ALUMINUM

ANNUAL SURVEY COVERING THE YEAR 1971

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The chemistry of organoaluminum compounds continues to expand and develop in many directions. Therefore the review for 1971 will be broken down into several areas in an attempt to systematize the material for the benefit of the reader. The literature is very extensive, and although an attempt has been made to cover all of the primary journals through Chemical Abstracts, there surely have been some oversights. The patent literature has not been included. The general breakdown of topics is as follows.

A. Structure, spectroscopic properties, and bonding of organo - aluminum compounds.

B. Studies of dissociation and exchange reactions and of addition compound formation

C. Synthesis and reactions of compounds containing Al-C bonds.

D. Nitrile addition reactions

E. Formation and reactions of other aluminum - nitrogen bonded compounds.

F. Formation and reactions of aluminum-oxygen bonded compounds.

G. Formation and reactions of S, Se, and P derivatives.

   H.   Cleavage and exchange reactions of alkyl- and alkylaluminum

        halides.

   I.   Formation and reactions of hydridic Compounds.

   J.   Aluminum-transition metal derivatives.

   K.   Polymerization reactions and catalysts.

A.   Structure, Spectroscopic Properties, and Bonding of Organo-

     aluminum Compounds.

     The discussion started in 1970 concerning the structure and bonding

in trimethylaluminum has stimulated work on this compound and a

number of papers have appeared.   A three dimensional x-ray structural

determination carried out at $-170^\circ$ provide good evidence for the locations

of the hydrogen atoms in the trimethylaluminum dimer [1].



I
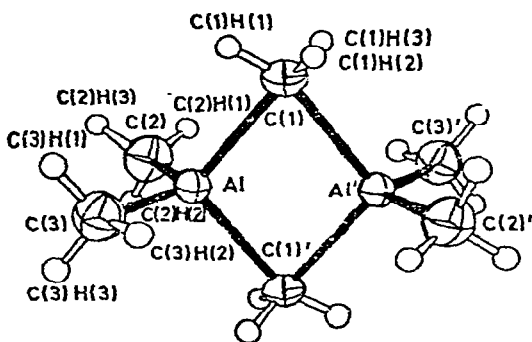
The Structure of $Me_6Al_2$ Dimer After Hoffman and Streib, ref. 1.

     The structure shows that the hydrogens are not in a position to

bond strongly with the aluminum atom and supports the three centered

Al-C-Al bridged bond originally postulated.   Electron diffraction studies

were carried out on both the monomer and dimer in the gas phase [2].

These results showed that the terminal Al-C distance (1.957$^{\circ}$) in the

dimer and the Al-C distance in the monomer were the same. Further-

more, these bond distances are within experimental error of the terminal

Al-C distance reported from the x-ray crystallographic determinations.

The bridge Al-C distance determined for the gas phase was 2.140Å [2],

again very close to the value obtained in the crystal (2.125Å) [1]. It

would appear, therefore, that little difference in structure occurs between

the gaseous and crystalline dimer. The data from the electron diffraction

study were also interpreted to mean that in monomeric $Me_3Al$ nearly

free rotation of the methyl groups take place, while substantial rotation

and other vibrational motions occur in the dimeric molecule. The Raman

spectrum has also been reported for both the monomeric and dimeric

$Me_3Al$ in the gas phase [3]. The monomer was found to have a spectrum

very similar to that of the other $Me_3M$ derivatives of Group III. The

force constants were calculated assuming $D_{3h}$ symmetry and free

rotation of the methyl groups, and were then compared to those observed

for the other Group III methyl derivatives.

The structure of the dimeric $Me_4Al_2H_2$ was studied by electron

diffraction and the molecule was shown to have hydrogen bridging

groups [4]. The Al-Al distance (2.62Å) was equal to that reported in

$Me_6Al_2$ dimer in the gas phase and only 0.02Å longer than that

reported in the solid. The terminal Al-C bonds were equal to those in

the $Me_6Al_2$ dimer.

Two studies have been reported on adducts of $Me_3Al$. The first

records the crystal structure of trimethyl(quinuclidine)aluminum [5]

as indicated in II.  The Al-C distances were found to be 2.02Å which



II
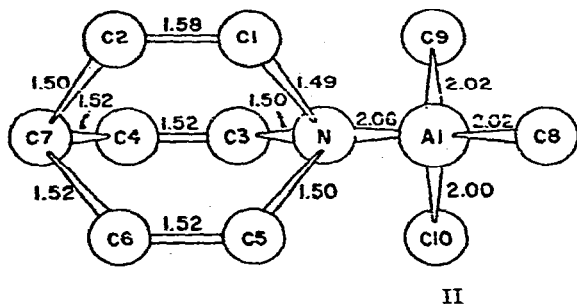
The Structure of $Me_3Al \cdot NC_7H_{13}$ after

C. D. Whitt, et al., ref. 5.

is very similar to that observed in trimethylaluminum.  The $Me_3Al$

portion of the molecule is somewhat flattened with C-Al-C angles of

approximately 113-114°, slightly larger than the tetrahedral angle.  A

brief discussion of the causes for this distortion is presented.  An

electron diffraction study on the trimethylaluminum-trimethylamine

adduct gave similar results for geometry and bond lengths around the

aluminum atom [6].  The crystal structure of hexacyclopropyldi-

aluminum has also been reported and yields similar Al-Al and Al-C

bond distance to those recorded for trimethylaluminum dimer [7].

An interesting feature of this structure is that the bridging cyclopropane

rings are to the same side of the Al-C four membered ring as indicated

in III giving rise to the magnetic nonequivalence of the terminal groups

observed in the nmr spectrum.  This feature is discussed further under

exchange studies .  Several other structures were determined in which

different groups were attached to the aluminum which gave  rise either

to bridged species or monomeric derivatives with Al-C terminal
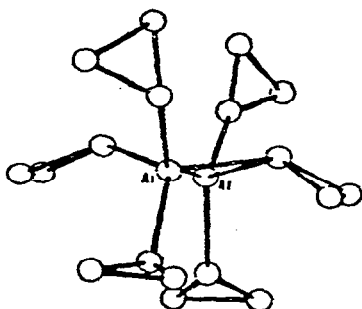
III

The Structure of $(c\text{-}C_3H_5)_6Al_2$ after

J. W. Moore, et al., ref. 7.

groups [8, 9]. Kai, et al. [8] determined the structure of the stereo-

specific polymerization catalyst of acetaldehyde, dimethylaluminum

N-phenylbenzimidate dimer, $[Me_2AlOC(Ph)NPh]_2$ as shown in IV.

Two features of this structure should be noted, first the Al-C bond

distance remains the same and second, and of more interest, that this

stereospecific catalyst contains an eight membered ring with apparent

delocalization of electrons over the N-C-O linkage. The structure of

$[Me_2AlOC(Ph)NPh \cdot ONMe_3]$ has also been reported [9]. This compound

has been shown to be monomeric with the oxygen atoms in each

coordinating group bound to the aluminum atom forming a slightly dis-

torted tetrahedral coordination. It, unlike the compound noted above,

does not have catalytic activity in the polymerization of acetaldehyde.
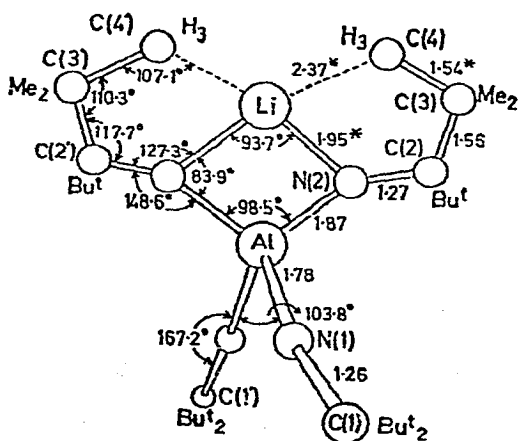
Shearer, et al. [10] prepared the compound, $LiAl[N=C(t\text{-}Bu)_2]_4$

by reaction of $AlCl_3$ with $(t\text{-}Bu)_2C=NLi$. They determined its

structure to be that shown in V by x-ray crystallography. Two interesting

points were made. First the Al-N distances observed for the

*References* p. 200
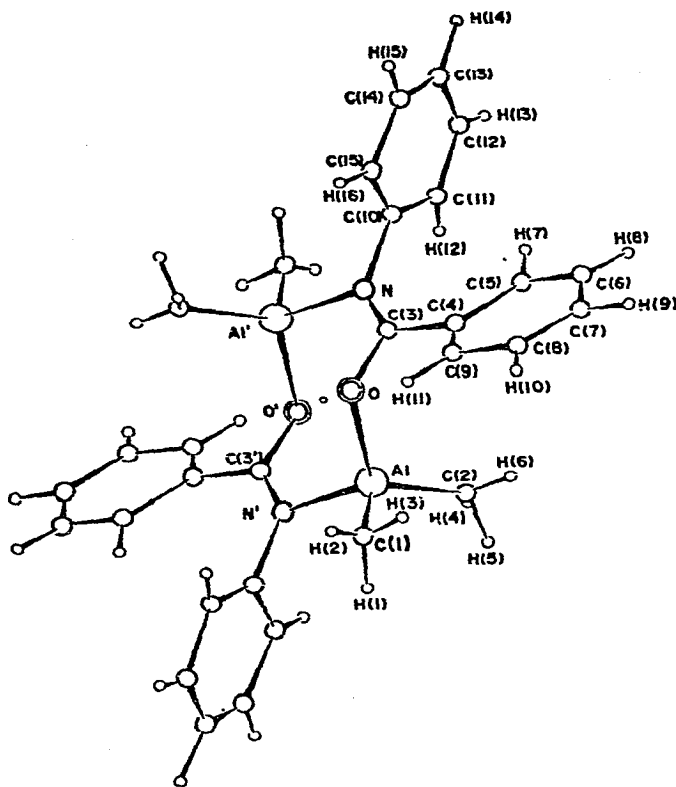
IV

The Molecular Structure of $[Me_2AlOC(Ph)NPh_2]_2$

After Kai, et al., ref. 8.



V

The Molecular Structure of $LiAl[(N=C(t-Bu)_2]_4$

After Schearer, et al., ref. 10.

non-bridging groups were found to be appropriate for appreciable

$N\rightleftharpoons Al$ (p→d) dative $\pi$-bonding and second, the two groups bridging the

Al to the Li also appeare to be involved in a novel Li... H-C interaction.

The final crystal structure of an organoaluminum compound

reported in 1971 is that of $B_9C_2H_{12}AlMe_2$ [11]. The $Me_2Al$ group is

bound to the edge of the $B_9C_2$ moiety as indicated in VI. The hydrogen
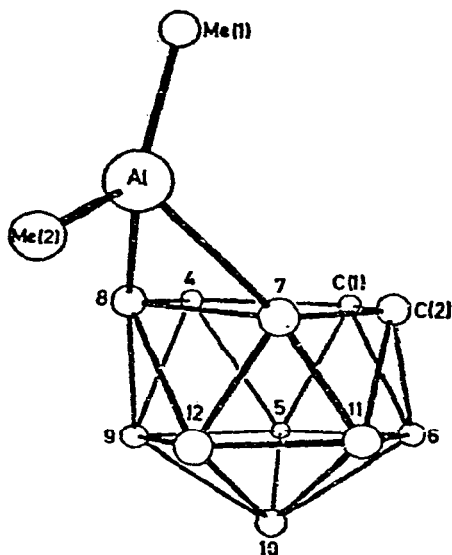


VI

The Molecular Framework of $B_9C_2H_{12}AlMe_2$ After
Churchill, et al., ref. 11.

atoms in the structure have not been located but from the similarity to

the B-Al bond length (2.15Å) in $Al(BH_4)_3$ and that observed in the present

compound (1.94Å) as well as from an interpretation of the ^{1}H and [11]B

nmr spectra, the authors concluded that the aluminum atom was held

to the cage by two Al-H-B bridge bonds. The [11]B nmr spectrum also

was temperature dependent and this was interpreted in terms of a rapid

exchange of hydrogens bridged to the Al atom.

Other studies providing structural information about organo-

aluminum compounds include work on the $^{27}$Al nqr studies on $R_nAlX_{3-n}$

(X = Cl or Br; R = Me, Et, Pr , i-Bu, or Ph)[12]. It was shown

that the three trialkylaluminum species had similar asymmetry parameters

($\lambda$ ) and coupling constants $e^2Q_q$ indicating that in the solid state all

had similar dimeric structures. The data supported halide bridges

for $R_4Al_2X_2$ species as shown in VII, and trans oriented halogens in
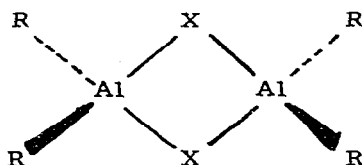


VII

the $R_2Al_2X_4$ derivative as shown in VIII. The relationship between the

observed quadrupolar coupling constants and electron distribution

within the various orbitals was discussed.
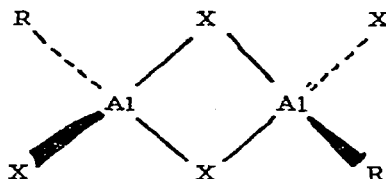


VIII

Ohkubo, et al. [13] have reported extended Huckel calculations

on trimethylboron and aluminum, and calculated a significant difference

in bonding. Unfortunately, their results predicted that both species

should be more stable in monomeric form, however they did order

the stabilities correctly with monomeric $Me_3B$ more stable than $Me_3Al$.

Wilkie has examined the ir and Raman spectra of $LiAlMe_4$ [14]

and of both $LiAlEt_4$ and $NaAlEt_4$ [15] in some detail. After a variety

of isotopic substitutions it was shown that Li interacted strongly with

the organic groups in both cases. It was concluded that a bridged

structure, as indicated in IX, was the form present in the solid

for both methyl and ethyl derivatives. $NaAlEt_4$ gives a much simpler

spectrum which appears to be consistant with little interaction of the

cation with the metal alkyl anion leaving the Al atom in $T_d$ symmetry.
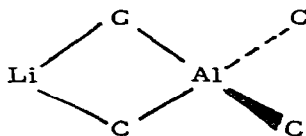


IX

Ruch'eva, et al. [16] have recorded the ir spectra of the Group III

derivatives of the type $(C_6D_5)_3M$ including Al between 200 and 2,600 $cm^{-1}$

They have reported calculations of in-plane and out-of-plane normal

vibrations with use of the force field observed in the undeuterated

molecule.

Bürger et al. [17] carried out a complete normal coordinate

analysis of the silylamides, $Al[N(SiMe_3)_2]_3$, $Ga[N(SiMe_3)_2]_3$, and

$In[N(SiMe_3)_2]_3$. They found that the compounds were all monomeric and

the central metal atom was in a trigonal environment. Good agreement

of calculated and observed frequencies was achieved with the following

M-N stretching force constants;  Al-N, 2.09; Ga-N, 1.95; and In-N,

1.77 $\frac{mdyn}{\mathring{R}}$  .

Finally epr spectroscopic measurements were made on a series

of radicals produced by the irradiation of a series of hydrides and

alkyls of Al, Si and P [18].  The results of these studies showed that

the series changed from nearly flat $AlR_3^-$ radical to a pyramidal

$PR_3^+$ radical.  This change was accentuated  when R = alkyl as opposed

to a hydrogen atom.  This result was interpreted in terms of an

increasing 3p to 3s ratio of orbitals used in bond formation.

B.  Studies of Dissociation and Exchange Reactions and of Addition

    Compound Formation.

Hay, Hooper and Robb [19] presented a critical review of both

the kinetic and thermodynamic data available in the literature dealing

with the dissociation of trimethyl- and triethylaluminum dimers.  Their

best estimates of these parameters for reaction 1 are summarized as

follows

$$R_6Al_2 \rightleftharpoons 2R_3Al \qquad (1)$$

For trimethylaluminum:

$$\Delta H_{d(g)} = 20.2 \pm 0.3 \text{ kcal/mole of dimer} \qquad (2)$$

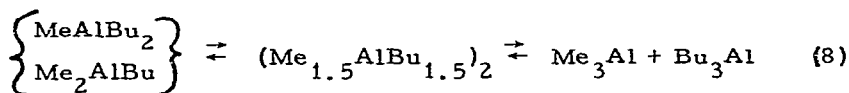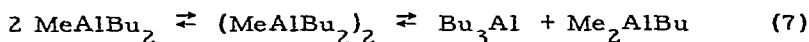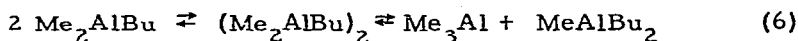$$\text{and } \Delta H_{d(l)} = 16.5 \pm 1.5 \text{ kcal/mole of dimer} \qquad (3)$$

while for triethylaluminum the values are:

$$\Delta H_{d(g)} = 10.2 \pm 1.0 \text{ kcal/mole of dimer} \qquad (4)$$
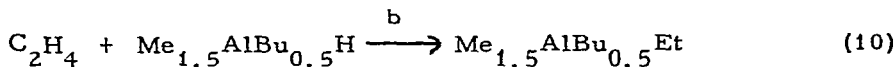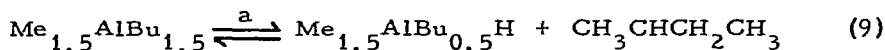
$$\text{and } \Delta H_{d(l)} = 8 - 14 \text{ kcal/mole of dimer} \qquad (5)$$

Egger and Cocks [20] have studied the thermal decomposition of

$Me_2AlBu$ in the presence of excess ethylene between $401-478^\circ K$.  On

the basis of their studies, they proposed the following rapidly established

equilibria.

$$2 \text{ Me}_2\text{AlBu} \rightleftharpoons (\text{Me}_2\text{AlBu})_2 \rightleftharpoons \text{Me}_3\text{Al} + \text{MeAlBu}_2 \qquad (6)$$

$$2 \text{ MeAlBu}_2 \rightleftharpoons (\text{MeAlBu}_2)_2 \rightleftharpoons \text{Bu}_3\text{Al} + \text{Me}_2\text{AlBu} \qquad (7)$$

$$\left\{ \begin{matrix} \text{MeAlBu}_2 \\ \text{Me}_2\text{AlBu} \end{matrix} \right\} \rightleftharpoons (\text{Me}_{1.5}\text{AlBu}_{1.5})_2 \rightleftharpoons \text{Me}_3\text{Al} + \text{Bu}_3\text{Al} \qquad (8)$$

with the elimination reaction described by

$$\text{Me}_{1.5}\text{AlBu}_{1.5} \xrightleftharpoons[b]{a} \text{Me}_{1.5}\text{AlBu}_{0.5}\text{H} + \text{CH}_3\text{CHCH}_2\text{CH}_3 \qquad (9)$$

$$\text{C}_2\text{H}_4 + \text{Me}_{1.5}\text{AlBu}_{0.5}\text{H} \longrightarrow \text{Me}_{1.5}\text{AlBu}_{0.5}\text{Et} \qquad (10)$$

In the presence of excess ethylene the elimination reaction in $\underline{9}$ was the

slow, irreversible, and rate controlling step, as $k_b \gg k_a > k_{-a}$. The

parameters for this reaction were given as the observed rate

constants, $\log k \text{ (sec}^{-1}) = (10.85 \pm 0.18) - (27.80 \pm 0.36 / \ominus)$, where $\ominus$

equals $4.58 \times 10^{-3}$ T in kcal/mole resulting in a negative intrinsic

entropy of activation of 13.0 cal/$^\circ$K mole.

This reaction was compared with earlier studies on $R_3\text{Al}$ derivatives

made by these authors and discussed in terms of the tight four centered

transition state shown in X.
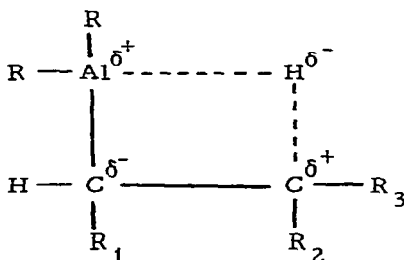


X

A brief study of the mass spectrum of $(Me_3Al)_2$ was presented in a discussion of other groups III alkyls which confirmed earlier mass spectral investigations of $(Me_3Al)_2$ [21]. In addition several new fragments were identified and it was shown that the abundance of the molecular ion decreased in the order $Al > B > Ga > In > Tl$. A more complete discussion is given in the review of indium and gallium.
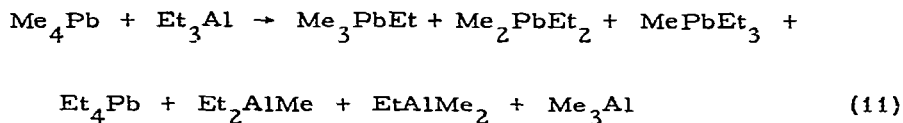
In the closely related aluminum alkoxides, Wilson [22] has presented a calorimetric investigation of the heat of formation of tri-isopropylaluminum and the energy required to dissociate an Al-O bridge bond. His estimates of these values were for the heat of formation of tetrameric tri-isopropoxyaluminum, $\Delta H_f^o = -5149.5$ kJ/mole, and for the heat of formation of the gaseous dimer, $\Delta H_f^o = -2466.9$ kJ/mole. These results led to a minimum value of $\Delta H_{het} = 131.5$ kJ/mole for the Al-O bridge bond.

The reports appearing on alkyl exchange reactions involving aluminum derivatives have decreased. Matteson [23] reinterpreted the self-exchange of trimethylaluminum and the exchange between trimethyl-aluminum and trimethylgallium. His analysis of the data supports the dissociative mechanism for the exchange processes involving tri-methylaluminum and does not require one to invoke a complex solvent cage effect to account for the behavior of any of the systems involved. It does predict a slight concentration dependence for the rate of exchange in the Al-Ga system which has not been observed due to the limited concentration ranges studied. A test of this would be of general interest.

A second paper dealing in part with exchange process in the

$\bigtriangledown_4$Al$_2$Me$_2$ system has shown that the cyclopropyl groups are located preferentially in the bridging cites and that the orientation of these groups give rise to non-equivalent terminal methyl groups [7]. In this instance, a pseudo rotational barrier involving the aluminum-carbon bridged bond has been reported of about 11 kcal/mole. This adds a new dimension to the study of exchange process involving bridged organometallic compounds and indicates some of the complexities of these reactions which are still not understood.
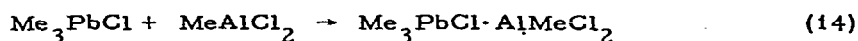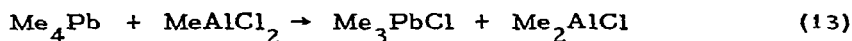
Boleslawski, et al. [24] have proposed a series of exchange reactions and the formation of several complexes between R$_3$AlX$_{3-n}$ derivatives and Me$_4$Pb. The first of these is described by 11.

$$Me_4Pb + Et_3Al \rightarrow Me_3PbEt + Me_2PbEt_2 + MePbEt_3 +$$
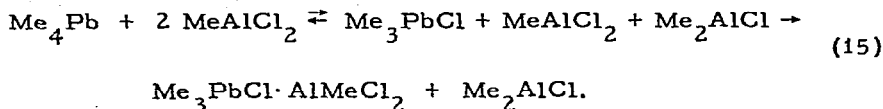
$$Et_4Pb + Et_2AlMe + EtAlMe_2 + Me_3Al \qquad (11)$$

This reaction is supported by nmr studies. They also reported reaction 12.

$$Me_3PbMe^* + Me_2AlCl \rightarrow Me_4Pb + Me^*MeAlCl \qquad (12)$$
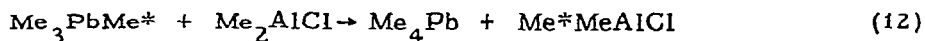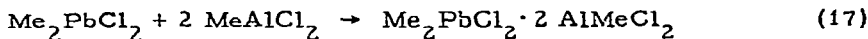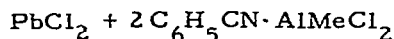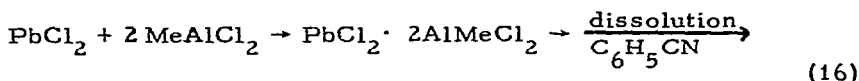
which was supported by observation of broadened nmr lines interpreted by the authors to be the result of exchange. No additional data was presented, however, and this result might also be accounted for in terms of exchange of complexes formed such as they proposed for MeAlCl$_2$ with Me$_4$Pb. They observed no chlorine exchange in reaction 12. With Me$_4$Pb and MeAlCl$_2$, two reactions were reported as seen in 13 and 14. These reactions are complicated by additional exchanges as

$$Me_4Pb + MeAlCl_2 \rightarrow Me_3PbCl + Me_2AlCl \qquad (13)$$

$$Me_3PbCl + MeAlCl_2 \rightarrow Me_3PbCl \cdot AlMeCl_2 \qquad (14)$$

indicated in 15 and therefore the nature of the system is dependent on

$$Me_4Pb + 2 MeAlCl_2 \rightleftarrows Me_3PbCl + MeAlCl_2 + Me_2AlCl \rightarrow$$
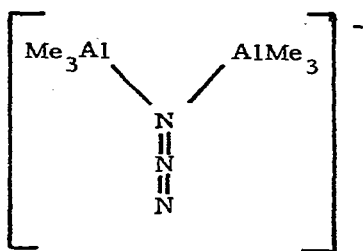
(15)

$$Me_3PbCl \cdot AlMeCl_2 + Me_2AlCl.$$

the stoichiometry used. Although not noted in the paper, it should be

clear that a variety of aluminum compounds will be present, such as

$Me_4Al_2Cl_2$, $Me_3Al_2Cl_3$, $Me_2Al_2Cl_4$. These authors also discussed the

path of exchange and influence that the formation of the benzonitrile-

aluminum adduct has on the exchange reaction. This same research

group [25] reported on the formation of complexes between $PbCl_2$ and

$Me_2PbCl_2$ with $MeAlCl_2$ as indicated in 16 and 17. They supported this

preliminary report with nmr data and with a cryoscopically determined

$$PbCl_2 + 2 MeAlCl_2 \rightarrow PbCl_2 \cdot 2AlMeCl_2 \rightarrow \xrightarrow[C_6H_5CN]{dissolution}$$

(16)

$$PbCl_2 + 2 C_6H_5CN \cdot AlMeCl_2$$

$$Me_2PbCl_2 + 2 MeAlCl_2 \rightarrow Me_2PbCl_2 \cdot 2 AlMeCl_2 \tag{17}$$
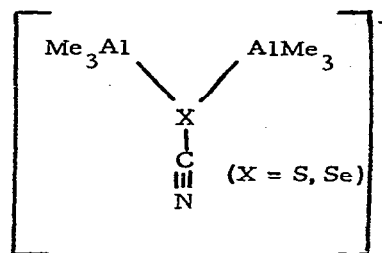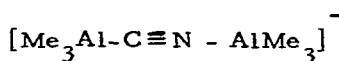
molecular weight of 530-540 for the latter complex (theoretical 534).

Weller, et al. [26] reported the formation and ir spectra of the

following complexes with the $[NMe_4]^+$ counter ions: $[(Me_3Al)_2N_3]^-$

$[Me_3AlN_3]^-$, $[(Me_3Al)_2SCN]^-$, $[Me_3AlSCN]^-$, $[(Me_3Al)_2CN]^-$,

$[(Me_3Al)_2SeCN]^-$, and $[(Me_3Al)_3C(CN)_3]^-$. These were prepared by

simple addition reactions and the structures indicated in XI, XII, XIII,

and XIV were proposed in addition to the normal four coordinate

aluminum complexes. Atwood, Milton, and Seale [26] have also prepared

the thiocyanate complex $K[(Me_3Al)_2SCN]$ and have shown that it de-

$$\left[ \begin{array}{c} \text{Me}_3\text{Al} \qquad \text{AlMe}_3 \\ \diagdown \qquad \diagup \\ \text{N} \\ \| \\ \text{N} \\ \| \\ \text{N} \end{array} \right]^-$$

XI

$$\left[ \begin{array}{c} \text{Me}_3\text{Al} \qquad \text{AlMe}_3 \\ \diagdown \qquad \diagup \\ \text{X} \\ | \\ \text{C} \\ \| \\ \text{N} \end{array} \right]^- \quad (X = S, Se)$$

XII

$$[\text{Me}_3\text{Al-C}\equiv\text{N} - \text{AlMe}_3]^-$$

XIII

$$\left[ \begin{array}{c} \text{Me}_3\text{Al} \qquad\qquad \text{AlMe}_3 \\ \diagdown \qquad\qquad \diagup \\ \text{N}\equiv\text{C} \qquad \text{C}\equiv\text{N} \\ \diagdown \quad \diagup \\ \text{C} \\ | \\ \text{C} \\ \| \\ \text{N} \\ \text{AlMe}_3 \end{array} \right]^-$$
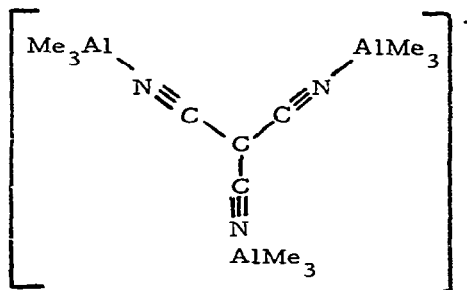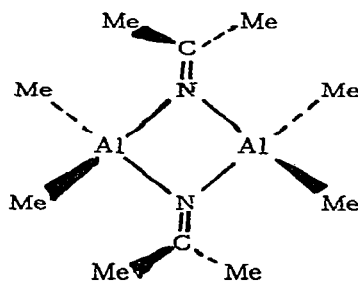
XIV

composes thermally to yield a compound which has the empirical

formula corresponding to $\text{Me}_2\text{CNAlMe}_2$ with the proposed structure

given in XV.

$$\begin{array}{c} \text{Me} \diagdown \quad \diagup \text{Me} \\ \text{C} \\ \| \\ \text{N} \\ \text{Me} \diagdown \quad \diagup \quad \diagdown \quad \diagup \text{Me} \\ \text{Al} \qquad \text{Al} \\ \text{Me} \diagup \quad \diagdown \quad \diagup \quad \diagdown \text{Me} \\ \text{N} \\ \| \\ \text{C} \\ \text{Me} \diagup \quad \diagdown \text{Me} \end{array}$$
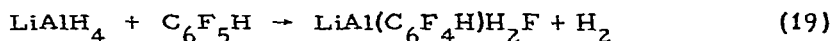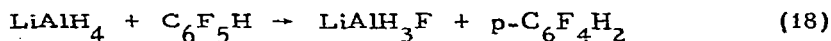
XV

## C. Synthesis and Reactions of Compounds Containing Al-C Bonds.

In a single report on perfluoroaluminum compounds, Dickson and

Sutcliffe [28] stated that $\text{LiAlH}_4$ reacts with fluorobenzenes in different

manners depending on the degree of substitution to yield fluorophenyl-

aluminum derivatives. With $C_6F_5H$ reactions 18 and 19 was observed

in which a fluorophenylaluminum compound was produced. With $C_6F_6$,

$$LiAlH_4 + C_6F_5H \rightarrow LiAlH_3F + p\text{-}C_6F_4H_2 \qquad (18)$$

$$LiAlH_4 + C_6F_5H \rightarrow LiAl(C_6F_4H)H_2F + H_2 \qquad (19)$$

the additional reaction noted in 20 took place while 1, 2, 4, 5-tetra-

$$LiAlH_4 + C_6F_6 \rightarrow LiAlH_3F + C_6F_5H \qquad (20)$$
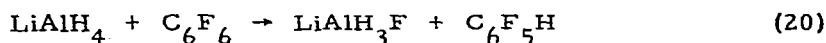
fluorobenzene was shown to react via 21. The aluminum compounds

$$LiAlH_4 + n(p\text{-}C_6F_4H_2) \rightarrow LiAl(C_6F_4H)_nH_{4-n} \qquad (21)$$
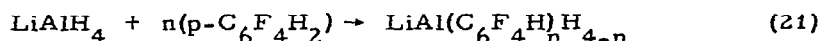
could not be isolated free of THF but were characterized by their nmr

spectra and by chemical reactions.

Eisch and Considine reported [29] on the specific ortho-arylation

in the photochemical rearrangements of the tri-m-tolyl- and tri-p-tolyl-

aluminum systems. The reaction observed is indicated in 22.

Kroll and Hudson [30] investigated the metalation of cyclopenta-

diene with $(i\text{-}Bu)_3Al$ and found that this reaction proceeded as indicated in 23.



$$(i\text{-}Bu)_3Al + C_5H_6 \rightarrow (i\text{-}Bu)_2AlC_5H_5 + i\text{-}BuH \qquad (23)$$
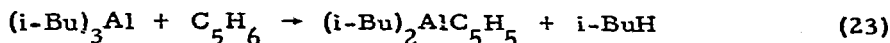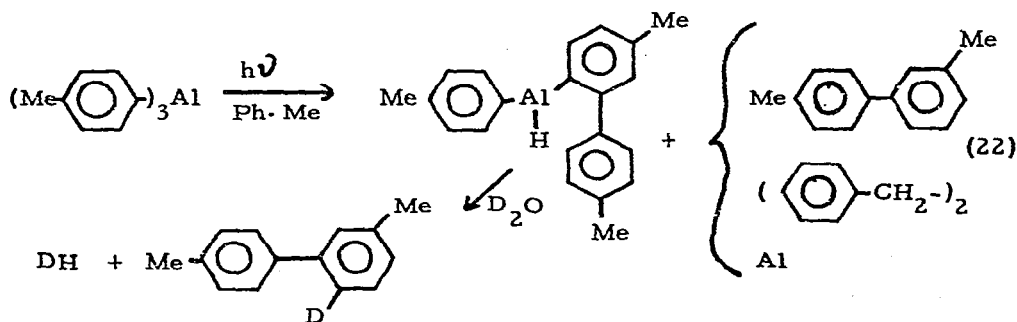
The reaction was extremely sluggish and only occurred at elevated temp-

eratures in the gas phase where a number of side reactions also occurred.

In addition, they reported on the reaction of endo-dicyclopentadiene

with $(i-Bu)_3Al$. This compound was found to undergo carboalumination as

seen in 24 very readily. A similar reaction was also noted with

$(i-Bu)_2AlH$ at $60°$.

$$AlR \quad + \quad \text{[structure]} \quad \longrightarrow \quad \text{[structure]} \qquad (24)$$
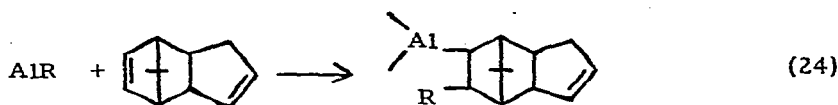
Eisch and Biedermann [31] examined the reactions of pure

tribenzylaluminum, $(PhCH_2)_3Al$, and its etherate in order to evaluate

the structural factors leading to either normal or allylic reactions with

allylic C-Al bonds. $(PhCH_2)_3Al$ was found to be most readily prepared

by reaction 25 or alternately by the reaction of $AlCl_3 \cdot Et_2O$ with

$$3(PhCH_2)_2Hg \;+\; 2Al \xrightarrow{\Delta} 2(PhCH_2)_3Al \;+\; 3\,Hg \qquad (25)$$
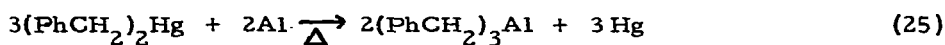
$PhCH_2MgX$. An investigation of the nmr spectra between +25 to $-90°$

gave rise only to a single nmr spectrum interpreted to mean that

benzylaluminum is monomeric. Its reaction with $D_2O$ and $CO_2$ were

normal and its addition to $PhC \equiv CPh$ yielded the cis addition product.

The reaction of unsolvated $(PhCH_2)_3Al$ to benzophenone anil was studied

and found to proceed as indicated in 26. All of the products which were

$$(26)$$
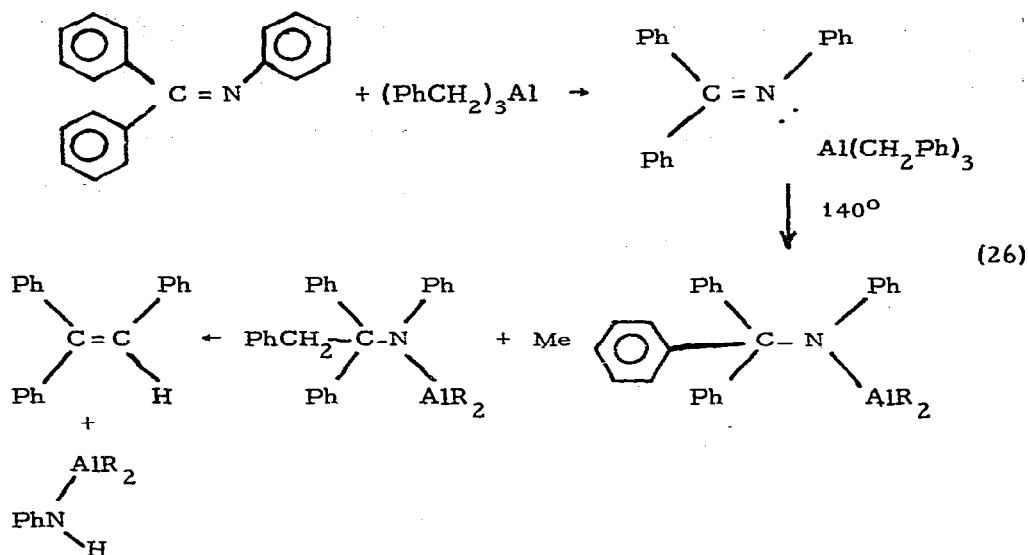
observed point to exclusive 1, 2-addition of $(PhCH_2)_3Al$ to benzophenone

anil. Possible reasons for this are discussed.

The basis of many of the industrial polymerization reactions and

the synthesis of long chain organic species is often dependent on the

addition of Al-C bonds to multiple bonded species. Typical of this type

of application is the report by Mischenko, et al. [32] who studied the

addition of $Et_3Al$ to ethylene to yield $\alpha$-olefines under a variety of

conditions.

Eisch and Hordis [33, 34] have attempted to evaluate a number

of factors related to this general topic. They have investigated both

the stereochemical [33] and kinetic [34] effects of the substitutent on

the addition of $Ph_3Al$ to para-substitute diphenylacetylenes. The para

substituents (Z) employed were the $Me_2N$, MeO, Me, MeS, H, Cl,

$CF_3$ and $MeSO_2$ groups, but the acetylenes with the latter two substituents

fail to react normally.  The others underwent stereospecific cis addition

to yield mixtures of the two isomers XVI and XVII.  The logarithm of

the ratio of these isomers correlated linearly with the Hammett $\sigma$ values
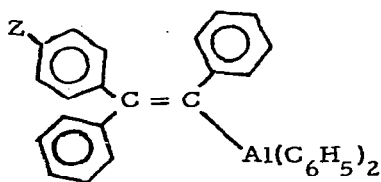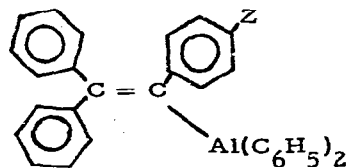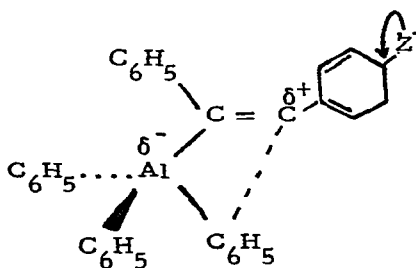
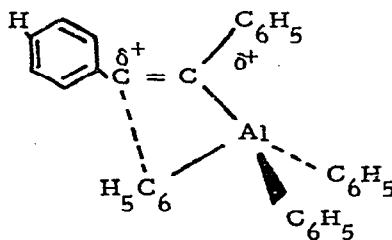XVI                                         XVII

of the para substituent ( $\rho$ =-0.713).  The regioselectivity and cis

stereospecificity, as well as the rate retarding effect of donor solvents,

were shown to be in accord with a kinetically controlled electrophilic

attack of the aluminum center on the triple bond.  The proposed

transition states for the additions are shown in XVIII and XIX.  The

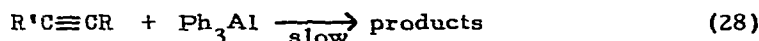XVIII                                       XIX

small $\Delta \rho$ value may occur as the result of participation of the phenyl

group as a $\pi$ base.

Kinetic studies provided additional information concerning the

course of the reaction.[34].  It was shown that if the substituent, Z,

was a Lewis base, i. e., $Me_2N$, MeO, etc., the rates of reaction

were not readily analyzable; however, for the diphenylacetylene itself

and for the p-chloro and p-methyl derivatives, it was shown that the

overall rate was 3/2 order, first order in acetylene and 1/2 order in

triphenylaluminum. The p-chloro group modestly retarded and the

p-methyl definitely enhanced the reactivity of the diphenylacetylene

moiety to carboalumination. These data, along with the strong retarding

influence of donor molecules on the rate, lead to the suggested mechanism

in which initial dissociation of dimer occurs followed by the electro-

philic attack of the tricoordinate aluminum on the acetylene in the rate

determining step.

$$Ph_6Al_2 \rightleftharpoons 2Ph_3Al \qquad\qquad (27)$$

$$R'C\equiv CR + Ph_3Al \xrightarrow{\text{slow}} \text{products} \qquad\qquad (28)$$

In addition to the transition states cited above in XVIII and XIX,

the possability of the initial formation of an Al-$\pi$ complex as seen in
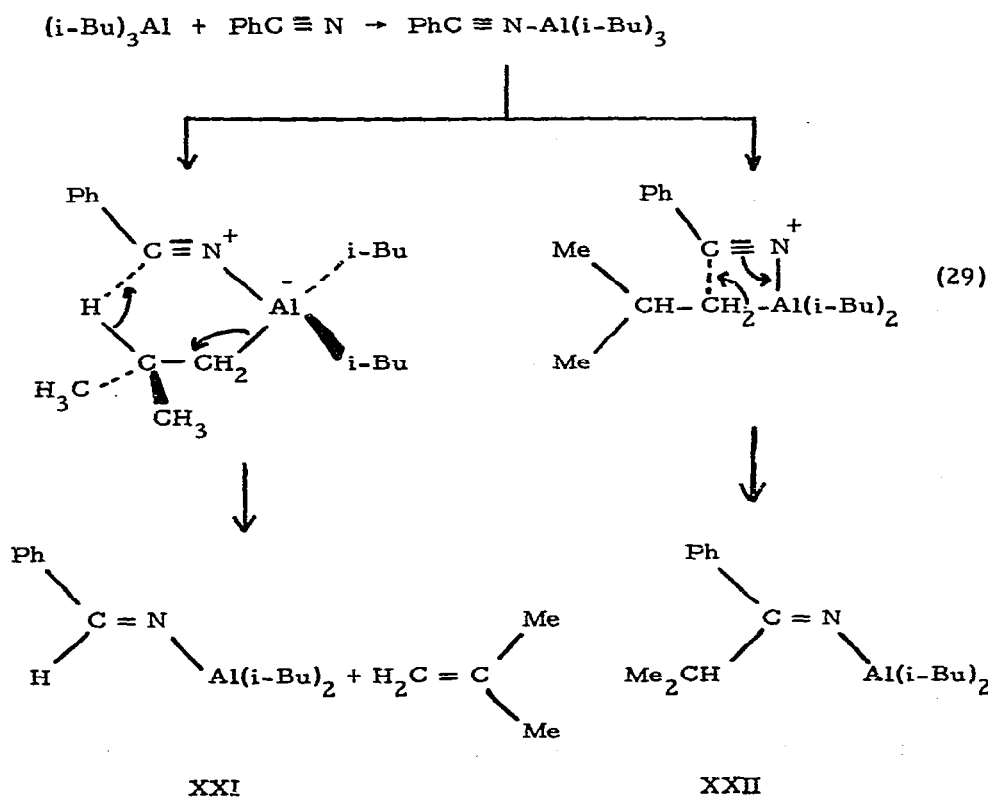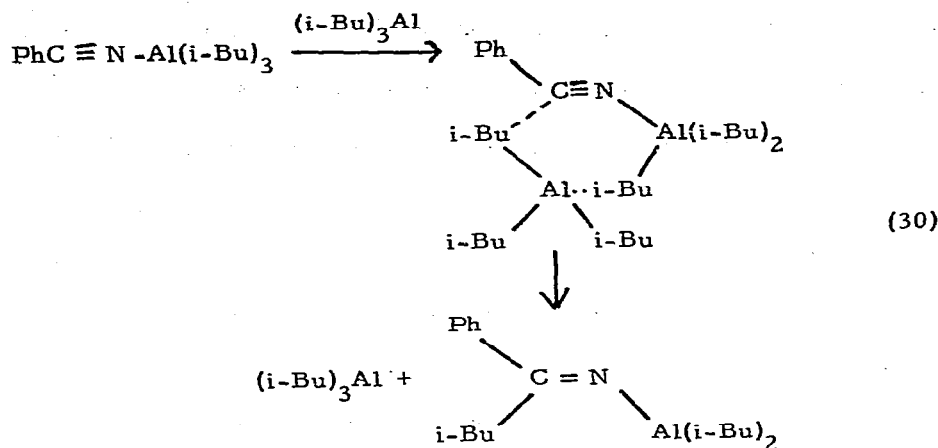
XX was considered.



XX
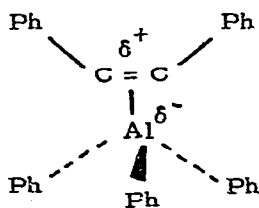
D. Nitrile Additon Reactions

The reaction of triisobutylaluminum, $[(i-Bu)_3Al]_2$ with benzo-

nitrile has been investigated by Lardicci and Giacomelli [35]. They have

shown that both reduction and addition products are formed with the

reduction products always in excess. It was shown that the reactants

formed a complex which then proceeded to the products through a thermal

rearrangement. This is illustrated in 29. An alternate path in 29, was

also proposed for the formation of the addition product XXII which

was consistent with the experimental observations when excess

(i-Bu)$_3$Al was present. This path involves a six centered transition

state. This latter mechanism is also consistent with the partial

racimization observed in the reaction of (+) tris [(S)-2-methylbutyl]-

aluminum with benzonitrile.

$$(i-Bu)_3Al \ + \ PhC \equiv N \ \rightarrow \ PhC \cong N-Al(i-Bu)_3$$

(29)

XXI                                                    XXII

$$PhC \equiv N - Al(i-Bu)_3 \xrightarrow{(i-Bu)_3Al}$$

(30)

The reaction of benzonitrile with methylaluminum derivatives, $Me_n AlCl_{3-n}$, has been studied by Kuran, et al. [36]. The reaction, as studied by these workers, yields a variety of different products dependent upon the method of work up. These include acetophenone, 3, 5-diphenyl-2-pypazoline hydrochloride or tris(1, 3-diphenylpropane-1, 3, -dionato)aluminum, 2, 4, 6-triphenylpyrimidine, triphenyl-s-triazine, and methane. The reactions are postulated to go through addition compound formation as previously noted followed by various rearrangement or further addition steps. Some of the reactions which were proposed and the products arizing from them are illustrated in 31.

Hoberg[37] also has shown that on warming n-benzylamino-alanes ring closure occurs between the aluminum and the ortho position of the phenyl ring as seen in 32. If substituents are present in both ortho positions, then reaction occurs by a different route as indicated in 33. The compounds were identified by their ir and mass spectra.

Hoberg and Mur [38, 39] have investigated a number of reactions of Al- N bonded species with nitriles. They have found that compounds of the type $Cl_n Et_{2-n} AlN = CHR$ (n = 0, 1, 2) react initially with aromatic

nitriles by addition to the $-C\equiv N$ as seen in **34**. The subsequent reactions

of Al-C, Al-N, or cycloaddition are influenced by, n, the number

of Et and/or Cl groups. Previously these authors [39] had reported

on the reaction of benzonitrile with dialkyl- or alkylarylamino-

aluminum derivatives. They observed that for the sterically hindered
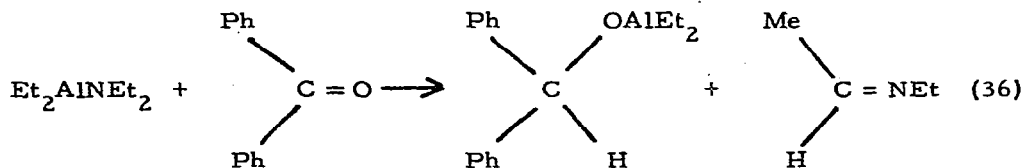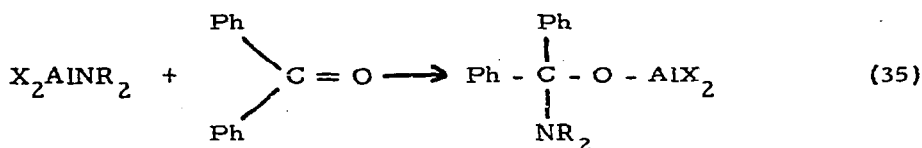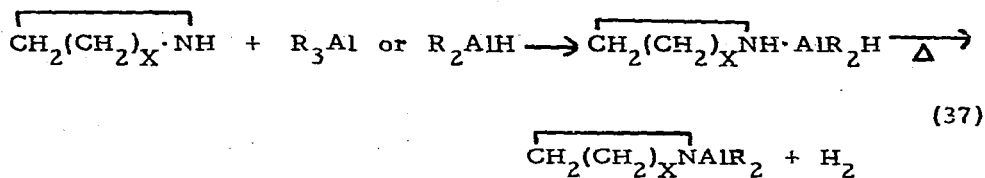


(31)

(32)

(33)

(34)
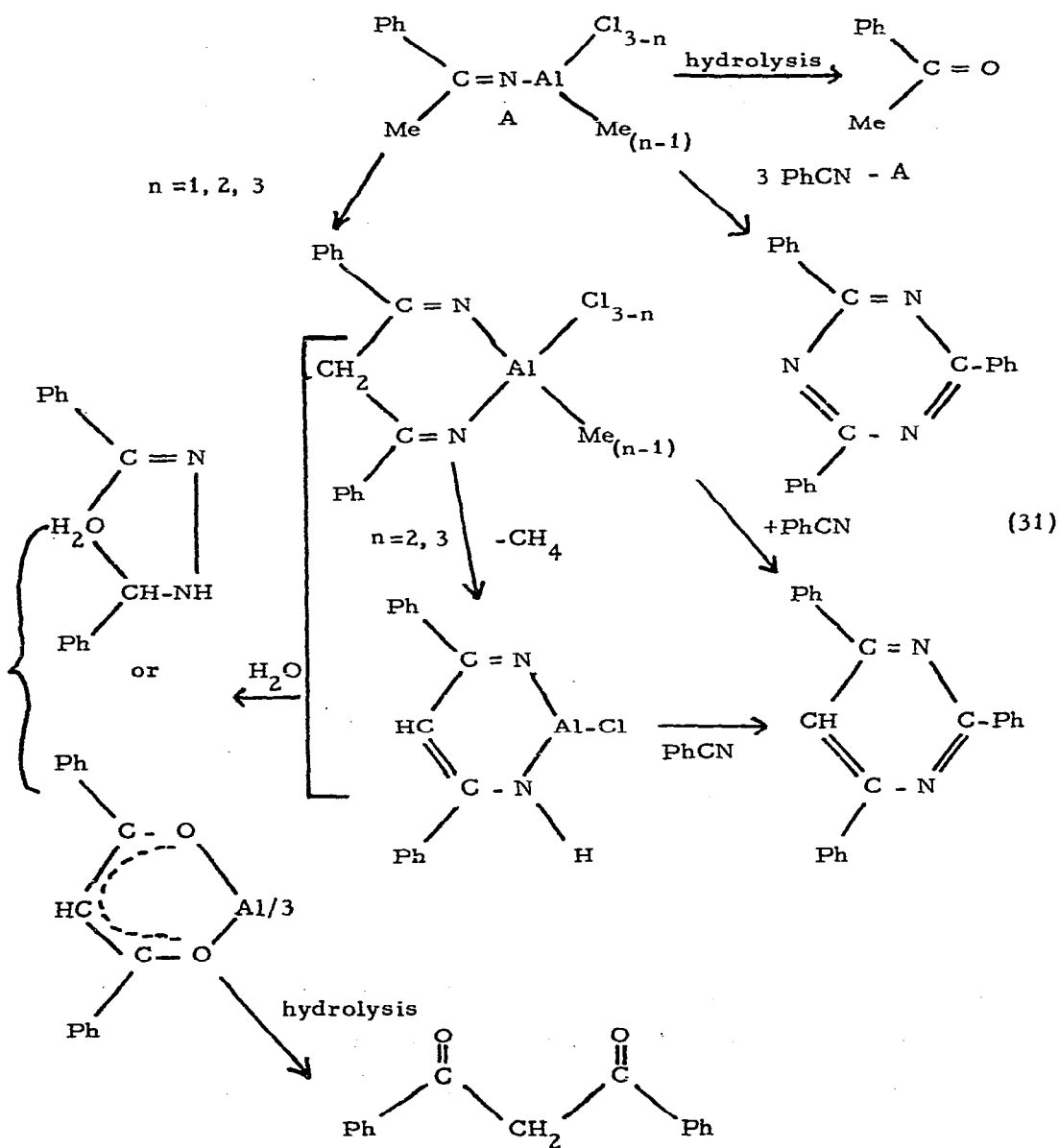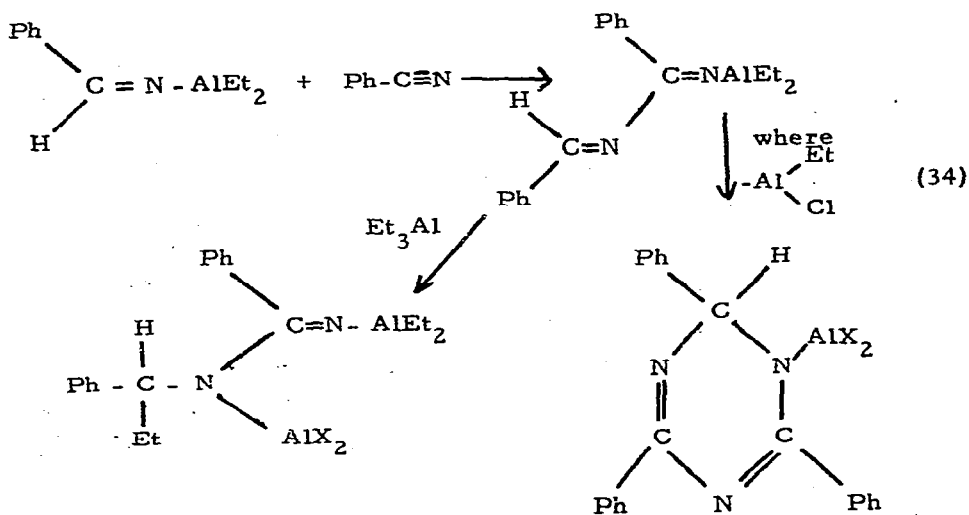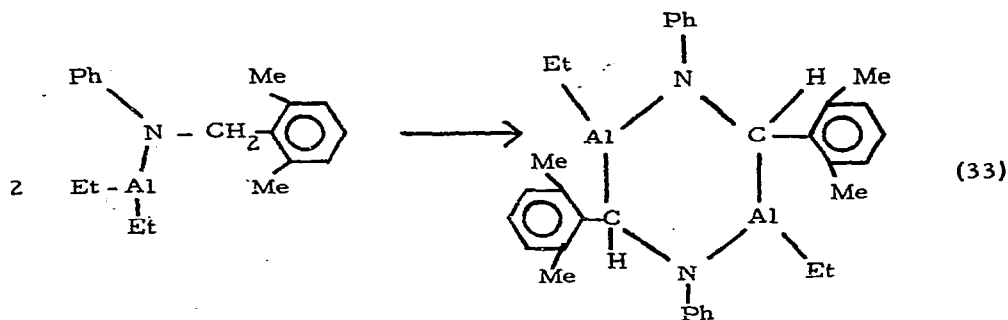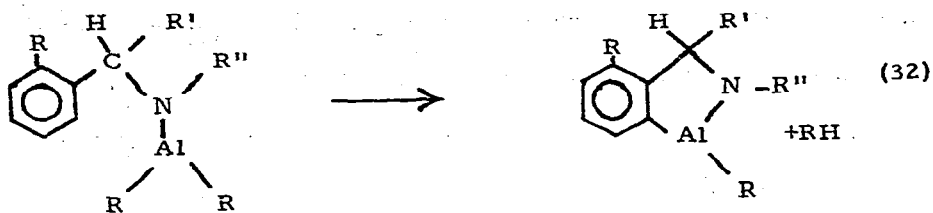
compounds $Et_2AlNPh_2$ and $Et_2AlN(C_6H_{11})_2$ the addition reaction was suppressed substantially (50% yield) and side reactions occurred. The general addition reactions of these derivatives were discussed.

E.  Formation and Reactions of other Aluminum Nitrogen Bonded

   Compounds.

   Hoberg and Tkatchenko [40] also investigated the reaction of

aluminum amides $X_2AlNR_2$ (R = Me, Et and 1-pyraolidienyl) with benzo-

phenone and found different reaction paths depending upon the other (X)

substituents on the aluminum.  For X = Cl, the main reaction was

1, 2-addition of the Al-N to the C=O bond, leading to $Ph_2C(NR_2)OAlCl_2$

which on addition of $R_2AlH$ gave $Ph_2CHNR_2$.  For X = Et, the reduction

by N-alkyl groups was promoted and gave a main product $Ph_2CH(OH)$.

These reactions are shown in 35 and 36.

$$X_2AlNR_2 \ + \ \overset{Ph}{\underset{Ph}{>}}C = O \ \longrightarrow \ Ph - \overset{Ph}{\underset{NR_2}{\overset{|}{\underset{|}{C}}}} - O - AlX_2 \qquad (35)$$

$$Et_2AlNEt_2 \ + \ \overset{Ph}{\underset{Ph}{>}}C = O \ \longrightarrow \ \overset{Ph}{\underset{Ph}{>}}C\overset{OAlEt_2}{\underset{H}{<}} \ + \ \overset{Me}{\underset{H}{>}}C = NEt \qquad (36)$$

   Storr and Thomas [41] have investigated the preparation and

structure of a series of cyclic imino-compounds of aluminum, gallium

and indium.  For the aluminum compounds, they reported two general

preparative reactions as described in 37 with the hydride providing a

smoother route.  The products were characterized by cryoscopic

$$CH_2(CH_2)_X \cdot NH \ + \ R_3Al \ \text{ or } \ R_2AlH \longrightarrow CH_2(CH_2)_X NH \cdot AlR_2H \xrightarrow{\Delta}$$

$$(37)$$

$$CH_2(CH_2)_X NAlR_2 \ + \ H_2$$

X = 1, 2, 3, 4

R = Me, Et, i-Bu

molecular weight measurements, nmr, and mass spectral studies. They were found to vary between dimer and trimer with the more sterically hindered derivatives in the dimeric state. It was found that in the cases where both existed in equilibrium, conversion from one form to the other was slow. The proposed structures for the species are given in XXIII and XXIV. The equilibrium constant and the mechanism of conversion between these two forms is discussed. It was also suggested that rapid confirmational changes occurred with the ring systems which gave rise to magnetic equivalence of the cites on the rings.
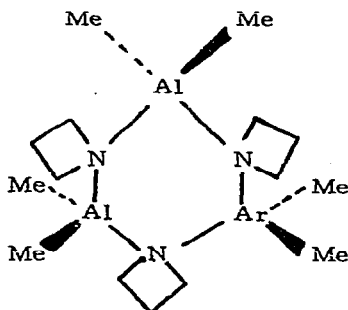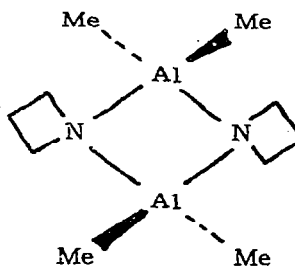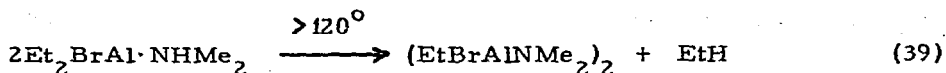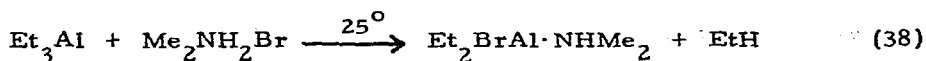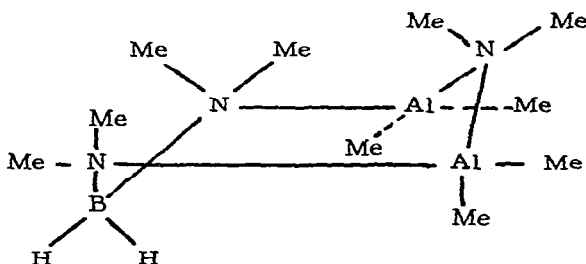


XXIII                                           XIV

Preparation of the derivative $(EtBrAlNMe_2)_2$ by the reaction sequence indicated in 38 and 39 has been reported [43]. Studies on the
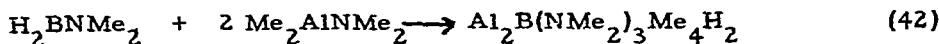
$$Et_3Al + Me_2NH_2Br \xrightarrow{25^{\circ}} Et_2BrAl \cdot NHMe_2 + EtH \qquad (38)$$

$$2Et_2BrAl \cdot NHMe_2 \xrightarrow{>120^{\circ}} (EtBrAlNMe_2)_2 + EtH \qquad (39)$$

nmr spectrum of the final product were interpreted to mean that the

$NMe_2$ group occupied the bridging position, and that the Br atoms were

trans to one another. The appearance of two methylene quartets for

$Et_2BrAl \cdot NHMe_2$ was interpreted in terms of restricted rotation about the

C-Al bond.

Hall and Schram [43] have prepared the novel compound $Al_2B(NMe_2)_3$-

$Me_4H_2$ and proposed the structure shown in XXV based on $^1H$ and $^{11}B$

nmr spectra and on ir studies. The proposed sequence of reactions for

the preparation of the compound is given in 40, 41 and 42.

XXV

$$Me_6Al_2 + 2HB(NMe_2)_2 \rightarrow 2\ MeHBNMe_2 + 2\ Me_2AlNMe_2 \qquad (40)$$

$$2\ MeHBNMe_2 \rightarrow H_2BNMe_2 + Me_2BNMe_2 \qquad (41)$$

$$H_2BNMe_2 + 2\ Me_2AlNMe_2 \rightarrow Al_2B(NMe_2)_3Me_4H_2 \qquad (42)$$
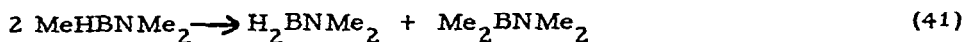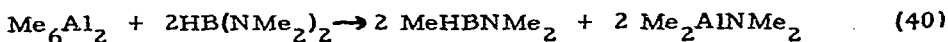
A variety of other reactions have been reported which involve

nitrogen containing compounds. Danilov, et al. [44] have noted that

$BuN_3$ reacts with $Et_3Al$ in benzene (10 hr. at $40^{\circ}$) to give the adduct

$C_{10}H_{24}AlN_3$ which on hydrolysis with $NH_4Cl-NH_4OH$ in $Et_2O$ gave ethane

and $BuN=NNHEt$. Similarly, $PhN_3$ gave the 1:1 adduct which was con-

verted in 50% yield to $PhN=NNHEt$.

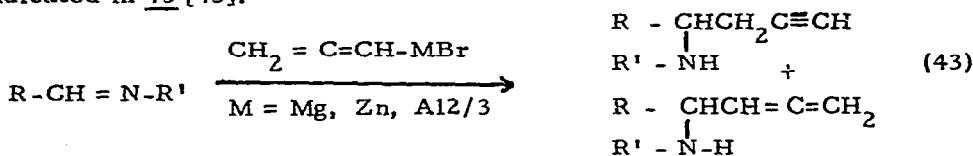Aldimines, $RCH=CNR'$ (R = Me, $Me_2CH$, $Me_2CHCH_2$, Ph; R' = Me, Bu,

$Me_2CH$, Ph) were treated with $CH_2=C=CHMBr$ and gave products as

indicated in 43 [45].

$$R-CH = N-R' \xrightarrow[\text{M = Mg, Zn, Al2/3}]{CH_2 = C=CH-MBr} \begin{array}{l} R - \underset{|}{C}HCH_2C\equiv CH \\ R' - NH \\ \\ R - \underset{|}{C}HCH=C=CH_2 \\ R' - N-H \end{array} + \quad (43)$$

It has also been shown [46] that either $Ph_3Al$ or $Ph_2Zn$ react with

$RNHPPh_2$ (R = 2, 3-$Me_2C_6H_3$; 4-$MeC_6H_4$, or 2-pyridyl) in $Et_2O$ to give

the corresponding $Ph_2AlNRPPh_2$ and $PhZnNRPPh_2$. The addition

compounds of $Me_3Al$ and $Me_3In$ with $(R_3P=N)_2SiR_2$ have been shown to

undergo the interesting rearrangement in 44 leading to cationic four



(44)
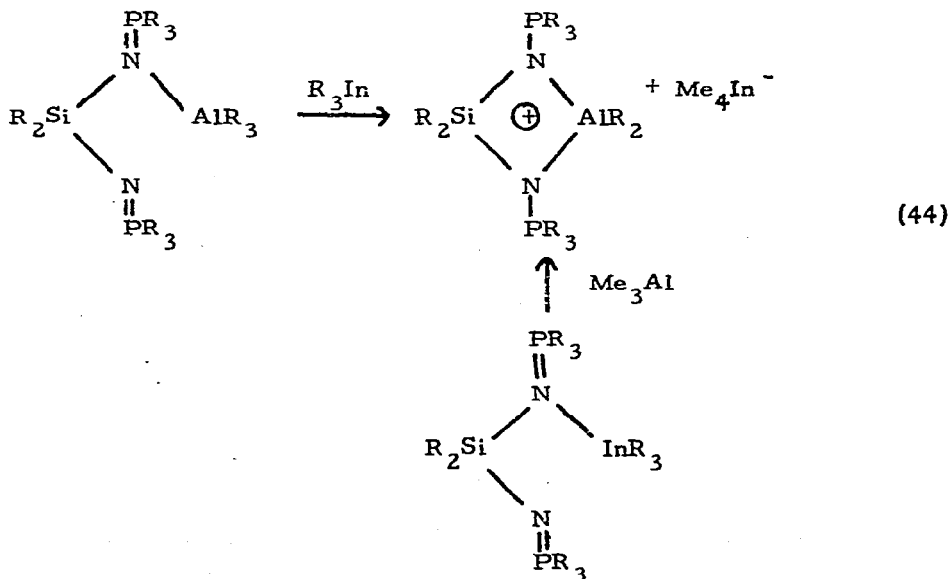
membered rings and $Me_4In^-$ [47]. The ionic species was characterized by its ir and nmr spectra.

Two other studies involving the reactions of aluminum adducts with nitrogen containing compounds have been reported. Buczkowski, et al. [48] reported ^{1}H nmr studies on the adducts of i-PrN(Me)Ph with $MeAlCl_2$ and $Me_2AlCl$ in which they observed that nitrogen inversion was slowed on adduct formation. They suggested that exchange processes involving the adducts were similar to those which have been reported in past years for Al, Ga, and In amine addition compounds.

Hirabayashi and co-workers [49] concluded from variable temperature nmr studies on the dimethylaluminum derivative of n-phenyl carbamate that a 1,3-shift occurred as illustrated in 45.



(45)
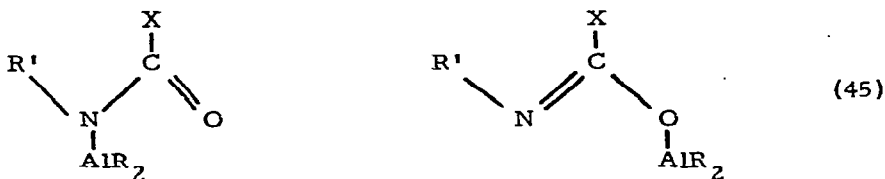
F. Formation and Reactions of Aluminum-Oxygen Bonded Compounds.

The reactions which involve attack of aluminum on oxygen derivatives, ketones, acids, etc., are of major importance because of synthetic value. In addition the alkoxides often formed play an important role in the formation of stereospecific catalysts.

A variety of reactions of aluminum alkyls with ketones and epoxides have been reported. Namy [50] has shown that reactions of $Me_3Al$ proceed via 46.

$$ + Me_3Al \xrightarrow{H_2O} \quad (46) $$
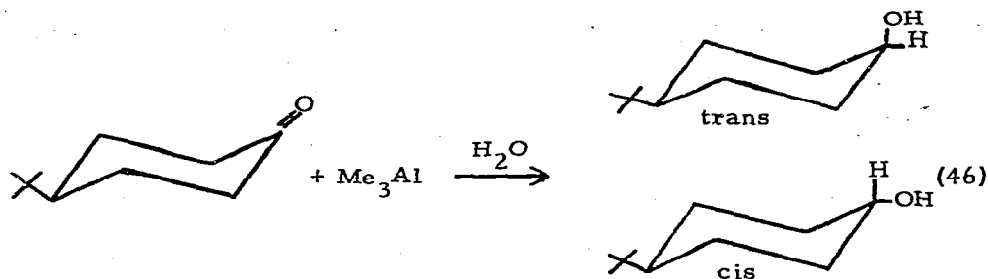
When the Al/ C=O ratio is 2/1, the cis compound is the major product;
when the ratio is 1/1, then the trans product predominates. The former
is thought to be formed via a six centered transition state while the
latter occurs through a four centered process. He has also investigated
the reaction of $Me_3Al$ and $Et_3Al$ with cis-1-phenyl-1, 2-epoxypropane
and observed retention of configuration [51]. This general
reaction with epoxides was discussed further in papers by Namy, et al.
[52, 53] and appears to be governed by solvent coordination and by the
metal alkyl used.

Barbot and Miginiac observed that reaction of the ketones
$R_2C = O$ (R = $Me_2CH$, Et, Pr, or Bu) with Mg or Al derivatives of
$EtCH = CHCH_2Br$ yielded primarily branched chain alcohols while the
Zn derivative gave linear alcohols upon hydrolysis [54].

It has also been shown [55] that the reactions indicated in 47 gave



$$ R'COOR'' + 2 HAl \begin{array}{c} R' \\ R \end{array} \xrightarrow{H_2O} R'CH_2OH \qquad (47) $$

$$ \xrightarrow{} R'CH_2O\overset{O}{\overset{\|}{C}}Me $$

$$ MeC-O-C-Me $$
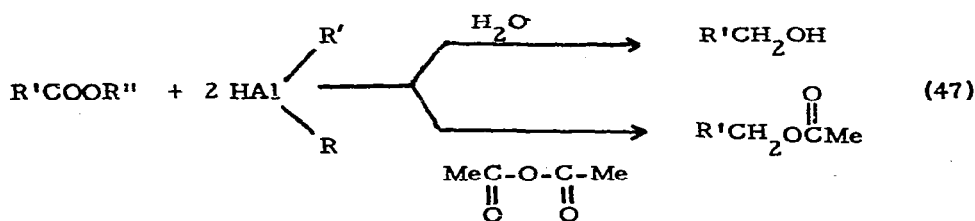
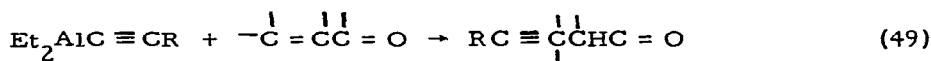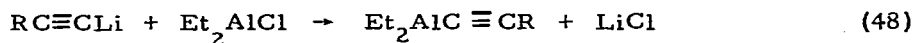higher yields of acetate then normally obtained by conventional hydrolysis

which yield the alcohol.

Ashby, et al. [56] have investigated the factors which determine

the stereoselectivity of $Li[AlH(O-t-Bu)_3]$ in the reduction of ketones. On

the basis of association data, the relative reactivities of $LiAlH(O-t-Bu)_3$

and of $HAl(O-t-Bu)_2$ and on the concentration dependence of the reduction

product, they concluded that the degree of aggregation of the reducing

species determines the stereoselectivity of this reagent.

Hooz and Layton [57] have described an interesting reaction sequence

given in 48 and 49 which provides a convenient route to $\gamma$ , δ-acetylenic

ketones which may then be used in subsequent synthetic procedures. This

$$RC\equiv CLi + Et_2AlCl \rightarrow Et_2AlC\equiv CR + LiCl \qquad (48)$$

$$Et_2AlC\equiv CR + {}^-\overset{|}{C}=\overset{|}{C}\overset{|}{C}=O \rightarrow RC\equiv \overset{|}{C}\overset{|}{C}HC=O \qquad (49)$$

route appears to be a fairly general one with the proposed path given in

XXVI. If the enone is transoid as in XXVII, then the geometry prohibits

the reaction and 1, 2-addition occurs.
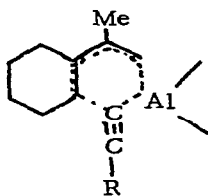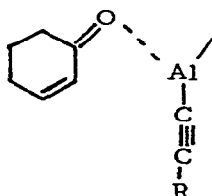


XXVI                          XXVII

It has been shown [58] that in the preparation of propargylcarbinols

and their diastereomers were different when the ketones,

RCH(OMe)COMe, were treated with $CH_2=C=CHMgBr$ or $(CH_2=C=CH)_2AlBr$.
The isomers indicated in XXIX were the major products when the
aluminum compound was used while XXVIII predominated with the
Grignard. The reaction of the aluminum compound was affected by



XXVIII

XXIX
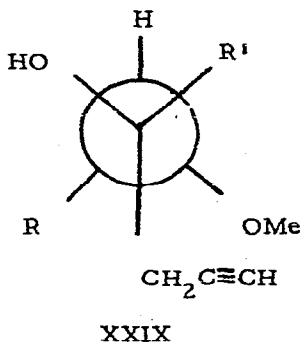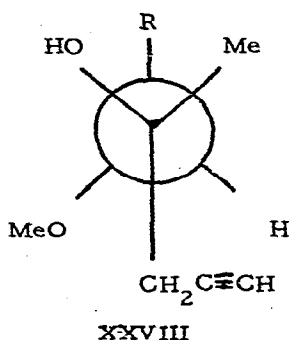
solvent (THF) and XXVIII was favored with decreased association (in-
creased solvation) of the aluminum compound.

Allen, et al. [59] have studied the reaction of $Et_3Al$ with methyl
methacrylate (MMA) and have shown that the stable complex indicated
in XXX was formed when the Al/MMA ratio was 1/1 or less. If



XXX
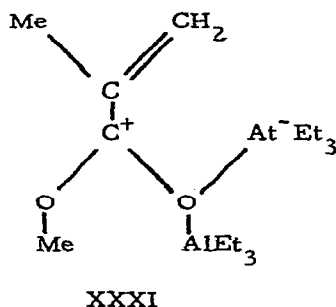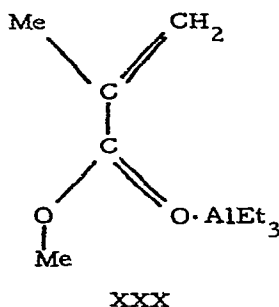
XXXI

excess $Et_3Al$ was present, complex XXXI was formed which proceeds to
addition products. The reaction was studied by following the nmr spectra
of reacting mixtures and by product analysis.

Dialkylaluminum β-diketonates and related compounds were prepared by Kroll, et al. [60] by reaction 50. It was reported that the

$$R_3Al + R' - \overset{\text{O}}{\underset{\|}{C}} - CH_2 - \overset{\text{O}}{\underset{\|}{C}} - R'' \longrightarrow R_2Al \overset{O-C}{\underset{O-C}{\overset{R'}{\diagup}}} \overset{R'}{\diagdown} CH + RH \qquad (50)$$
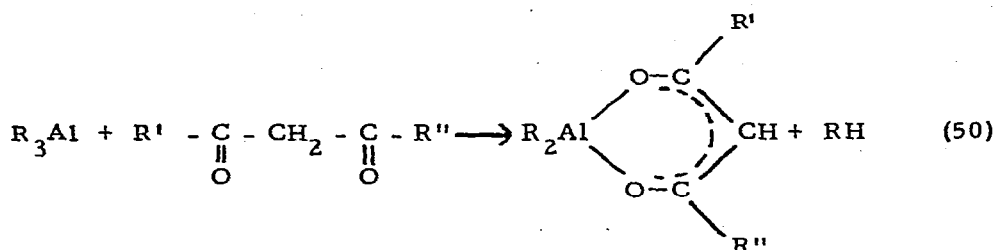
compounds were thermally stable and could be distilled, with the exception of the hexafluoroacetylacetonates which were unstable even at room temperature. The compounds were characterized by ^{1}H nmr spectroscopy and by their reactions. The methyl derivatives did not undergo rapid exchange with $Me_3Al \cdot$ p-dioxane or with $(Me_2AlOR)_n$. It was shown that the following reactions occurred:

$$Me_2Al \cdot acac + SnCl_4 \longrightarrow Me_2SnCl_2 + Cl_2Alacac \qquad (51)$$

$$2\ Me_2Alacac + SnCl_4 \longrightarrow Me_4Sn + 2\ Cl_2Alacac \qquad (52)$$
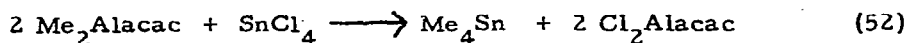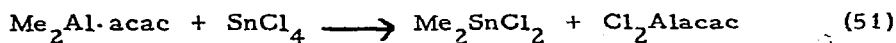
The dichloro derivatives were also prepared by exchange reactions. It was found that they, unlike the dialkyl derivatives, were relatively strong Lewis acids forming addition compounds.

Aluminum compounds containing alkoxy groups are of continuing interest in the field of organoaluminum chemistry, and a number of papers related to this topic have appeared. The phenyl derivatives have been prepared by addition of AcOH in ether to $Ph_3Al$ also in ether [61]. The product $Ph_2AlOAc$, or $PhAl(OAc)_2$ was dependent on the ratio of reactants. The same general procedure was also used to

prepare $Ph_2AlOBz$, $PhAl(OBz)_2$, $Ph_2Al(O_2CCH_2Cl)$, and $PhAl(O_2CCH_2Cl)_2$.

Starowieyski, et al. [62] have studied the formation, molecular

weight, and spectroscopic properties of mixed phenoxyaluminum

derivatives. They prepared the derivatives as indicated in 53. Their

$$Me_nAlCl_{3-n} + PhOH \rightarrow Me_{n-1}(PhO)AlCl_{3-n} + MeH \qquad (53)$$
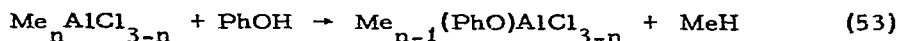
molecular weight studies indicated that the most stable form is trimeric

for all species, however, they did prepare material which contains

significant amounts of dimer by distillation. This material reverted to

trimer with time. On the basis of their ir and nmr studies, they claimed

that a variety of bridged compounds such as XXXII and XXXIII exist in
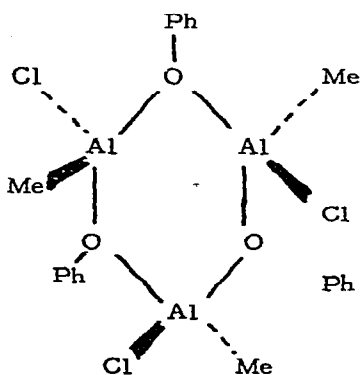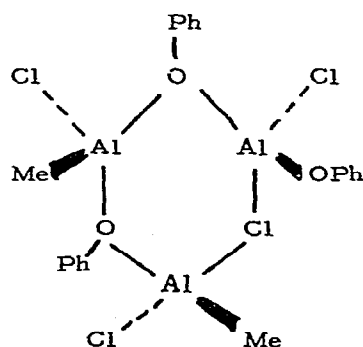


XXXII                                              XXXIII

the mixture.

Oliver and Worral [63] have studied the isopropoxides of Al, Ga,

and In. In this work they observed that the aluminum derivatives

formed an adduct with pyridine and proposed that this had either

structure XXIV or XXXV.

XXXIV                                    XXXV
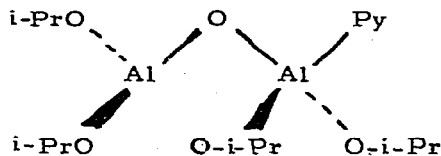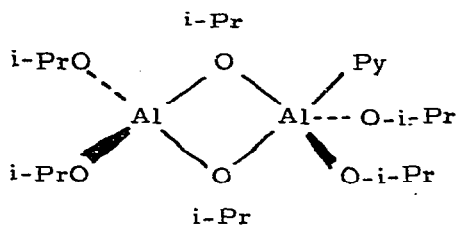
The Raman and ir spectra of aluminum isopropoxide were investigated by Fieggen and Gerding [64]. Their studies favored the tetrameric structure earlier proposed by Bradley for the higher melting form in which a central aluminum is six coordinate. They suggested cyclic and/or chain forms for the lower melting trimeric species. A series of chloroalkoxides have been prepared by the alcohol interchange method indicated in $\underline{54}$ [65]. The molecular weight and, therefore, the degree of aggregation of the chlorine substituted derivatives were reported to

$$[(i\text{-}PrO)_3Al]_n + 2\ HOCH_2CCl_3 \rightarrow HO\cdot i\text{-}Pr + [i\text{-}PrOAl(OCH_2CCl_3)_2]\quad (54)$$
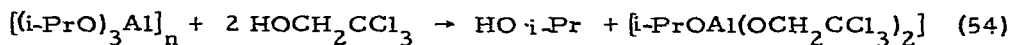
be less than for the simple alkoxides. Thus $Al(OCH_2CH_2Cl)_3$ and $Al(O\text{-}i\text{-}Pr)(OCH_2CCl_3)_2$ were dimeric while $i\text{-}PrOAl(OCH_2CH_2Cl)_2$ and $i\text{-}PrOAl(OCH_2CHCl_2)_2$ were trimeric. It was suggested that this was due to the increased electron withdrawing power of the chlorine derivatives. It was also suggested that the ability of these species to form adducts with pyridine, ethylenediamine, benzylamine, etc., was a result of this effect. The pyridine adduct $(Cl_3CCH_2O)_3Al\cdot Py$, was monomeric in benzene unlike the isopropoxide previously discussed.

A brief report on the conductance of sodium tetraethoxyaluminate

has also appeared which indicates that this material behaves as a weak

electrolyte in ethanol solution. It is monomeric in this media [66].

Related reactions include the preparation $(EtO)_2AlOOCH(OH)R$ from

the reaction of $EtAl(OEt)_2$ with $RCH(OH)(OOH)$ [67]. The product elim-

inates EtOH readily forming $[-Al(OEt)OOCHRO-]_n$ . This further

decomposes at room temperature yielding a complex mixture. $EtAl(OEt)_2$

also reacted with t-BuOOCH(OH)Me to give $t-BuOOCHMeOAl(OEt)_2$

which decomposed to t-BuOH and $(EtO)_2AlOAc$.

Aluminum hexafluoroisopropoxide and a series of Group IV

derivatives have been prepared by reactions similar to 55 [68]. The

$$AlCl_3 \; + \; 3 \, NaOCH(CF_3)_2 \; \rightarrow \; 3 \, NaCl \; + \; Al[OCH(CF_3)_2]_3 \qquad (55)$$
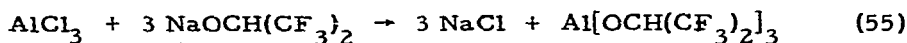
resulting compounds have been characterized by $^1H$ and $^{19}F$ nmr, by

ir and by mass spectral studies.


G. Formation and Reactions of S, Se, and P Derivatives.

Lalancette, et al. [69] studied the preparation of $(Me_2CHS)_2AlMe$

and $(t-BuS)_2AlMe$ and the reactions of these materials and of $(MeS)_2AlMe$

with ketones and aldehydes. The preparations were carried out by

reaction of the thiol with $Me_6Al_2$ at reflux temperatures yielding the

product directly. The methyl- and isopropylthiols were highly poly-

merized and were insoluble in non-distructive solvents. The

$(t-BuS)_2AlMe$, however, was soluble in benzene and other non-polar

solvents. The reaction with ketones is illustrated in 56. If a sterically

hindered ketone was reacted with a ratio of two carbonyl groups per

aluminum the normal product was formed, but if the ratio reached

two aluminum atoms per carbonyl, then reaction 57 prevailed.  With

aldehydes the predominate reaction is given in 58.

$$
\underset{\substack{\|\\O}}{MeC}\ Me\ +\ (MeS)_2AlMe\ \rightarrow\ \underset{Me}{\overset{Me}{\diagdown}}C=CH\underset{\substack{\|\\O}}{C}Me
$$

(56)

+

$$
\underset{Me}{\overset{Me}{\diagdown}}C-CH_2\underset{\substack{\|\\O}}{C}Me \\
\phantom{xxxxx}SMe
$$

$$
2\ (MeS)_2AlMe\ +\ t\text{-}Bu\text{-}\underset{\substack{\|\\O}}{C}Me\ \rightarrow\ t\text{-}Bu\underset{Me}{\overset{Me}{C}}=CH\underset{\substack{\|\\O}}{C}\text{-}t\text{-}Bu\ +
$$

$$
t\text{-}BuC=CHC=CH\underset{\substack{\|\\Me}}{C}\text{-}t\text{-}Bu
$$

(57)

$$
RCH_2C\underset{H}{\overset{O}{\diagup}}\ +\ (MeS)_2AlMe\ \rightarrow\ RCH_2C\underset{\diagdown SMe}{\overset{\diagup SMe}{-}}H\ +\ RCH=C\underset{\diagdown SMe}{\overset{\diagup H}{}}
$$

(58)
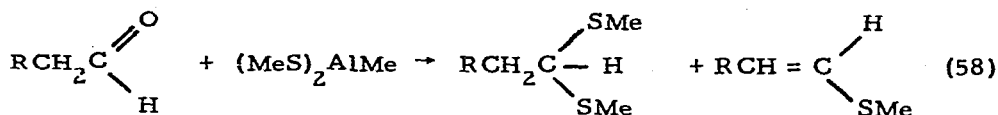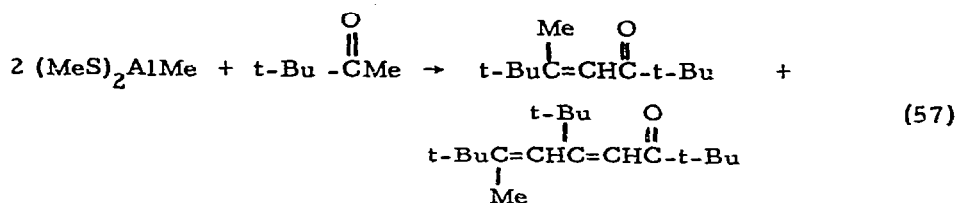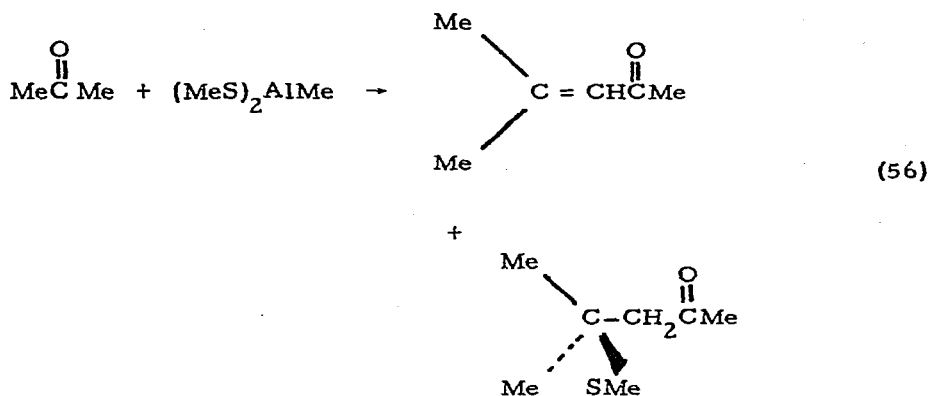
Other products were also observed dependent upon the ratio of reactants

and the exact nature of the aldehyde.  A discussion of the mechanisms

of these reactions was presented.

Vyazankin, et al. [69a] studied the reaction between Et$_3$Al and

Et$_3$SiSH in hexane.  The products were the colorless crystalline

materials $[Et_3SiSAlEt_2]_2$, $[(Et_3SiS)_2AlEt]_{1.4}$, or $(Et_3SiSAlS)_x$ formed

when $Et_3Al$ was reacted with one, two, or three mole of $Et_3SiSH$,

respectively. The first two complexes were found to be thermally

unstable and disproportionated into $\{Et\cdot AlS\}_x$, $(Et_3Si)_2S$ and $Et_3Al$

and into $(Et\cdot AlS)_x$ and $(Et_3Si)_2S$, respectively.

Imaeda, et al. [70] have investigated the reactions of bis(diethyl-

aluminum)sulfide with a variety of carbonyl compounds. The general

reaction observed is indicated in 59 in which an initial 1/1 adduct is



(59)
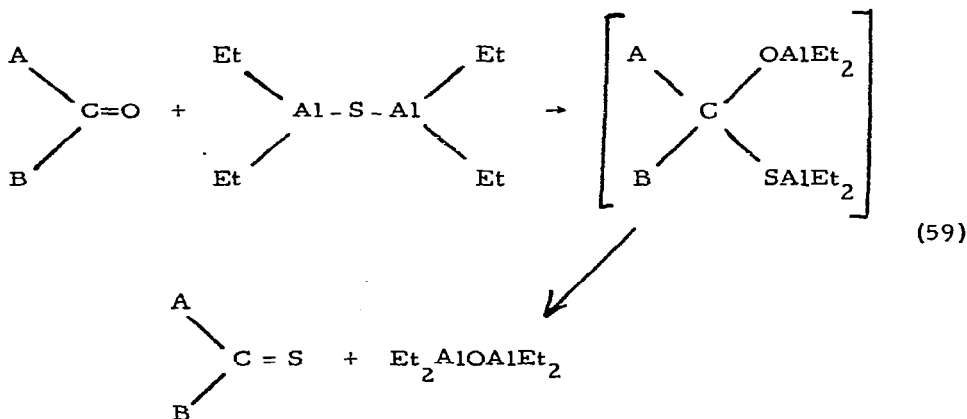
formed which is then converted to the corresponding thiocarbonyl

derivative. Several specific reactions were mentioned as indicated

in 60, 61, 62, and 63.



(60)

$$(61)$$



$$(62)$$



$$(63)$$
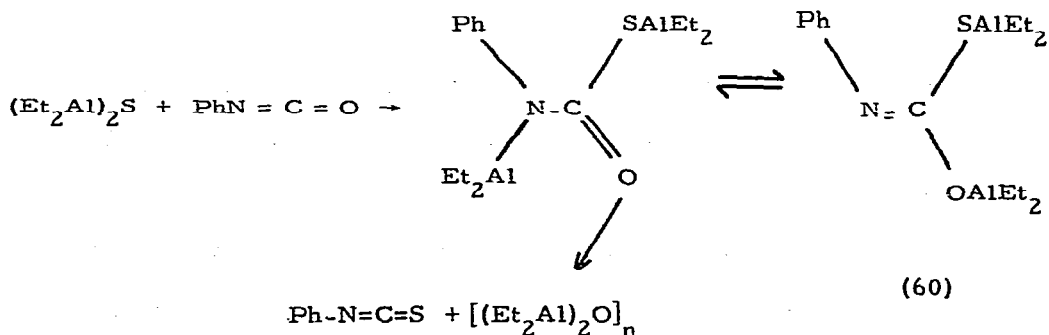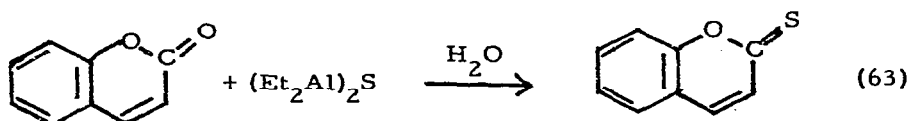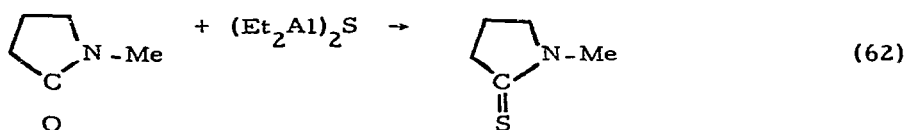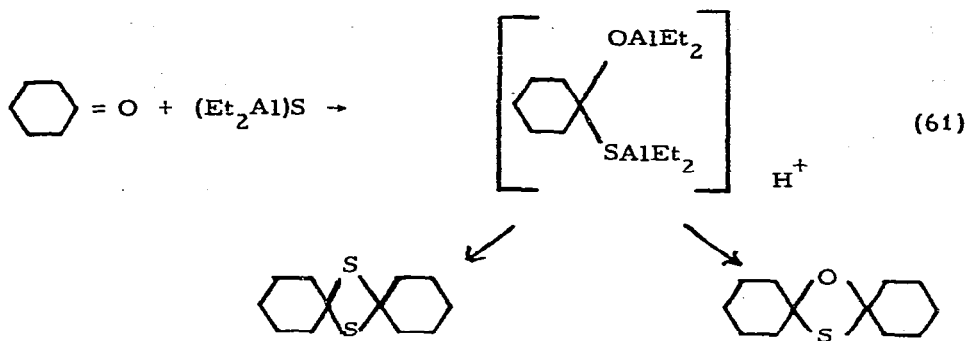
Other reactions were also discussed and it was suggested that the

driving force of the reaction depended not only on the formation of the

more stable Al-O-Al bonds, but also on the stability of the thiocarbonyl

compound formed which followed the order:
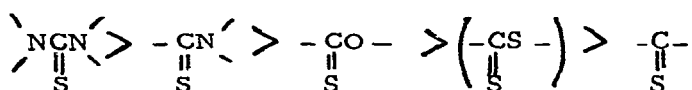


Weidlein [71] has investigated the reaction of gaseous COS with the

trialkyls of Al, Ga, and In, and has shown that one metal carbon bond is

cleaved. The aluminum derivative has been shown, by molecular weight

measurements in benzene, to be dimeric.   Infrared, Raman, and nmr

spectral measurements were made and on the basis of these data a

puckered eight membered ring structures were proposed as shown in

XXXVI and XXXVII.   The relative merits of each were discussed.
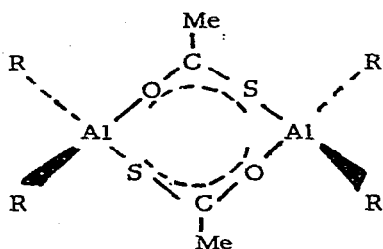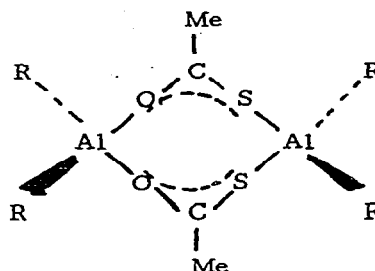


XXXVI                                                           XXXVII

He [72] also investigated the reactions of $R_3M$ (M = Al, Ga, In, R =

Me, Et) with $MeCS_2H$.   In all cases only one alkyl group was replaced.

The gallium and indium compounds were monomeric while the aluminum

was a dimeric species.   The structure in XXXVIII was proposed on
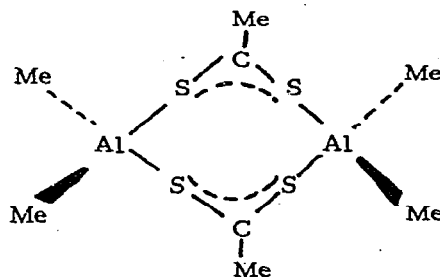


XXXVIII

the basis of ir spectral studies.

The influence of the para substituent on the reaction between aryl

sulfonic acid chlorides and $RAlX_2$ as indicated in 64 and 65 has been

$$ArSO_2Cl + EtAlX_2 \rightarrow ArSO_2AlX_2 + EtCl \qquad (64)$$

$$ArSO_2AlX_2 + RAlY_2 \rightarrow ArSO_2R + [X_2AlOAlY] \qquad (65)$$

$$(X = Et, \ Cl; \ Y = R, \ Cl; \ R = nC_4H_9, \ nC_6H_{13}, \ n\text{-}C_8H_{17})$$
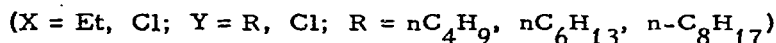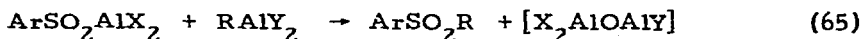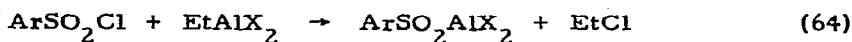
studied [73]. It was shown that p-chloro, p-bromo- and p-methoxyl-benzenesulfonyl chlorides gave poor yields of the sulfoxides and the aluminum sesquichloride did not give any product. p-t-Butyl and p-alkyl substituted derivatives gave good yields of the aryl-alkyl sulfoxides.

The preparation and reactions of several anionic derivatives of aluminum have been reported. Zakharkin, et al. [74] have studied the reaction of $NaAlEt_4$ and its hexyl-, heptyl-, and octyl- analogs and $LiAl(C_{10}H_{21})_4$ with $CO_2$ under moderate pressures. If 4-6 moles of $CO_2$ were used with 4-17 hour reaction time at 50-220° derivatives of the general type $MAl(O_2CR)_4$ were formed. These gave $RCO_2H$ on hydrolysis in high yield.

It has also been shown [75] that reactions of onium salts with $NaAlEt_4$, $Et_3Al$, and $NaAlEt_3H$ yield products such as $Et_4PAlEt_4$. Similar products were formed with $Ph_3MePI$, $Me_4AsI$, $Et_4AsI$, $Me_4SbI$, $Et_4SbI$, and $Me_4NI$.

The kinetics of the oxidation of $Et_2AlCl$, $Et_3Al$ and $NaAlEt_4$ in toluene were studied [76]. Similar data for the heptyl analogs were also obtained. In the latter case, formation of hydrocarbons was observed after 40-60% oxidation had occurred. The oxidation of $MAlR_4$ compounds proceeded through an $MAlR_3O_2R$ intermediate and gave yields of

primary alcohols up to 70% along with a variety of side products. The

first two Al-C bond reacted most readily and the side products were

formed primarily toward the end of the reaction. The reactivity with

oxygen rose in the series $NaAlR_4$, $R_3Al$ and $R_2AlCl$. Fritz and Schaefer

[77] prepared $NaAl(HPMe)_4$ and $NaAl(PH_2)_4$ by reaction of NaPHMe

and $NaPH_2$ with $AlCl_3$ in diglyme. These materials were then used to

prepare a series of compounds containing Si-P bonds by reactions such

as 66. The compounds were characterized by $^1H$ and $^{31}P$ nmr

$$4 R_3SiBr + NaAl(Ph_2)_4 \rightarrow 4 R_3SiPH_2 + NaAlBr_4 \qquad (66)$$
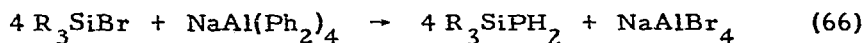
H. Cleavage and Exchange Reactions of Alkyl- and Alkylaluminum
   Halides.

Zenina, et al. [78] have reported formation of $Ph_2AlCl$, $Ph_2AlBr$,

$PhAlCl_2$ and $PhAlBr_2$ by exchange of $Ph_3Al$ with $AlX_3$ in benzene

solution. The chlorides were also prepared from $Ph_2AlOAc$ and

$PhAl(OAc)_2$ by reaction with $Me_2AlCl$. In all cases the appropriate

ratios of compounds were used.

Batalov [79] has studied the radical exchange between $Et_3Al$

and EtBr ($100^o$) in the presence of $SnCl_2$, $CoCl_2$, $FeCl_3$, $CuCl_2$, and

$BiCl_3$. The reaction was first order with respect to $Et_3Al$, and was

said to proceed through a four centered transition state involving $Et_3Al$,

EtBr, and the metal halide in equimolar amounts. The reaction was

inhibited by ether.

Alberola and Ferandez [80] have studied reactions between $Et_3Al$

in benzene with $MeCHClCH_2Cl$ which gave PrPh, $PhCH_2CHMePh$, and

$Ph_2CHEt$. $Me_2CClCH_2Cl$ under the same conditions yielded i-BuPh

and $Me_2C=CHPh$. PhCl, $p-MeC_6H_4Cl$, $1-C_{10}H_7Cl$, 9-bromophenanthrene,

and 9, 10-dibromoanthracene were unreactive toward $Et_3Al$-benzene but

other aromatic halides such as $p-MeC_6H_4CHClPh$ gave a variety of

products.

Nagata, et al. [81] in their studies on the synthesis of B-nor-$\Delta^4$-3-

ketosteroids from $\Delta^5$-3-β-hydroxysteroids, found that the hydrocyanation

of the enones with $Et_2AlCN$ was only successful for the 5-β vinyl

derivatives yielding the corresponding 5-keto-5-β-cyano derivatives.

Buchler, et al. [82] have investigated the formation of porphin com-

plexes of aluminum. The compounds were prepared by the reaction of

$R_3Al$ or $R_2AlH$ with octaethylporphin or by the displacement of $Cu^{+2}$

from the complex. The resulting product is indicated in XXXIX.

The compounds were characterized by nmr, ir, uv and mass spectral

measurements.
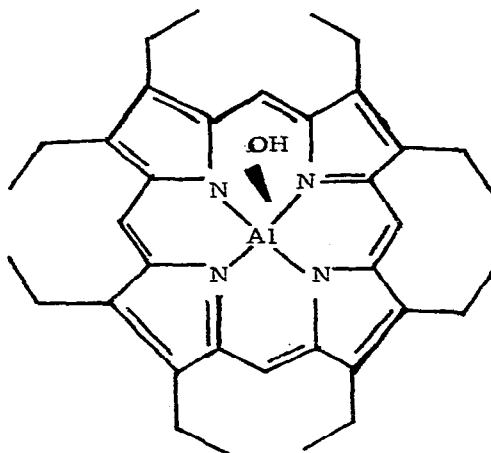


XXXIX

Young, et al. [83] have investigated the preparation and properties

of $1, 2-B_9C_2H_{12}MR_2$, $1, 2-B_9C_2H_{11}MR$ and $1, 7-B_9C_2H_{11}AlEt$ (M = Al,

R = Me, Et, M = Ga, R = Et). The structure of the $MR_2$ series has been

cited earlier as determined by x-ray crystolographing. These derivatives

appear to undergo a rapid tautomeric process and it has been proposed that

this involves some type of rotational or dissociation process which involve

exchange of position as indicated XL.



XL
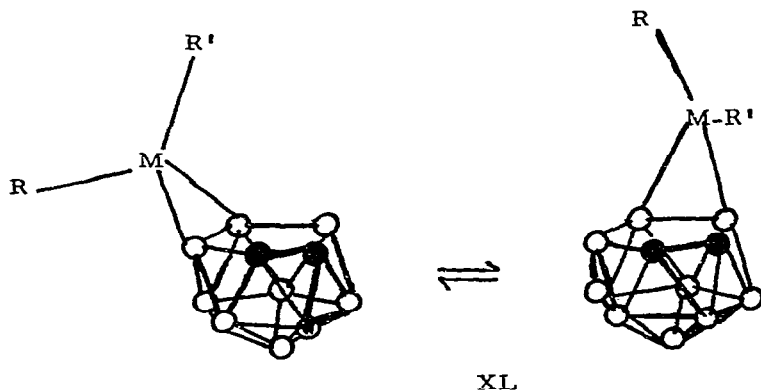
The process was shown to have a free energy of activation

$\Delta F^{\neq}$ = 10.6 ± 0.5 kcal/mole both from [11]B and ^{1}H nmr studies. All of

the compounds were fully characterized by [11]B and ^{1}H nmr, and ir spec-

troscopy and by chemical reactions.

The Si-Al bonded species, $EtAl(SiPh_3)_2 \cdot 2THF$, was propared by

Razuraev, et al. [83a] from the reaction of $Et_2AlBr$ with $Ph_3SiLi$. The

initially formed product underwent immediate disproportionation to give

the product which could only be isolated as the THF complex. The

compound was very sensitive to oxygen and gave $Al(OH)_3$, THF,

$C_2H_6$, $Br^-$ and $Ph_3SiH$ on hydrolysis. It also reacted with HOAc to give

$Ph_3SiH$ and aluminum acetate. Reaction of the compound with oxygen

in an organic solvent gave $Ph_3SiOH$, EtOH and $Al(OH)_3$ (on hydrolysis).

I.  Formation and Reactions of Hydridic Compounds.

A major area of organoaluminum chemistry deals with the
derivatives which contain metal -hydrogen bonds.  In this section of the
review only some aspects of this topic will be covered,  primarily
those dealing with formation and study of compounds containing new
Al-C bonds.  The use of reagents such as $LiAlH_4$ as a reducing agent
in organic synthesis will in general not be covered.  There will be some
additional information on the structure of the hydridic materials and
on formation of compounds with potential use as synthetic reagents.

Greenwood and Thomas [84] have investigated the preparation and
thermochemistry of 1/1 and 1/2 $AlH_3$-quinuclidine complexes and of 1/1
complexes of $AlH_3$ with 1, 4-dimethylpiperazine and NNN'N'-tetramethyl-
o-phenyl-enediamine.  They reported the heats of formation of these
compounds and discussed their results.

In another study [85] it has been shown that the loss of reducing
power of $LiAlH_4$ solutions in ether depends on both the degree of
aggregation and on solvolysis of the hydride.  The former dominates at
higher concentrations and at lower temperature,  whereas the latter
controls the rate of deactivation of dilute solution.

Srivastava and Ashby [86] have examined the reaction of $Et_2Mg$
and $AlH_3$ in THF.  On the basis of these studies they have proposed the
following sequence of reactions:

$$5\,Et_2Mg + 2\,AlH_3 \rightarrow 2\,EtMgAlEt_4 + 3\,MgH_2 \qquad (67)$$

$$2\,Et_2Mg + AlH_3 \rightarrow HMgAlEt_4 + MgH_2 \qquad (68)$$

$$3 \text{ Et}_2\text{Mg} + 2 \text{ AlH}_3 \rightarrow 2 \text{ HMgAlEt}_3\text{H} + \text{MgH}_2 \tag{69}$$

$$\text{Et}_2\text{Mg} + \text{AlH}_3 \rightarrow \text{HMgAlEt}_2\text{H}_2 \tag{70}$$

$$2 \text{ Et}_2\text{Mg} + 3 \text{ AlH}_3 \rightarrow 2 \text{ HMgAlEtH}_3 + \text{Et}_2\text{AlH} \tag{71}$$

$$2 \text{ Et}_2\text{Mg} + 4 \text{ AlH}_3 \rightarrow \text{HMgAlEtH}_3 + \text{Mg(AlH}_4)_2 + \text{Et}_3\text{Al} \tag{72}$$

$$3 \text{ Et}_2\text{Mg} + 8 \text{ AlH}_3 \rightarrow 3 \text{ Mg(AlH}_4)_2 + 2\text{Et}_3\text{Al} \tag{73}$$

$$\text{Et}_2\text{Mg} + 3 \text{ AlH}_3 \rightarrow \text{Mg(AlH}_4)_2 + \text{Et}_2\text{AlH} \tag{74}$$

$$\text{Et}_2\text{Mg} + 4 \text{ AlH}_3 \rightarrow \text{Mg(AlH}_4)_2 + 2\text{EtAlH}_2 \tag{75}$$
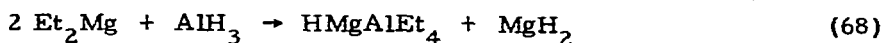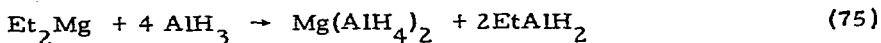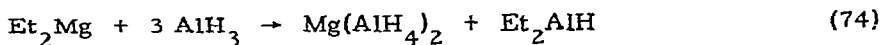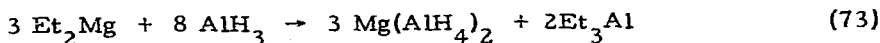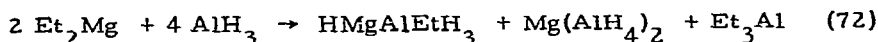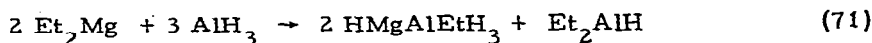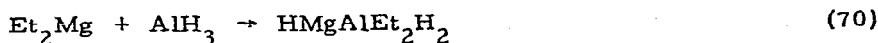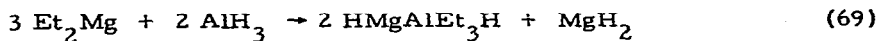
The reaction sequence is complex and leads to a variety of aluminum derivatives. Many of these have been followed by their ir spectra and the products characterized by elemental analysis. This placed the proposed reaction sequence on firm ground. The evidence was discussed in detail and in addition to the reactions given a number of possible equilibria were considered which involve many of these species.

Several papers have appeared dealing with hydroalumination of multiple bonds. Zweifel, et al [87, 88] have provided two very interesting results from their studies on the hydroalumination of alkynes. In the first of these papers [87] they showed that addition of diisobutylaluminium hydride to hexyne occurred via reaction 76. In the presence of excess $R_2\text{AlH}$ the reaction proceed as indicated in 77 with formation of a mixed bridged species. This derivative could further react or be equilibrated as noted.

$$(R_2AlH)_3 + 3\ HC \equiv CBu \rightarrow 3/2 \left( \begin{array}{c} H\ \alpha \\ \diagdown \\ R_2Al \end{array} C = C \begin{array}{c} Bu \\ \diagup \\ H\ \beta \end{array} \right) \tag{76}$$

$$4/3\ (R_2AlH)_3 + 3\ HC \equiv CBu \rightarrow 2\ R_2AlH \cdot R_2AlCH = CHBu$$

$$\tag{77}$$

$$\underset{(R_2AlH)_3}{\overset{HC \equiv CBu}{\rightleftharpoons}} \qquad (R_2AlCH = CHBu)_2$$
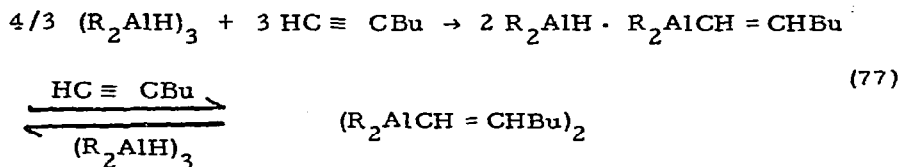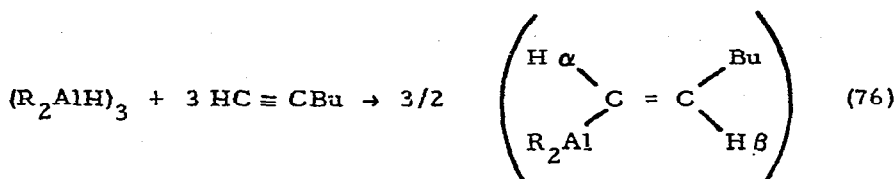
The structures proposed for the two species of interest are indicated

in XLI and XLII. The equilibrium constant strongly favors formation

of the mixed bridged derivative.



XLI                          XLII
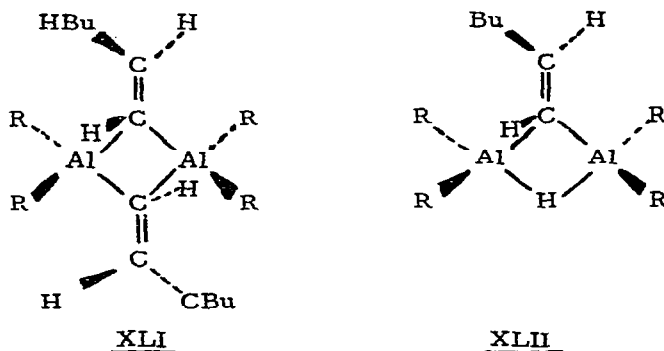
Further studies on the vinyl aluminum compounds produced

in these reactions indicated a carbene may be added to the double

bond producing cyclopopyaluminum derivatives as indicated in 78.



$$\tag{78}$$

R = Bu, t-Bu, ⬡ , Ph
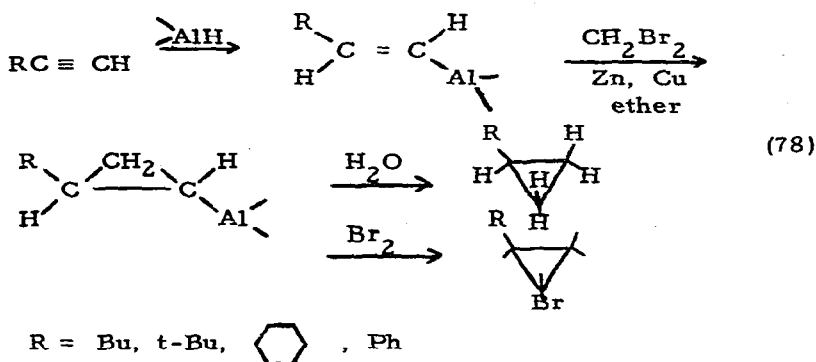
This sequence of reactions making cyclopropylaluminum derivatives

and trans substituted cyclopropanes available is of signifiance since they

provide a good route to these species. The unique structure of the

cyclopropylaluminum species already cited [7] clearly adds to the

significance of this work.

Eisch and Rhee [89] have investigated the kinetics of the hydro -

alumination of 4-octyne and have proposed a mechanism based on

their work. This is shown in 79 with a pre-equilibrium of monomeric

$(i-Bu)_2AlH$ followed by a rate controlling addition to the triple bond.



$$[(i-Bu)_2AlH]_3 \rightleftharpoons 3 \ (i-Bu)_2AlH$$

(79)
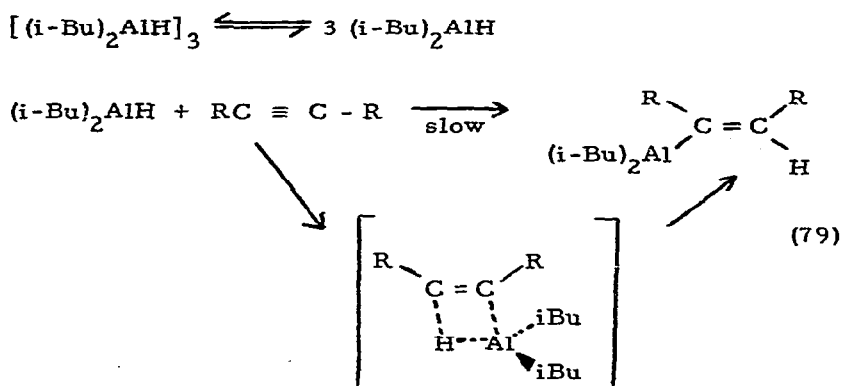
The dueterium isotope effect observed is in accord with initial

electrophilic attack of the aluminum on the $\pi$ -bond of the alkyne.

Zweifel, et al.[90] have shown that hydroalumination of hex-1-en-

5-yne in diethylether or triethylamine affords 2, $\alpha$ -bis-aluminomethyl-

cyclopentane  derivatives as proposed in 80 and 2, $\alpha$ -bis-alumino-

3-methyl-cyclopentene derivatives as proposed in 81 respectively.

(80)



(81)
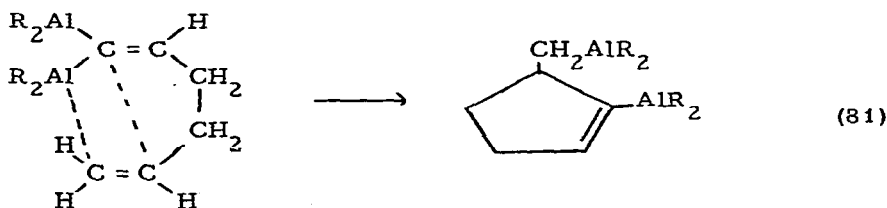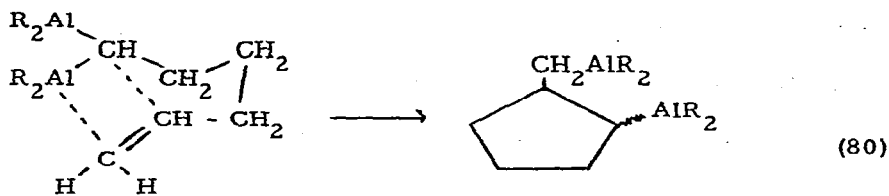
Kovar and Ashby [91] have reported on the direct formation, structure and stabilities of aminoalanes. The general reaction is given in **82.** The mono-(amino)alane does not appear to be produced

$$2 H_2 + 2 Al + 4 R_2NH \rightarrow 2 (R_2H)_2AlH + H_2 \qquad (82)$$
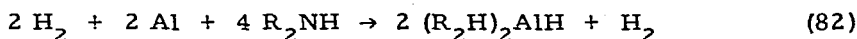
and was not formed by reaction of $H_2$, Al and the bis(amino)alane. The amines used successfully included $Me_2NH$, $Et_2NH$, piperidine and pyrolidine. Neither $(i-Pr)_2NH$ or $Ph_2NH$ reacted under the conditions used suggesting that the basisity of the amine played an important roll in the reaction. The products were characterized by ir, nmr, pyrolysis and thermogravemetric studies.

In the subsequent paper [92] on the synthesis of aminoboranes, it was proposed that reaction **82** was the initial step in the formation of aminoboranes followed by **83.** This was verified and the general reaction of the bis(amino)alanes with borate esters was discussed.

$$2 B(OPh)_3 + HAl(NEt_3)_2 \rightarrow HB(OPh)NEt_2 +$$

$$B(OPh)_2NEt_2 + Al(OPh)_3 \qquad (83)$$
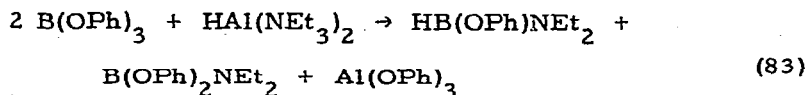
Synthesis of N-trialkylborazines have been reported [93] by essentially the same type of the reaction as indicated in 84. The latter reaction was carried out with a number of primary amines.

$$B(OPh)_3 + Al + RNH_2 \xrightarrow[\Delta \text{ pressure}]{H_2} 1/3 \text{ (HBNR)} + Al(OPh)_3$$

$$(84)$$
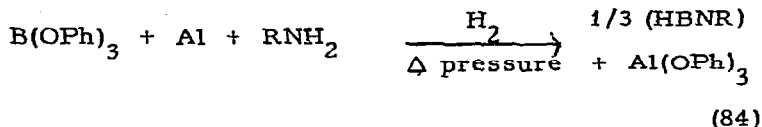
Beach and Ashby [94] have presented an extensive study on the reactions of the $LiAlH_4$ with secondary amines. The reaction of a 4/1 ratio of $Et_2NH/LiAlH_4$ over night (ether solution) is depicted by 85. The fourth hydride was only removed in this reaction by

$$LiAlH_4 + 3 Et_2NH \rightarrow LiAlH(NEt_2)_3 + 3 H_2 \qquad (85)$$
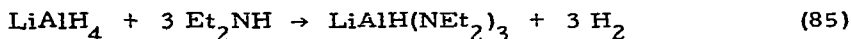
refluxing for two days, 86. Some of the intermediate reaction steps,

$$LiAlH_4 + 4 Et_2NH \rightarrow LiAl(NEt_2)_4 + 4 H_2 \qquad (86)$$
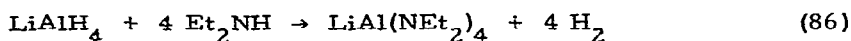
which were supported by independent studies are indicated in 87 to 90. This sequence also accounts for the formation of $Li_3AlH_6$ and equation 91 represents the overall stoichiometry of the formation of this compound. Possible structures for the second compound resulting from this sequence, $Al_2H_6NEt_2$, were discussed.

$$2 LiAlH_4 + 2 Et_2NH \rightarrow 2 LiH + 2 Et_2NH \cdot AlH_3 \qquad (87)$$

$$2 LiH + LiAlH_4 \rightarrow Li_3AlH_6 \qquad (88)$$

$$2 Et_2NH \cdot AlH_3 \rightarrow 2 Et_2NAlH_2 + 2 H_2 \qquad (89)$$

$$2 Et_2NAlH_2 + LiAlH_4 \rightarrow 2 LiAl_2H_6NEt_2 \qquad (90)$$

$$5 LiAlH_4 + 2 Et_2NH \rightarrow Li_3AlH_6 + 2 Al_2H_6NEt_2 + 2 H_2 \qquad (91)$$
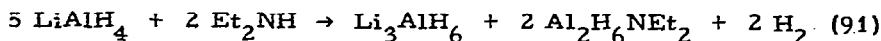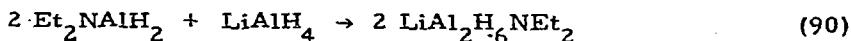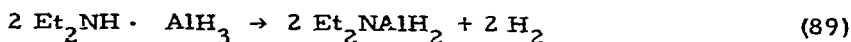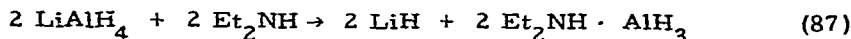
An interesting sequence of reactions has been observed in which

a stable complex indicated in   92   was formed [95]. This complex,

$$3 R_2BOMe + AlH_3 \rightarrow [(MeO)_3Al \cdot 3 R_2BH] \tag{92}$$
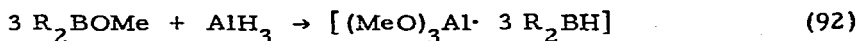
which contains an aluminum alkoxide complex serves as a hydro-

genation agent as seen in 93.   This reaction should prove to be very

$$(MeO)_3Al \cdot 3 R_2BH + 3 \text{ olefin} \rightarrow 3 R_2BR' + (MeO)_3Al \tag{93}$$
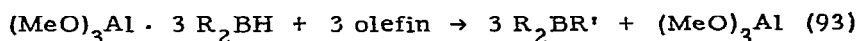
useful as a means of hydroboration.  The complex may also be

broken up by addition of strong bases such as pyridine via reaction 94.

$$(MeO)_3Al \cdot 3 R_2BH + 3 Py \rightarrow (MeO)_3Al + 3 R_2HBPy \tag{94}$$
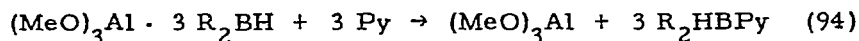
<u>Aluminum - Transition Metal Derivatives</u>

The study of aluminum transition metal complexes holds a

special position in organoaluminum chemistry.  Derivatives of this

type are interesting structually, in terms of their bonding and cer-

tainly because of their ability to serve as catalysts.  A number of

reports on new species and on the structure and properties of these

have appeared in the literature.  Petersen et al [96] have prepared

a compound containing aluminum and $Hg[W(CO)_3\pi Cp]_2$ by reaction 95.

$$Hg[W(CO)_3\pi Cp]_2 \xrightarrow[\text{Al}]{\text{THF}} Al[W(CO)_3\pi Cp]_3 \cdot 3 \text{ THF} \tag{95}$$
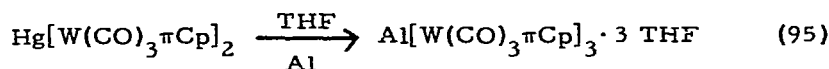
Several reactions of this derivative are indicated in 96.  The compound

$$
\begin{array}{c}
Al[W(CO)_3\pi Cp]_3 \cdot THF \xrightarrow{3H_2O} 3 \ HW(CO)_3\pi Cp \\
\Big\downarrow Bu_4N^+ \ Br^- \qquad \searrow (CF_3CO)_2O \\
Bu_4N^+W(CO)_3\pi Cp^- \qquad \qquad CF_3COW(CO)_3\pi Cp
\end{array}
\tag{96}
$$
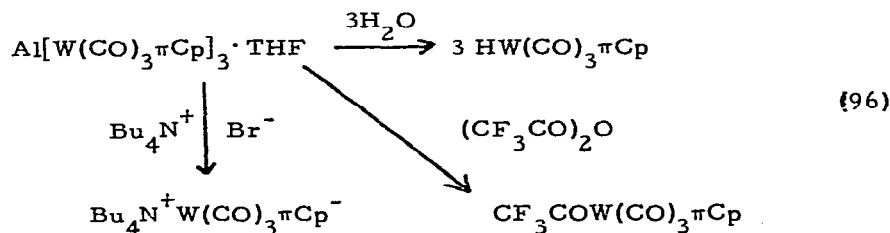
was also characterized by ir and by an x-ray crystal structure

determination. A partial structure obtained from this is depicted in

XLIII, which shows the coordination around the aluminum center.
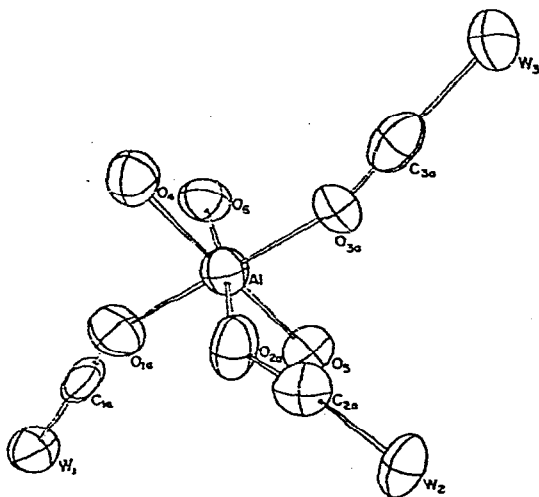


XLIII

A Partial Structure for $Al[W(CO)_3C_4H_5]_3 \cdot 3$ THF

After Petersen, et al., ref. 96.

Schrieke and Smith [97] have prepared another tungsten con-

taining compound via reaction 97. They characterized the product

$$R_2AlH + HW(CO)_3\pi\text{-Cp} \rightarrow R_2AlW(CO)_3\pi\text{-Cp} + H_2 \qquad (97)$$
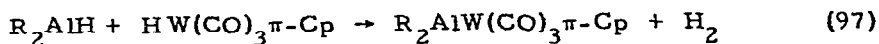
R = Me, Et

by ir, nmr and mass spectral studies and on the basis of these

preferred one of the structures indicated in XLIV and XLV which

$$\pi\text{-Co(CO)}_3\text{W} - \text{AlR}_2 \qquad\qquad \pi\text{-Cp(CO)}_2\text{W} - \text{CO} - \text{AlR}$$
$$\big| \qquad \big| \qquad\qquad\qquad\qquad\qquad \big|$$
$$\text{R}_2\text{Al} - \text{W(CO)}_3\pi\text{-Cp} \qquad\qquad \text{R}_2\text{Al} - \text{OC-W(CO)}_2\pi\text{-Cp}$$
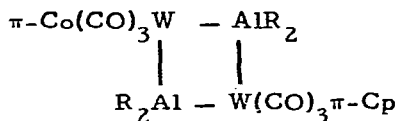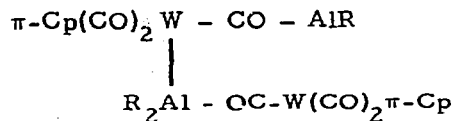
$$\qquad\qquad \text{XLIV} \qquad\qquad\qquad\qquad\qquad\qquad \text{XLV}$$

contain different bridging groups. The choice between these is not

clear since with the methyl derivative XLIV appears to be more

favorable while with the ethyl derivative XLV is indicated by ir studies.

Other structures were also proposed but eliminated on the basis

of the nmr or ir work.

Kroll and McVicker [98] have reported the preparation of a com-

pound containing a metal-aluminum bond from the reaction indicated

in 98. This reaction was also observed with formation of the tungsten

$$\text{R}_2\text{AlR'} + \text{HMo}(\pi\text{-Cp})(\text{CO})_2\text{L} \rightarrow \text{R}_2\text{AlMo}(\pi\text{-Cp})(\text{CO})_2\text{L} \qquad (98)$$
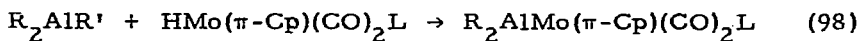
$$\text{R = alkyl, L = CO or phosphine}$$

analogues presumably with the structures cited above. The reaction

proceeded with the order $i\text{-Bu}_2\text{AlH} > \text{Et}_3\text{Al} > \text{Me}_3\text{Al}$. It was also

shown that the Al-M bond was cleaved by the reaction given in 99.

$$\text{R}_2\text{AlY} + \text{R'OH} \rightarrow \text{R}_2\text{AlOR'} + \text{HY} \qquad \text{Y} = \text{Mo}(\pi\text{Cp})(\text{CO})_3 \quad (99)$$
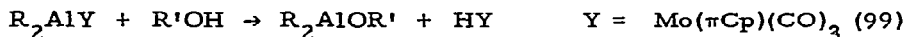
Alich, et al. [99] have observed a different type of aluminum trans-

ition metal complex in which the $\text{R}_3\text{Al}$ group is bound to a carbonyl

oxygen. They investigated the ir spectra of the species of known

structure shown in XLVI and studied the equilibrium indicated in

equation 100. This equilibrium, and the subsequent structural change

indicated, were governed by the basic character of the bridging carbonyl

group.



XLVI



(100)
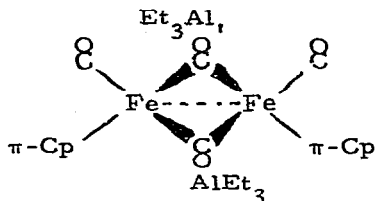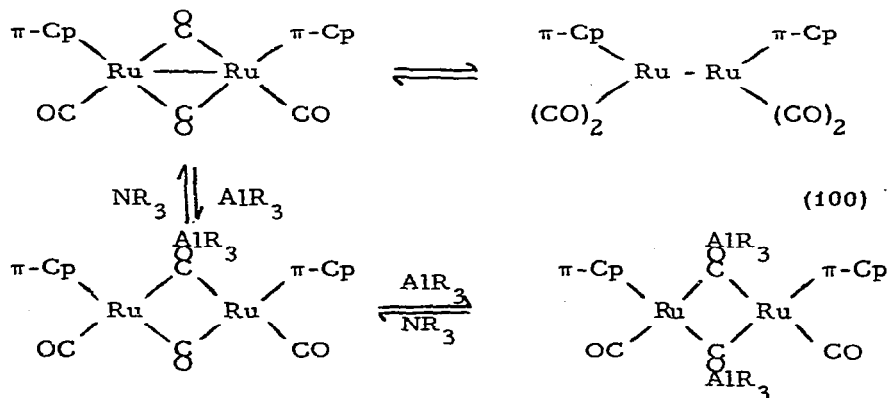


## Polymerization Reactions and Catalysts

One of the major uses of aluminum alkyls and related compounds

is in the polymerization of various unsaturated derivatives. The

aluminum compounds are used by themselves and in conjunction

with transition metal compounds. Many of the papers dealing

with these systems are covered, however, a majority of this work

is reported in patent literature which is not included in this review.

Lyons and Catterall [100] studied the kinetics and mechanisms

of $Et_3Al$ initiated polymerization of methyl isopropenyl ketone in

toluene and THF. The formation of the active catalyst sites are indicated

in 101. It is suggested that only the first two species were formed in

large concentrations. The subsequent polymerization reaction was
discussed in some detail. In a second paper [101] these authors
discuss the use of the preformed catalyst for polymerization of
vinyl ketones and further describe the mechanism of polymer formation.



$$(Et_3Al)_2 \rightleftharpoons 2\ Et_3Al\ + \begin{array}{c} Me \\ H_2C \end{array} C - C \begin{array}{c} O \\ Me \end{array}$$

(101)

$$\begin{array}{c} Me \\ H_2C \end{array} C - C \begin{array}{c} + \ Me \\ O - AlEt_3 \end{array}$$

| conjugate adduct | carbonyl adduct | reduction | enolization |
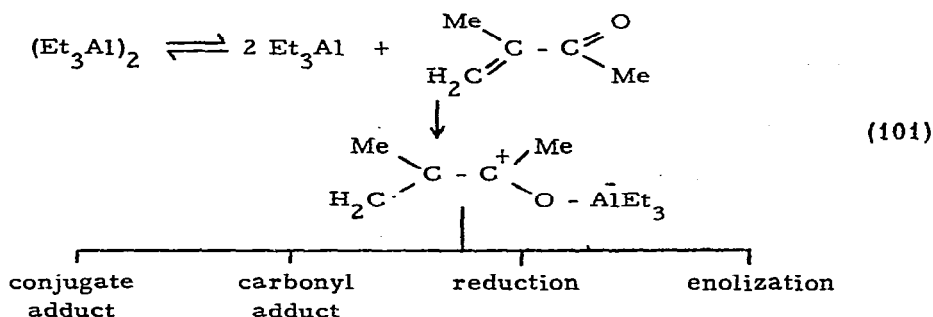
Solomon, et al. [102] studied the catalylic activity of $Et_2AlCl$
and $Et_3Al$ and the type of polymers formed in the polymerization of
acrylic and methacrylic esters of 2-allylphenol. The polymerization
occurs exclusively or predominantly through (meth) acrylic C = C
bonds in all of the cases reported. In a study on related systems
Patnaik and Gaylord [103] discussed the effect of solvent, temper-
ature and complex formation on the copolymerization of styrene with
methacrylate or acrylonitrile in the presence of ethylaluminum
sesquichloride.

Konomi and Tani [104] have investigated the polymerization
catalysts formed on reaction of $Et_3Al$, $NaAlEt_4$ and $KAlEt_4$ with
lactams and N-acetylacetams. They observed formation of $MAl(lac)_n$-
$Et_{4-n}$ which served as the catalyst. The compounds were characterized

by ir and nmr spectroscopy. A discussion of their formation and

reactions was presented.

Turning now to systems containing transition metals, Pino, et

al.[105] have investigated the nickel-catalyzed displacement reaction

between optically active organometallic compounds of Be, Zn, B and

Al and $\alpha$-olefins under homogeneous conditions. They observed

that there was little stereospecificity when the reaction was carried

out in the presence of nickel complexes containing optically active

ligands. Uv and CD studies showed the existance of interactions

among the reactants. On the basis of these results and the different

catalytic activities of Ni(acac) and Ni(mesal)$_2$, (mesal = N-methyl-

salicylaldimino), it was concluded that at least one of the ligands

originally present in the nickel complex is contained in the catalytic

species. The different reactivities of the organometallic compounds

used and the lack of catalytics activity on Ni(mesal)$_2$ in the racemization

of optically active 2-methylbutyl beryllium and aluminum derivatives

indicated that the alkylation and the subsequent hydride formation of

the nickel do not play an important role in the catalytic process. On

the basis of these studies a mechanism for the reaction is proposed

as indicated in 102, 103, and 104.

$$Ni(mesal)_2 \; + \; XR_3Al \; \rightarrow \; L_nNi$$

$$Li_nNi \; + \; CH_2 = CHR' \; \rightarrow \; CH_2 \underset{L_nNi}{\overset{\mid}{=}} CHR'$$

(102)

$$CH_2 = CHR' \quad + \quad \searrow AlCH_2 \overset{*}{C}HEt \quad \longrightarrow$$
$$L_n Ni \qquad\qquad\qquad\qquad\qquad Me$$

$$\begin{array}{c} Me \searrow \overset{*}{C} \diagup Et \\ CH_2 — C \\ \searrow Al \diagup \qquad \diagdown H \\ \diagdown CH_2 = CH-R \\ L_n Ni \end{array} \longrightarrow \left\{ \begin{array}{c} \searrow AlCH_2 CH_2 R \\ \diagup \\ + \\ CH_2 = C \diagup^{Et} \\ L_n Ni \diagdown Me \end{array} \right. \qquad (102)$$

$$CH_2 = C \diagup^{Et} \qquad + \qquad CH_2 = CHR \quad \rightarrow \left( \begin{array}{c} CH_2 = C \diagup^{ET} \\ \diagdown Me \\ \\ CH_2 = CHR' \\ L_n Ni \end{array} \right. \qquad +$$
$$L_n Ni \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (104)$$
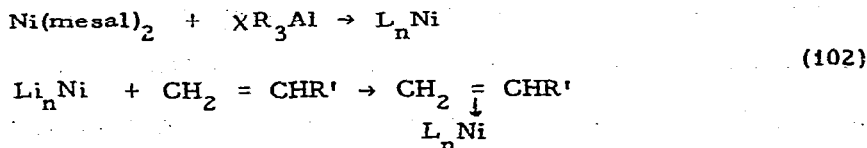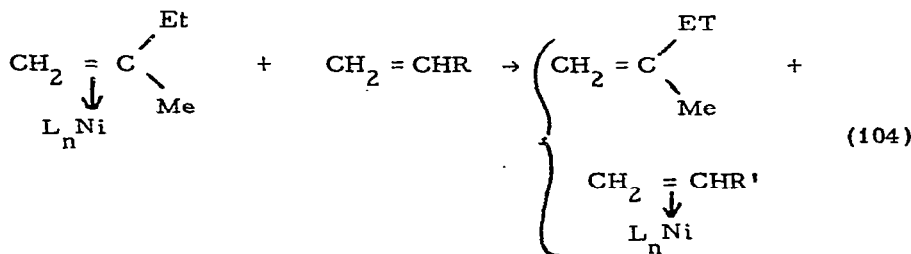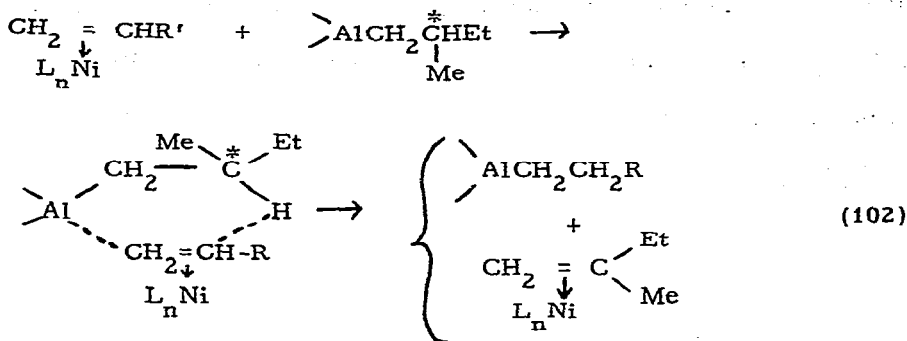
In a subsequent paper Giacomelli and Lardicci [106] reported that the kinetics of the displacement reaction between (+)tris[(S)-2-methylbutyl] aluminum and (RS)-4-methyl-1-hexene in the presence of soluble nickel catalyst was complex. The reaction was character-ized by an induction period followed by a first order dependence of the reaction rate on the concentrations of the nickel, the olefin and of the aluminum linked 2-methylbutyl groups. A possible mech-anism was discussed.

Jones [107] and Jones and Symes [108] have examined dimeri-zation reactions of $\alpha$-olefins with various aluminum-transition metal catalyst systems. Jones [107] considered several proposals which have been presented to account for the dimerization of propene and concluded that for reactions catalyzed by alkyl aluminum halides,

cobalt (or nickel)halide-aluminum alkyls, cobalt chloride-aluminum

chloride, or cobalt chloride-aluminum chloride-aluminum alkyl

systems, the dimerization proceeds through a cationic mechanism

indicated in 105 .

$$Cat^+An^- + CH_2 = CHCH_3 \rightarrow Cat - CH_2\overset{+}{C}H - CH_3$$
$$\underset{An^-}{}$$

$$Cat - CH\overset{+}{C}HCH_3 + CH_2 = CHCH_3 \rightarrow Cat - CH_2$$

(105)

$$\diagdown CH-CH_2\overset{+}{C}H-CH$$
$$\diagup \quad An^-$$
$$CH_3$$

$$Cat - CH_2 \qquad \downarrow$$

$$\diagup CH-CH=CH-CH_3 + H^+An^-$$
$$CH_3$$

$$\downarrow$$

$$CH_3$$
$$\diagdown CH-CH=CH-CH_3 + Cat^+An^-$$
$$\diagup$$
$$CH_3$$
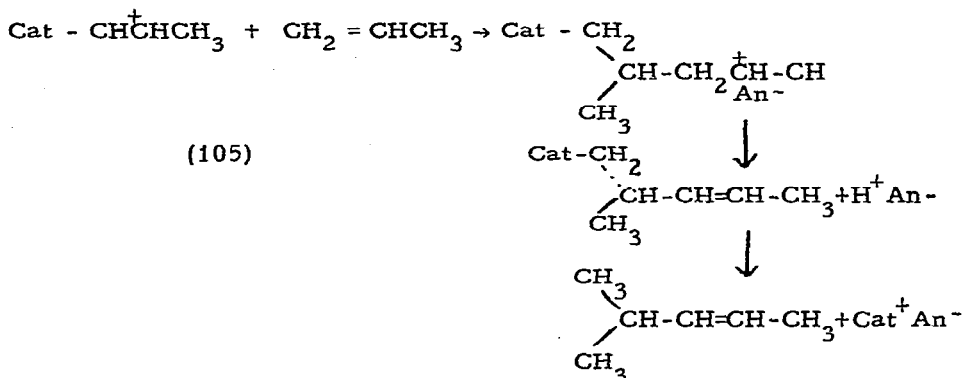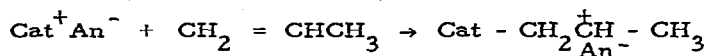
Since the charge separation on the propene is not complete they also

proposed that 106 occurred to some extent in order to account for all

of the products observed. An extensive discussion considering the

effect of the aluminum species and type of complexes formed was

presented.

In the second paper [108], in which the dimerization was catalyzed

by nickel β-diketonates and aluminum alkyls, it was shown that the

predominate product was hex-2-ene. To account for this change in

product distribution and in activity of the catalyt systems, the authors

proposed that the active catalyst was some complex species such as

$$CatCH\begin{array}{c}CH_3\\ \diagup\\ \diagdown\\ CH_2^+\\ An^-\end{array} \quad + \quad CH_2 = CH - CH_3 \rightarrow Cat - \begin{array}{c}CH_3\\ |\\ C - H\\ |\\ CH_2 - CH_2 - CH^+ CH_3\end{array}$$

$$\downarrow \quad An^-$$

(106)

$$CH_3CH_2CH_2CH=CHCH_3$$

$$+ Cat^+ An^-$$
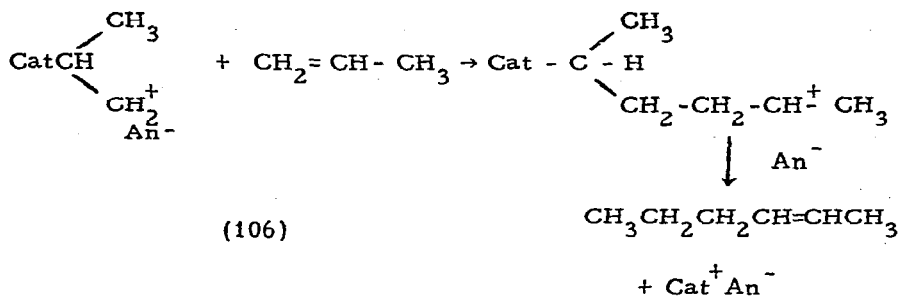
indicated in XLVII. They proposed a reaction scheme based on this type of catalyst to account for the reaction of 1-methyl-1-vinyl-2-dichlorocyclopropane in the presence of $R_3Al(R=Et,$ Bu or $Me_2CHCH_2)$ and $TiCl_4 \cdot SnCl_4$ or $WCl_6$. Three different oligomers were obtained



XLVII
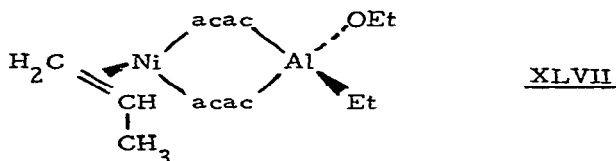
as indicated and characterized by nmr and molecular weights in the range of 1420 - 4800.



XLVIII            XLIX            L
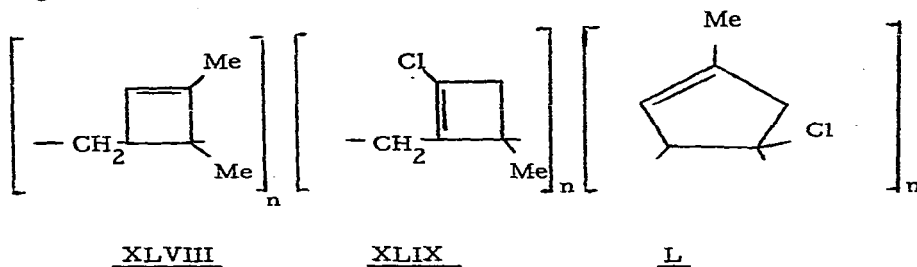
The $Ti(OBu)_4$ - $Bu_2AlH$ catalyst systems were reacted with $C_{11-16}$ internal olefins to yield primary aluminum compounds [114]. Another complex catalyst thought to be of the form indicated in LI was studied.



LI
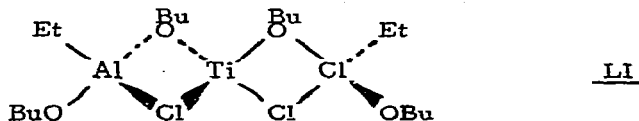
Many additional studies have been carried out to evaluate the

effects of complex metal catalysts. It has been shown for example

[109] that $Et_3Al$-transition metal salts (Fe, Co and Ni chlorides and

acac) isomerized α-olefins giving isomerization products and some

saturated hydrocarbons. It was suggested that this indicated formation

of a transition metal hydride as the active species.

The method of preparation of zinc and aluminum alkyl-active

methlene chelated compounds was studied by Kawakami and Tsuruta

[110]. The chelates include those formed with dimethylmalonate,

dimethyl chloromalonate, dimethyl methylmalonate, methyl cyanoacetate,

and others. The compounds were characterized by $^1H$ nmr spectroscopy

and by the $J_{^{13}C-^1H}$ for the methine protons. The compounds were also

studied by ir. Both zinc and aluminum derivatives were found to cause

a Michael-type addition with α, β-unsaturated esters or nitriles. The

aluminum derivatives exhibited lower activity than the zinc compounds.

Kinetic studies of the addition reactions showed that first-order rate

laws with respect to both the metal compound on the α, β-unsaturated

carbonyl derivative. It was proposed that the reaction may proceed

through the steps in 107. Substituent effects were studied and various

other correlations were made. It was concluded that the stability of

the complex was of major importance.

$$Et(Y)Al[DMM] \rightarrow Et(Y)Al --- (DMM)$$
$$\underset{\underset{MeCCH=CH_2}{\overset{\|}{O}}}{\vdots} \qquad |$$

(107)

$$\rightarrow Et(Y)AlO\overset{Me}{\underset{}{C}}=CHCH_2-DMM$$
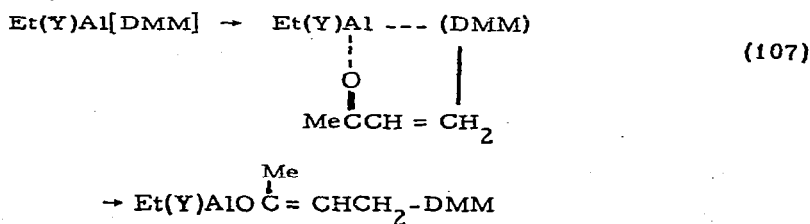
Graham and Slaugh [111] showed that $EtAlCl_2$-$WCl_6$ system enhanced
the rate of alkylation of benzene in the reaction with ethylene over that
observed for the transition metal halide alone while Srab, et al. [112]
studied the effect of $Et_3Al$, $Et_2AlCl$, $(i-Bu)_2AlCl$ and $(i-Bu)_3Al$ as
co-catalysts with $VCl_4$ and $VOCl_3$ in the polymerication of propylene.

Several papers dealt with the use of titanium containing derivatives.
Pinazzi, et al. [113] studied the polymerization by ir, electrical con-
ducing measurements, and by gas chromatography of evolving gases
[115]. This system was formed on addition of $Ti(O-Bu)_4$ with $Et_2AlCl$
or $EtAlCl_2$.

Furukawa [116] has investigated the catalytic activity of a variety
of $R_{3-n}AlCl_n$-transition metal catalysts in copolymer formation between
vinyl chloride and α-olefins or acrylic compounds. He has shown that
when equimolar or greater amounts of the aluminum compound are
present, one obtains a 1/1 copolymer with vinyl chloride and acrylonitrile
regardless of the monomer composition. This was interpreted by
an assumption that copolymerization takes place between free acrylo-
nitrile, and a ternary complex of vinyl chloride, acrylonitrile and
aluminum compounds.

Dixit, et al. [117] have investigated the polymerization of acrylo-
nitrile with $Et_3Al$-$VCl_4$ catalyst systems and found that the rate of
polymerization was first order with respect to monomer and inversely
proportional to the catalyst concentration. This fact was attributed to
the permanent complex formation between the catalyst complex and
acrylonitrile. A reaction scheme was proposed.

The use of $V(acac)_3$-$Et_2AlCl$ as a catalyst has been studied for

polymerization, copolymerization and terpolymerization of 1-isopropylidene-dicyclopentadiene [118]. The reaction and polymers produced were characterized by a variety of techniques.

Kawai, et al. [119] investigated the polymerization of methylacrylate with $Et_3Al$-CuCl catalyst. On the basis of kinetic studies and epr investigations they proposed that the polymerization was a radical process and postulated a reaction scheme.

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