight-membered coplanar ring. The geometry around magnesium is slightly distorted trigonal bipyramidal and the significant feature of this complex is its dimeric nature compared with the reactivity of other heterocumulenes like CS_2/NCS etc.



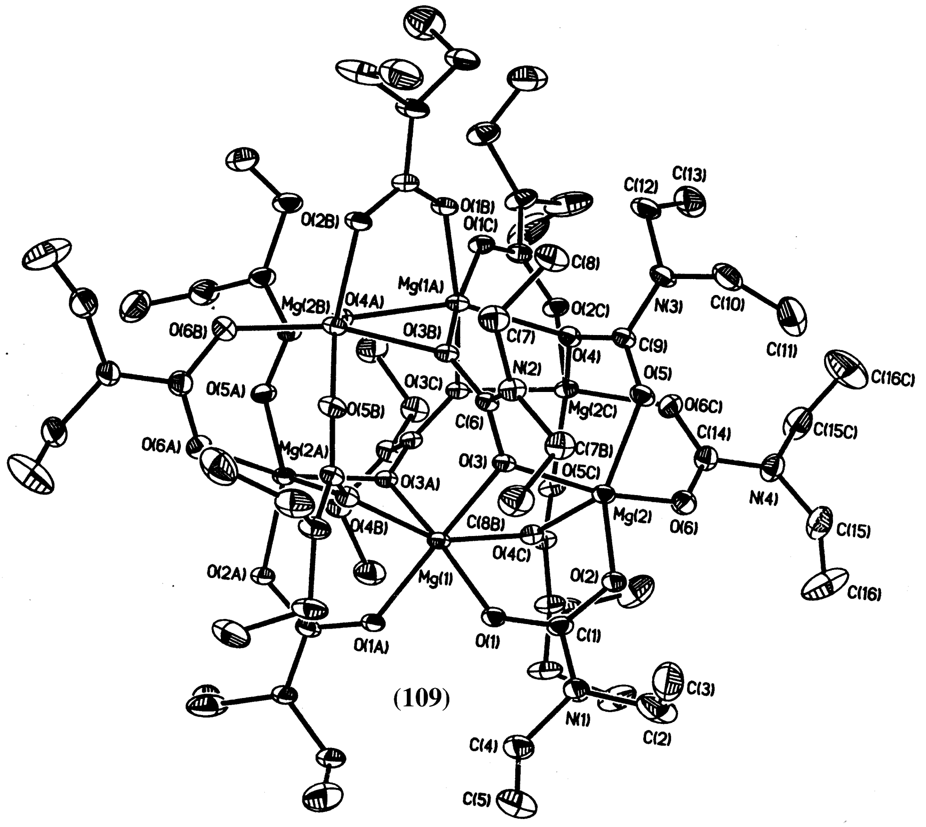
(107)

The spontaneity or randomness of the reactivity of CO_2 with Mg/Al systems finds no limits. The reaction of CO_2 with $Mg(NEt_2)_2$ leads to the formation of a novel cage structure $Mg_6(OOCNEt_2)_{12}$ (**109**) as a result of insertion into Mg–N bond [96]. The X-ray structure of this compound has revealed that it contains two types of Mg centers viz. octahedral and square–pyramidal with three different types of CO_2 bonding modes. It was found that the insertion of O_2 into the Mg–R bond of Al–Mg complex **74** resulted in the formation of alkoxide derivatives **75**.

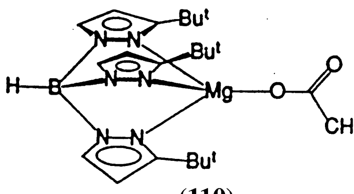
Parkin et al. reported that CO_2 and O_2 insert into the Mg–R bond of $\{\eta^3\text{-}HB(3\text{-}^tBupz)_3\}MgR$ to give the η^1-acetato complex $\{\eta^3\text{-}HB(3\text{-}^tBupz)_3\}Mg\{\eta^1\text{-}OC(O)CH_3\}$ (**110**) and alkylperoxo derivatives $\{\eta^3\text{-}HB(3\text{-}^tBupz)_3\}MgOOR$ (**111**), respectively, whereas ketones like $CH_3C(O)CH_3$ and $CH_3C(O)^tBu$ give the enolate complexes $\{\eta^3\text{-}HB(3\text{-}^tBupz)_3\}Mg\{\eta^1\text{-}OC(=CH_2)CH_3\}$ and $\{\eta^3\text{-}HB(3\text{-}^tBupz)_3\}Mg\{\eta^1\text{-}OC(=CH_2)^tBu\}$ accompanied by the elimination of ethane [33]. The reaction of the magnesium (trimethylsilyl)methyl complex $\{\eta^3\text{-}HB(3\text{-}^tBupz)_3\}MgCH_2SiMe_3$ with O_2 gives the trimethylsiloxide derivative $\{\eta^3\text{-}HB(3\text{-}^tBupz)_3\}MgOSiMe_3$ as a result of facile cleavage of the Si–C bond upon autooxidation.


C10
C9
C9
C10
C11
C8
C8
C11
O3
C6
C5
C4
O3
C2
C7
C3
C1
O1
O2
O2
Mg
Br
Br
Mg
C1
O1
C3
C7
C2
O3
C4
C5
C6
O3
C11
C8
C8
C11
C10
C9
C9
C10

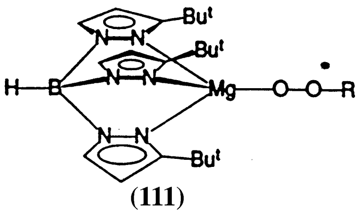
(108)


C(12)
C(13)
O(2B)
O(1B)
O(1C)
C(8)
Mg(1A)
N(3)
C(10)
Mg(2B)
O(4A)
O(2C)
O(6B)
O(3B)
C(7)
O(4)
C(9)
C(11)
N(2)
O(5)
C(16C)
O(5A)
O(3C)
Mg(2C)
O(6C)
O(5B)
C(6)
C(14)
C(15C)
O(6A)
Mg(2A)
C(7B)
O(3)
O(5C)
O(3A)
N(4)
C(8B)
Mg(2)
O(6)
O(4B)
O(4C)
C(15)
O(2A)
Mg(1)
O(2)
C(16)
O(1A)
O(1)
C(1)
C(3)
N(1)
C(2)
C(4)
C(5)

(109)

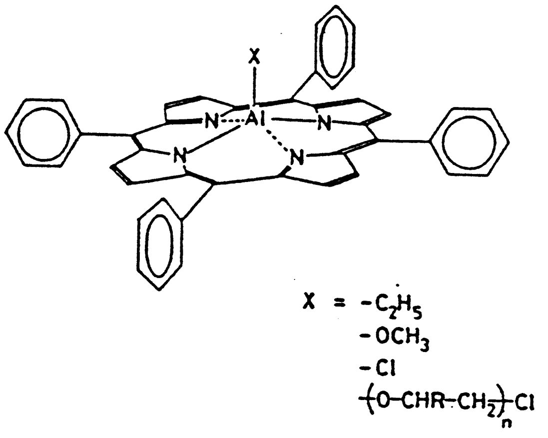


(110)



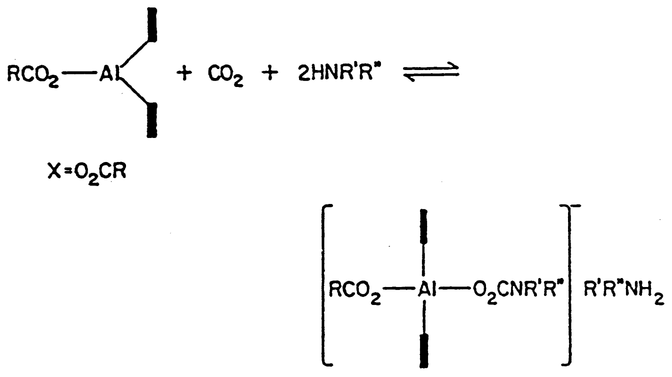
(111)

An interesting reaction with potential utility is the reaction of carbon dioxide and epoxide using organometallic catalyst systems to give alternating copolymer, an aliphatic polycarbonate from the monomers. It was discovered by Inoue et al. that α,β,γ,δ-tetraphenylporphinatoaluminium methoxide (TPP)AlOMe (**112**) traps carbon dioxide readily and reversibly at r.t. in the presence of 1-methylimidazole [97]. The trapped carbon dioxide is activated enough to react with epoxide at r.t. to afford the corresponding cyclic or alkylene carbonate. Thus, the (TPP)AlOMe-1-methylimidazole system is a good catalyst for the synthesis of alkylene carbonate from carbon dioxide and epoxide under mild conditions. The spectroscopic investigation of the reaction system indicated the formation of aluminum alkoxide (TPP)Al–O–CHR–CH2–O–CO–OR and subsequent intramolecular attack of this aluminum alkoxide toward the adjacent linear carbonate linkage regenerating the starting alkoxide, (TPP)AlOR.



(112)

Carbon dioxide is also reported to be trapped by (5,10,15,20-tetraphenylporphinato)aluminum acetate in the presence of a secondary amine in the form of an aluminum carbamate on the opposite side to the acetate group with respect to the porphyrin plane to form the comparatively unstable hexacoordinate complex **113** [98]. This undergoes a catalytic reaction involving secondary amine and epoxide to afford dialkylcarbamic ester under atmospheric pressure at r.t. Although the insertion of carbon dioxide into the transition metal (Ti, Zr, V, Nb, Ta and W)–nitrogen bond to form metal carbamate, actually proceeding via the substitution of the metal–nitrogen bond by carbamic acid, the observations strongly indicate that the dialkyl carbamate formed from carbon dioxide and dialkylamine coordinates directly to the aluminum atom of $Al(TPP)O_2CCH_3$ (1, $X = O_2CCH_3$).

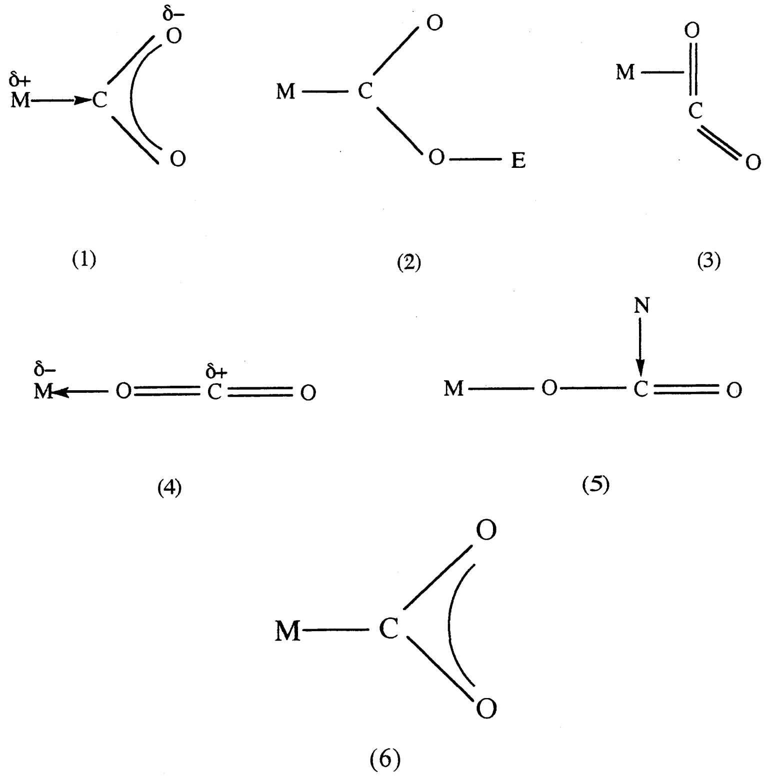


(113)

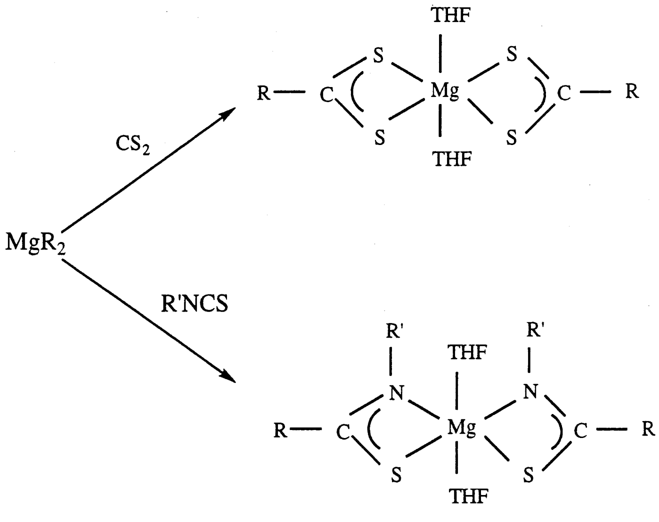
6. Comparison of heterocumulene reactivities

The notion of activation of carbon dioxide by transition metal complexes is traditionally associated with coordination of CO_2 to the metal center. The mechanisms of the reactions of CO_2 with different organometallic compounds often referred to as the insertion reactions, were barely defined for a long time. But the extensive use of physical and chemical methods, especially X-ray crystallography, has greatly facilitated progress in this area. The dominant characteristic of carbon dioxide is the electrophilic nature of the carbon atom as exemplified by its ready reaction with nucleophiles [99]. Depending upon the polarity of the M–H or M–C bond the metal–ligand bond may add to the carbon–oxygen bond of CO_2 to give M–C and M–O bonded products. Carbon dioxide insertion into organotransition complexes leads to different types of products formed as a result of the adventitious presence of a second reagent (O_2, ROH, H_2O, etc.). All these products are potential intermediates in the catalytic transformation of CO_2; therefore the study of their formation and of their evolution in the presence of substrate (H_2 etc.) remains a fruitful field of research [100]. Thus, CO_2-transition metal complexation can be expected to occur by electron donation from electron-rich low valent metal centers to give oxycarbonyl–metal compounds (1); the concomitant presence of an electron accepting center (E) would favor this reaction by forming complexes of the type (2). Also, carbon–oxygen π-bonds may interact with the requisite vacant metal orbital to give π-complexes of the type (3). The oxygen atoms of carbon dioxide could also act as weak (or potential) electron donors to electron deficient metals, e.g. (4); the presence of an electron donating center (N) would aid this reaction, e.g. (5) as shown in Scheme 9.

Recent reviews [99a, 100b] on the organo transition metallic chemistry of carbon dioxide and the reactivities of other heterocumulenes provide rich information on the various bonding modes involved and the catalytic activation of CO_2 and other heterocumulenes. Hence, it is not reviewed in this paper. The insertion reactions of heterocumulenes in general and CO_2 in particular, with the main group metals like magnesium and aluminum received less attention from the scientists. The main technical difficulties faced are high air sensitivity and the involvement of efficient vacuum and inert atmospheric conditions. Often, polymers are obtained in the



Scheme 9.

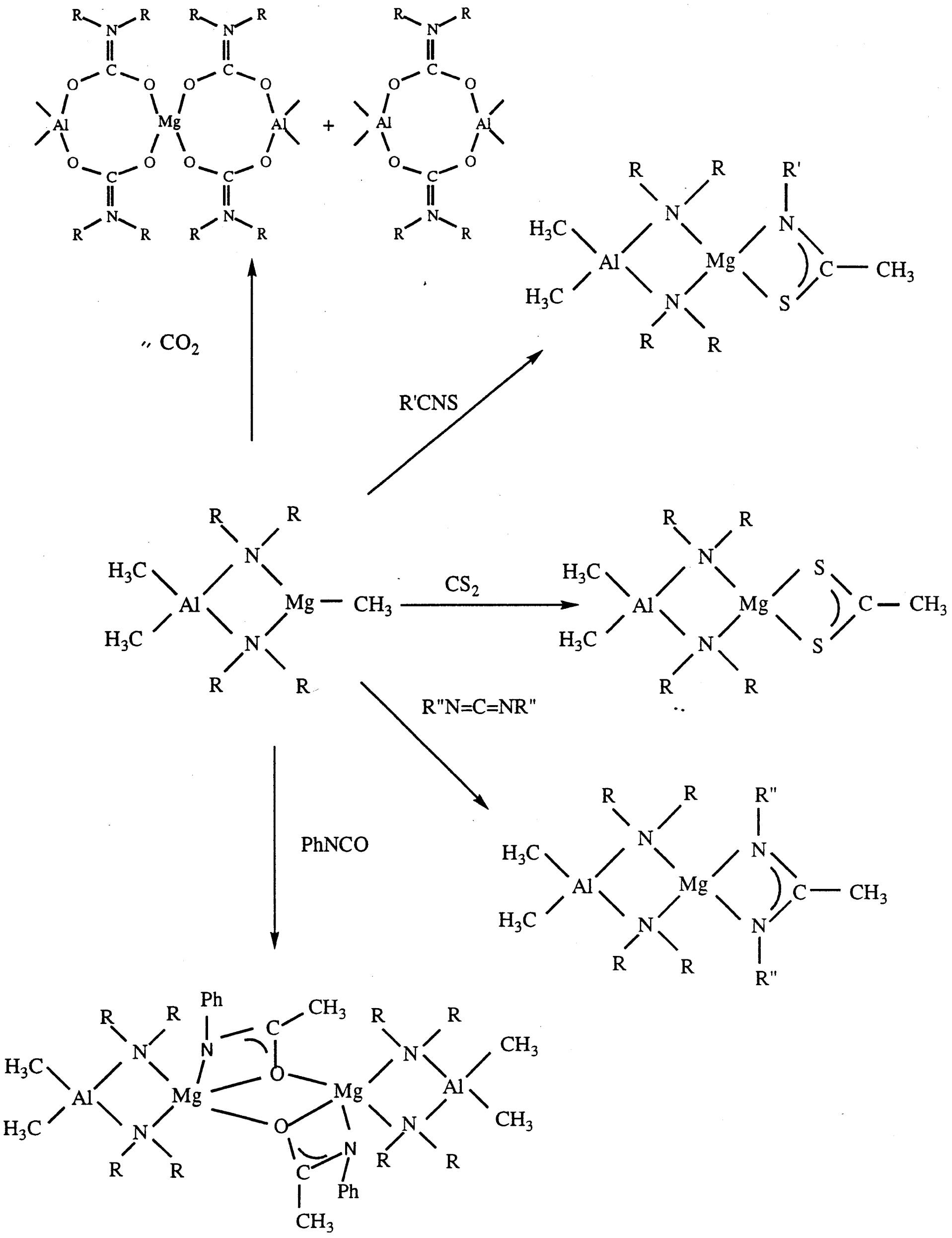


(10 a)

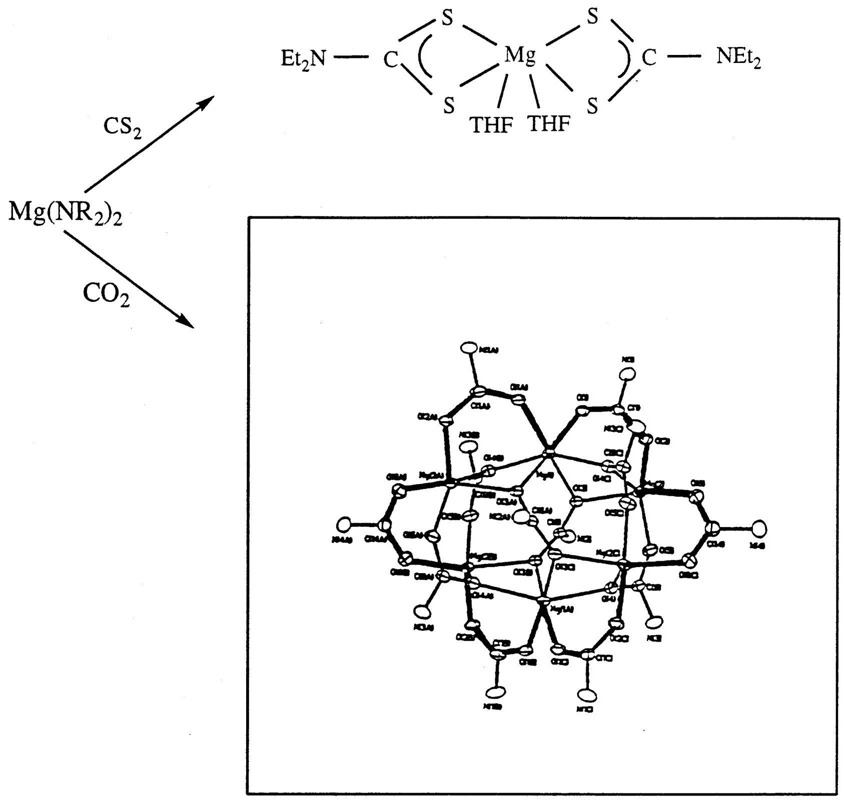
Scheme 10.

reactions of CO_2 with various magnesium diamides and it is not possible to get single crystals from these reactions. The other reason has been the inadequate information available from which any solid conclusion could not be achieved. From the information available on the insertion reactions of heterocumulenes like CO_2, CS_2, RNCNR, RNCO and RNCS with organomagnesium or organoaluminum, or mixed Mg–Al complexes, the following conclusions can be deduced. CS_2 forms monomeric complexes preferably whereas CO_2 prefers the bridging model and forms oiligomers or sometimes polymers. Both of the reactions are facile at r.t. conditions or more appropriately, exothermic. All of the heterocumulenes except CO_2 insert into the M–X (M = Mg or Al; X = C, N, Cl) to form four-membered twisted or planar rings. The planarity or twisted nature depends largely on the steric factor of the substituents. Carbon dioxide behaves uniquely in the formation of eight-membered rings or cages or polymers which is a an important observation that needs a thorough understanding of the reaction mechanisms. The Mg–Al oligomer $[Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg(\mu\text{-}Me)]_4$ reacts with CO_2, CS_2, RNCS, RNCNR to form the various complexes as shown in Scheme 10(b).

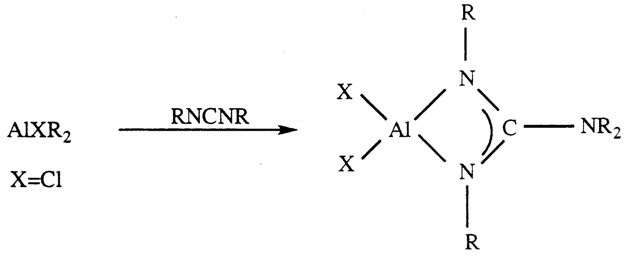
It should be noted from Scheme 10, all the heterocumulenes except CO_2 form four-membered rings with the metal ion preferably magnesium. In the case of CO_2 insertion, both of the metal ions (Mg and Al) are involved in the ring formation indicating that both are reactive centers for CO_2 which forms eight-membered rings with μ_2-η^2 coordination modes. The reaction of CS_2 or RNCS with MgR_2 proceeds through insertion into Mg–C bond giving the four-membered rings similar to the Mg–Al systems as shown in Scheme 10(c). CO_2 inserts into the Mg–N bond of $Mg(NEt_2)_2$ to form a very interesting cage structure incorporating six Mg atoms, 24 each of CO_2 molecules and (NEt_2) units each which is not common in transition metal chemistry. From the present data one can conclude that even though the formation of four-membered rings is very common in transition metal–CO_2



Scheme 10. (*Continued*)



(10 c)



(10 d)

Scheme 10. (*Continued*)

complexes, it is not observed in the Mg–Al systems. The reason for the random behavior of CO_2 towards metal centers is unclear which needs a great deal of concern over the theoretical approach as well as the wealth of structural data for CO_2–metal complexes. We must also accept that it is not the time to conclude the non-existence of the $M-CO_2-$ bonding shown in type (6) of Scheme 9. CO_2

insertion reactions play an important role in various catalytic processes. The most common insertion reaction is found in the preparation of organic acids via the Grignard reagent (Eq. (1)) wherein the metal–carbon is broken and CO_2 is inserted. The chemistry of heterocumulene insertion into the Mg–Al complexes promises an interesting theme for chemists not only for reducing the concentration of CO_2 in the atmosphere but also in displaying remarkable structural features that a chemist usually needs in the development of what is called ‘chemical architecture’.

References

[1] J.M. Brown, S.K. Armstrong, E.W. Abel, F.G.A. Stone, G. Wilkinson, Comprehensive Organometallic Chemistry II, vol. 11, Pergamon, Oxford, UK, 1995.
[2] J.F. Garst, Acc. Chem. Res. 24 (1991) 95.
[3] B.J. Wakefield, Organomagnesium Methods in Organic Synthesis, Academic Press, New York, 1995.
[4] E.C. Ashby, A.B.J. Goel, Inorg. Chem. 17 (1978) 1862.
[5] J.K. Stille, W.J. Scott, J. Am. Chem. Soc. 108 (1986) 3033.
[6] D. Bonafoux, M. Bordeau, C. Biran, P. Cazeau, J. Dunogues, J. Org. Chem. 61 (1996) 5532.
[7] P. Beak, A.I. Meyers, Acc. Chem. Res. 19 (1986) 356.
[8] P.E. Eaton, G. Castaldi, J. Am. Chem. Soc. 107 (1985) 724.
[9] P.E. Eaton, R.G. Daniels, D. Casucci, G.T. Cunkel, J. Org. Chem. 52 (1987) 2100.
[10] P.E. Eaton, H. Higuchi, R. Millikan, Tetrahedron Lett. 28 (1987) 1055.
[11] K.A. Swiss, C. Woo-Baeg, D.C. Liotta, A.F. Abdel-Magrid, C.A. Maryanoff, J. Org. Chem. 56 (1991) 5978.
[12] Y. Kondo, N. Takazawa, A. Yoshida, T. Sakamoto, J. Chem. Soc. Perkin Trans. 1 (1995) 1207.
[13] P. Beak, J.E. Hunter, Y.M. Jun, A.P. Wallin, J. Am. Chem. Soc. 109 (1987) 5403.
[14] M.G. Gardinger, C.L. Raston, Coord. Chem. Rev. 166 (1997) 1.
[15] L.V. Interrante, L.E. Carpenter, C. Whitmarsh, W. Lee, G.A. Slack, Mater. Res. Soc. Symp. Proc. 73 (1986) 986.
[16] M.F. Lappert, P.P. Power, A.R. Sanger, R.C. Srivastava, Metalloid Amides, Ellis Horwood, Chichester, UK, 1980.
[17] N. Kuramoto, H. Taniguchi, J. Mater. Sci. Lett. 3 (1984) 471.
[18] H. Schnidbaur, M. Schmidt, Angew. Chem. Int. Ed. Engl. 6 (1962) 327.
[19] B. Liao, Y. Li, Y. Lu, J. Mater. Chem. 3 (2) (1993) 117.
[20] E.J. Vandenberg, J. Polym. Sci. 7 (A-1) (1969) 525.
[21] V.R. Magnuson, G.D. Stucky, J. Am. Chem. Soc. 90 (1968) 3269.
[22] M.W. Lunch, J.T. Pullukat, U.S. Pat., 4 455 386, (1984) (Chem. Abstr., 1985, 101152510h).
[23] (a) W. Leitner, Coord. Chem. Rev. 153 (1996) 257. (b) J. Barker, M. Kilner, Coord. Chem. Rev. 133 (1994) 219. (c) P.V. Yaneff, Coord. Chem. Rev. 23 (1977) 183. (d) A.G. Pinkus, Coord. Chem. Rev. 25 (1978) 173. (e) G.J.M. Gruter, G.P.M. van Klink, O.S. Akkerman, F. Bickelhaupt, Chem. Rev. 95 (1995) 2405. (f) P. Braunstein, D. Matt, D. Nobel, Chem. Rev. 88 (1988) 747.
[24] D.H. Gibson, Chem. Rev. 96 (1996) 2063.
[25] W. Leitner, Angew. Chem. Int. Ed. Engl. 34 (1995) 2207.
[26] P.G. Jessop, T. Ikariya, R. Noyori, Chem. Rev. 95 (1995) 259.
[27] D.A. Palmer, R. van Eldick, Chem. Rev. 83 (1983) 651.
[28] K.K. Pandey, Coord. Chem. Rev. 140 (1995) 37.
[29] G.E. Coates, D. Ridley, J. Chem. Soc. A (1967) 56.
[30] W. Clegg, F.J. Craig, K.W. Henderson, A.R. Kennedy, R.E. Mulvey, P.A. O’Neil, D. Reed, Inorg. Chem. 36 (1997) 6238.
[31] R. Han, G. Parkin, Organometallics 10 (1991) 1010.

[32] R. Han, G. Parkin, J. Am. Chem. Soc. 114 (1992) 748.

[33] T.Y. Her, C.C. Chang, G.H. Lee, S.M. Peng, Y. Wang, J. Chin. Chem. Soc. 40 (1992) 315.

[34] Y. Kondo, A. Yoshida, T. Sakamoto, J. Chem. Soc. Perkin Trans. 1 (1996) 2331.

[35] P.E. Eaton, C.H. Lee, Y. Xiong, J. Am. Chem. Soc. 111 (1989) 8016.

[36] K. Kobayashi, K. Yokota, H. Akamatsu, O. Morikawa, H. Konishi, Bull. Chem. Soc. Jpn. 69 (1996) 441.

[37] P. Hubberstey, Coord. Chem. Rev. 102 (1990) 111.

[38] A.W. Duff, P.B. Hitchcock, M.F. Lappert, R.G. Taylor, J. Organomet. Chem. 293 (1985) 271.

[39] L.M. Englehardt, P.C. Junk, W.C. Patalinghug, R.E. Sue, C.L. Raston, B.W. Skelton, A.H. White, J. Chem. Soc. Chem. Commun. (1991) 930.

[40] (a) LM. Englehardt, B.S. Jolly, P.C. Junk, C.L. Raston, B.W. Skelton, A.H. White, Aust. J. Chem. 39 (1986) 1337. (b) N. Kuhn, M. Schulten, J. Organomet. Chem. 421 (1991) 1.

[41] K. Henderson, R.E. Mulvey, W. Clegg, P.A. O'Neil, J. Organomet. Chem. 439 (1992) 237.

[42] C.R. Hauser Jr., H.G. Walker, J. Chem. Soc. 69 (1947) 295.

[43] E.C. Ashby, Pure Appl. Chem. 54 (1980) 545.

[44] R.A. Bartlett, M.M. Olmstead, P.P. Power, Inorg. Chem. 33 (1994) 4800.

[45] T. Hascall, K.R. Senge, P.P. Power, Angew. Chem. Int. Ed. Engl. 33 (1994) 356.

[46] M.D. Li, C.C. Chang, S.T. Liu, G.H. Lee, Y. Wang, S.M. Peng, Organometallics 13 (1994) 1994.

[47] L.V. Interrante, G.A. Sigel, M. Garbauskas, C. Hejna, G.A. Slack, Inorg. Chem. 28 (1989) 252.

[48] (a) G.E. Coates, Organometallic Compounds, Methuen, London, 1967, p. 397. (b) T. Mole, E.A. Jeffery, Organoaluminum Compounds, Elsevier, London, 1972, 236.

[49] Jr.O.T. Beachley, K.C. Racette, Inorg. Chem. 15 (1976) 2110.

[50] S. Amirkhalili, P.B. Hitchcock, A.D. Jenkins, J.Z. Nyathi, D. Smith, J. Chem. Soc. Dalton Trans. (1981) 377.

[51] K. Ziegler, B.P. 799 (1958) 823.

[52] (a) M.F. Lappert, P.P. Power, A.R. Sanger, R.C. Srivastava, Metal and Metalloid Amides, Ellis Horwood-Wiley, Chichester, UK, 1979. (b) M.J. Taylor, P.J. Brother, in: A.J. Downs (Ed.), The Chemistry of Aluminum, Gallium, Indium and Thallium, Blackie-Chapman Hall, New York, 1993, Ch. 3. (c) G.H. Robinson, in: G. Robinson (Ed.), Coordination Chemistry of Aluminum, VCH, New York 1993, Ch. 5.

[53] (a) P.J. Brothers, R.J. Wehmschulte, M.M. Olmstead, Ruhlandt-Senge, S.R. Parkin, P.P. Power, Organometallics 13 (1994) 2792. (b) D.M. Choquette, M.J. Timm, J.L. Hobbs, M.M. Rahim, K.J. Ahmed, R.P. Planalp, Organometallics 11 (1992) 529.

[54] S. Amirkhalili, P.B. Hitchcock, A.D. Jenkins, J.Z. Nyathi, J.D. Smith, J. Chem. Soc. Dalton Trans. (1981) 377.

[55] T.Y. Her, C.C. Chang, J.O. Tsai, Y.Y. Lai, L.K. Liu, H.C. Chang, J.H. Chen, Polyhedron 12 (1993) 731.

[56] (a) J.C. Huffman, W.E. Streib, J. Chem. Soc. Chem. Commun. (1971) 911. (b) J.F. Malone, W.S. McDonald, J. Chem. Soc. Dalton Trans. (1972) 2646. (c) R.G. Vranka, E.L. Amma, J. Am. Chem. Soc. 89 (1967) 3121. (d) J.W. Moore, D.A. Sanders, P.A. Scherr, M.D. Glick, J.P. Oliver, J. Am. Chem. Soc. 93 (1971) 1035. (e) G.H. Robinson, S.A. Sangokoya, Polyhedron 7 (1988) 2727. (f) L. Cocco, D.P. Eyman, J. Organomet. Chem. 18 (1979) 3188. (g) V.H. Hess, A. Hinderer, S. Steinhauser, Z. Anorg. Allg. Chem. 377 (1970) 1. (h) V.R. Maagnuson, G.D. Stucky, J. Am. Chem. Soc. 91 (1969) 2544. (i) V.R. Maagnuson, G.D. Stucky, J. Am. Chem. Soc. 28 (1989) 252. (j) M.E. O'Neil, K. Wade, Comprehensive Organometallic Chemistry., vol. 1, Pergamon Press, Oxford, 1982, Chapters 11 and 12.

[57] C.C. Chang, M.D. Li, M.Y. Chiang, S.M. Peng, Y. Wang, G.H. Lee, Inorg. Chem. 36 (1997) 1955.

[58] J.L. Atwood, G.D. Stucky, J. Am. Chem. Soc. 89 (1967) 5362.

[59] M. Zaworotko, J.L. Atwood, Inorg. Chem. 19 (1980) 268.

[60] V.R. Magnuson, G.D. Stucky, J. Am. Chem. Soc. 91 (1969) 2544.

[61] (a) M.J. Taylor, P.J. Brothers, in: A.J. Downs (Ed.), Chemistry of Aluminum, Gallium, Indium and Thallium, Blackie-Chapman Hall, London, 1993, p. 118. (b) A.J. Downs, C.R. Pulham, Chem. Soc. Rev. (1994) 175.

[62] R.J. Wehmschulte, P.P. Power, Inorg. Chem. 33 (1994) 5612.
[63] R.J. Wehmschulte, P.P. Power, J. Chem. Soc. Chem. Commun. (1998) 335.
[64] S. Schulz, L. Haming, R. Herbst-Irmer, H.W. Roesky, G.M. Sheldrick, Angew. Chem. Int. Ed. Engl. 33 (1994) 969.
[65] M.G. Gardiner, S.M. Lawrence, C.L. Raston, J. Chem. Soc. Dalton Trans. (1996) 4163.
[66] J.F. Janik, E.N. Duesler, R.T. Paine, Inorg. Chem. 26 (1987) 4341.
[67] J. Pinkaas, B. Gaaul, J.G. Verkade, J. Am. Chem. Soc. 115 (1923) 3925.
[68] J. Pinkas, T. Wang, R.A. Jacobson, J.G. Verkade, Inorg. Chem. 33 (1994) 4202.
[69] P.B. Hitchcock, J.D. Smith, K.M. Thomas, J. Chem. Soc. (1976) 1433.
[70] (a) D.A. Atwood, J.A. Jegier, D. Rutherford, J Am. Chem. Soc. 117 (1995) 6779. (b) D.A. Atwood, J.A. Jegier, D. Rutherford, Inorg. Chem. 35 (1996) 63.
[71] C.C. Chang, C.C. Huang, J.O. Tsai, M.D. Li, L.K. Liu, Polyhedron 12 (1993) 2125.
[72] M.D. Li, C.C. Chang, S.T. Liu, G.H. Lee, Y. Wang, S.M. Peng, Organometallics 13 (1994) 1504.
[73] F.K. Schmidt, G.V. Ratovskii, T.V. Dmitrieva, I.N. Ivleva, G. Yu. Borodko, J. Organomet. Chem. 256 (1983) 309 and references therein.
[74] S.-J. Dzugan, V.L. Goedken, Inorg. Chem. 25 (1986) 2858.
[75] G.H. Robinson, S.A. Sangokoya, J. Am. Chem. Soc. 109 (1987) 6852.
[76] A.W. Laubengaver, J.D. Smith, G.G. Ehrlich, J. Am. Chem. Soc. 83 (1961) 542–546.
[77] Z. Jiang, L.V. Interrante, D. Kwon, F.S. Tham, R. Kullnig, Inorg. Chem. 30 (1991) 995.
[78] J.H. Wengrovius, M.F. Garbauskas, E.A. Williams, R.C. Going, P.E. Donahue, J.F. Smith, J. Am. Chem. Soc. 108 (1986) 982.
[79] M.D. Li, C.C. Chang, M.Y. Chiang, S.T. Liu, Inorg. Chem. 37 (1998) 1655.
[80] K. Ziegler, E. Holzkmap, Ann. 605 (1957) 93.
[81] D.B. Malpass, L.W. Fannin, J. Organomet. Chem. 93 (1975) 1.
[82] M. Vieth, W. Frand, F. Toner, H. Lange, J. Organomet. Chem. 326 (1987) 315.
[83] C.C. Chang, S.C. Lin, C.N. Tsai, L.K. Liu, J. Chin. Chem. Soc. 39 (1992) 55.
[84] T.Y. Her, C.C. Chang, L.K. Liu, Inorg. Chem. 31 (1992) 2291.
[85] T.Y. Her, C.C. Chang, G.H. Lee, S.M. Peng, Y. Wang, Inorg. Chem. 33 (1994) 99.
[86] C.C. Chang, T.Y. Her, F.Y. Hsieh, C.Y. Yang, M.Y. Chiang, G.H. Lee, Y. Wang, S.P. Peng, J. Chin. Chem. Soc. 41 (1994) 783.
[87] C.C. Chang, W.H. Lee, T.Y. Her, G.H. Lee, S.M. Peng, Y.J. Wang, J. Chem. Soc. Dalton Trans. (1994) 315.
[88] C.C. Chang, T.Y. Her, M.D. Li, R. Williamson, G.H. Lee, S.M. Peng, Y. Wang, Inorg. Chem. 34 (1995) 4296.
[89] C.C. Chang, B. Srinivas, M.L. Wu, W.H. Chiang, M.Y. Chiang, C.S. Hsiung, Organometallics 14 (1995) 5150.
[90] J.A. Meese-Marktscheffel, R.E. Cramer, J.W. Gilje, Polyhedron 13 (1994) 1045.
[91] M.D. Li, C.C. Chang, Y. Wang, G.H. Lee, Organometallics 15 (1996) 2571.
[92] C.C. Chang, J.H. Chen, B. Srinivas, M.Y. Chiang, G.H. Lee, S.M. Peng, Organometallics 16 (1997) 4980.
[93] B. Srinivas, C.C. Chang, C.H. Chen, M.Y. Chiang, I.T. Chen, Y. Wang, G.H. Lee, J. Chem. Soc. Dalton Trans. (1997) 957.
[94] C.C. Chang, C.H. Hsiung, H.L. Su, B. Srinivas, M.Y. Chiang, G.H. Lee, Y. Wang, Organometallics 17 (1998) 1595.
[95] C.C. Chang, B. Srinivas, M.L. Wu, W.H. Chiang, M.Y. Chiang, C.S. Hsiung, Organometallics 14 (1995) 5150.
[96] C.C. Chang, K.C. Yang, S.M. Peng, G.H. Lee, in preparation.
[97] T. Aida, S. Inoue, J. Am. Chem. Soc. 105 (1983) 1304.
[98] F. Kojima, T. Aida, S. Inoue, J. Am. Chem. Soc. 108 (1986) 391.
[99] (a) W. Leitner, Coord. Chem. Rev. 153 (1996) 257. (b) K.K. Pandey, Coord. Chem. Rev. 140 (1995) 37. (c) D.A. Palmer, R.V. Eldik, Chem. Rev. 83 (1983) 651.
[100] (a) P. Braunstein, D. Matt, D. Nobel, Chem. Rev. 88 (1988) 747. (b) D.H. Gibson, Chem. Rev. 96 (1996) 2063. (c) W. Leitner, Angew. Chem. Int. Ed. Engl. 34 (1995) 2207.