ALUMINUM

ANNUAL SURVEY COVERING THE YEAR 1972

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The chemistry of organoaluminum compounds has continued at about the same level as in 1971 with a wide variety of topics covered. For this reason and for the benefit of the reader, the material has been broken down into a series of broad topics as indicated below. There is some overlap in areas and the choice of location for the discussion of a particular paper has been made arbitrarily by the author. As in the past, an attempt has been made to cover all of the primary literature through Chemical Abstracts although there surely are some oversights. The general breakdown of topics is as follows:

A) Structural and spectroscopic studies

B) Thermodynamic and kinetic studies

C) Syntheses of aluminum compounds

D) Labeling and exchange reactions catalyzed by aluminum derivatives

E) Syntheses of alkyllead derivatives from aluminum species

F) Bridged and complex organoaluminum derivatives

G) Unsaturated organoaluminum compounds

H) Reaction of aluminum derivatives with carbon-oxygen bonds

I) Formation and reactions of compounds containing Al-X bonds (X = $-NR_2$, $-SR$, $-SiR_3$, $-I$, $-Cl$, etc.)

J) Systems containing aluminum bound to another metal either directly or by bridging

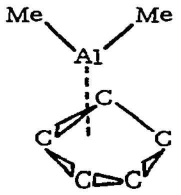
K) Aluminum alkyl complexes and addition compounds

L) Aluminum alkoxides and related compounds

Structural and Spectroscopic Studies

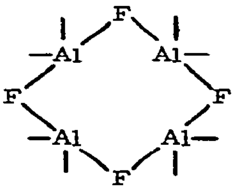
A variety of structural studies have been reported on organoaluminum derivatives. These include structural determinations both in the solid state by X-ray techniques and in the gas phase by electron diffraction as well as ir, Raman and nmr studies which led to structural assignments.

One of the more interesting of these studies was the determination of the gas phase structure of dimethyl(cyclopentadienyl)aluminum monomer from electron diffraction data.[1] In this report, Drew and Haaland concluded that the cyclopentadienyl ring is bonded to the aluminum in an unsymmetrical fashion as indicated in I with overall molecular symmetry of C_s.



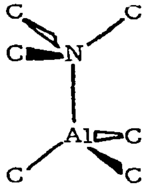
I

The molecular structure of $(Me_2AlF)_4$ has been determined by gas phase electron diffraction studies which confirm the cyclic four-membered ring structure shown in II.[2] The electron diffraction data indicate low symmetry (C_s) and further suggest a large amount of intramolecular motion.



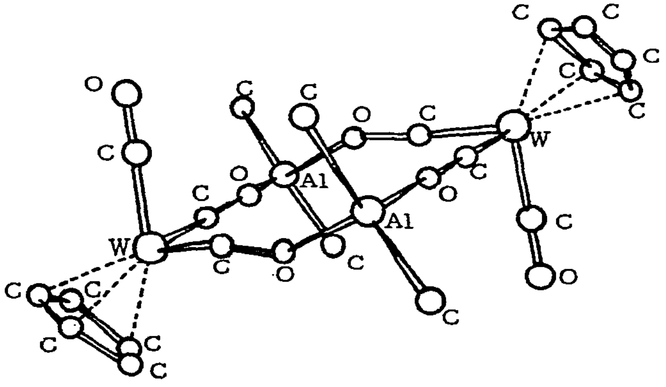
II

In another paper the gas phase structure of the adduct $Me_3Al\text{-}NMe_3$ was established as indicated in III with the carbon atoms in a staggered conformation.[3] In this paper variations in the Al-N and Al-C bond distances and in the various bond angles were discussed in some detail.



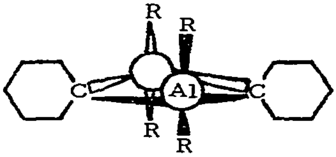
III

Gainsford et al.[4] have used X-ray diffraction methods to determine the structure of $[CpW(CO)_3AlMe_2]$ which shows some very interesting features that are illustrated in IV. One should note especially that the central portion of the molecule is composed of a twelve-membered ring with CO bridging units between tungsten and aluminum. The chemistry of derivatives of this type is discussed in section J.



IV

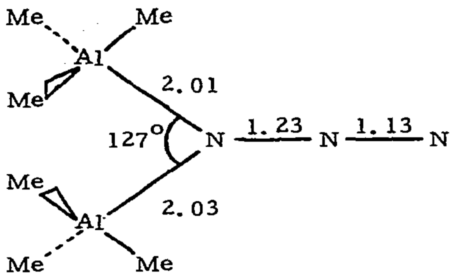
Malone and McDonald have presented the detailed analysis on the structures of Ph_6Al_2[5] and $Me_4Ph_2Al_2$.[6] In both cases bridging phenyl groups are observed with the phenyl group perpendicular to the four-membered AlCAlC ring as indicated in V. Discussion of the structures was presented. It was noted that in Ph_6Al_2 all of AlCAlC rings were planar while in the $Me_4Ph_2Al_2$ molecule 1/3 of the rings are planar while the remainder are folded by about 14°. This was discussed in terms of repulsions within the molecular unit.



V

Atwood and Newberry[7] have determined the crystal structure of $K[Al_2(Me)_6N_3]$ and have found that there are two chemically nonequivalent molecules in the asymmetric unit. The differences are best shown in the following diagrams viewed down the nitrogen chain and result from the change in the conformation of the carbon atoms of the methyl groups. The structure of the C_{2v} form of the anion is given in VII. It was also noted that compounds

VI



VII

of the general type $M[Al_2Me_6X]$ ($M = K$, Cs, Me_4N^+; $X = N_3$, SCN, Cl, I) form nonstoichiometric complexes with small aromatic molecules such as benzene, toluene and p-xylene with from two to five aromatic molecules loosely associated with the $K[Al_2Me_6X]$. The behavior was stated to be reminiscent of a clathrate type behavior.

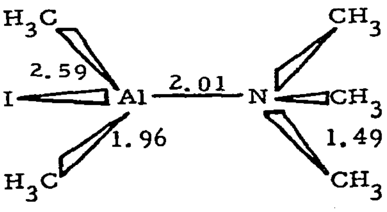
Atwood and Milton[8] have reported the reaction indicated in 1 forming

$$Me_4NI + Me_3Al \xrightarrow{90^\circ} [Me_4N][AlMe_3I] \qquad (1)$$

the trimethyliodoaluminate. At 280° this decomposes via the process illustrated in eq. 2. The crystal structure for the latter compound was reported

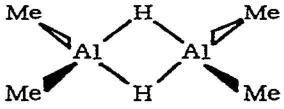
$$[Me_4N]\ [AlMe_3I] \xrightarrow{280^\circ} Me_3N\cdot AlMe_2I + C_2H_6 \qquad (2)$$

in a preliminary fashion and shows the molecular geometry to be that indicated in **VIII**.



VIII

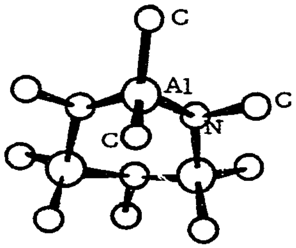
In another study the molecular structure of the dimeric molecule $(Me_2AlH)_2$ has been determined by electron diffraction.[9] The molecule was shown to have D_{2h} symmetry with the structure given in IX. The most



IX

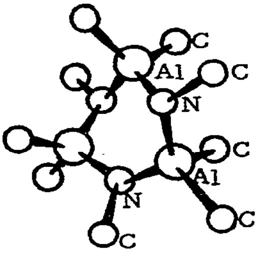
interesting feature of this study is that it was shown that the Al-Al distance was the same as that observed in Me_6Al_2 and that this distance is only 0.010Å greater than the value calculated for a single bond by doubling the tetrahedral covalent radius and is 0.24Å smaller than the Al-Al distance in aluminum metal. It was suggested that these observations strongly support metal-metal bonding in electron difficient systems.

McLaughlin et al.[10] have determined the structures of the stereoisomers of cyclotri-μ-methylamidotris(dimethylaluminum) by single crystal X-ray studies. The molecular geometry of the cis form is indicated in X and the



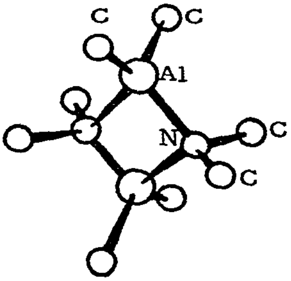
X

trans form is indicated in XI. The molecules have the same general dimensions but the cis form occurs in the chair conformation while the trans form



XI

exists in a skrewboat configuration for the six-membered ring. A third form having an Al_2N_2 ring system was also described and the molecular geometry for it is indicated in XII. The influence of the intramolecular interactions



XII

influencing the conformations observed and the degree of aggregation in the molecular unit was discussed.

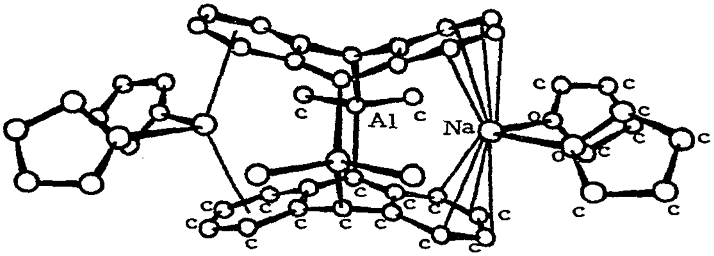
In a subsequent paper the spectral properties of the cis and trans isomers were discussed including work on the variable temperature nmr, ir and mass spectra of these derivatives.[11] It was shown that a distinction could be made between the isomeric forms in solution and estimates of the equilibrium established between the cis and trans isomers in solution were determined as a function of temperature. It was noted that the spectra of the pure isomers could not be obtained due to the fairly rapid interconversion between the isomers upon solution. The interconversion, however, is slow on the nmr time scale so that distinct spectra could be obtained for each isomer present. It was noted that at higher temperatures the trans isomer was predominant while at lower temperatures the cis species became dominant. Various studies were also made on the Al-Et and N-Et substituted derivatives which were interpreted in terms of similar isomers being formed. The nmr spectra were difficult to interpret on a quantitative base for the ethyl derivatives due to the overlap observed in many of the reasonance signals.

Both the ir and mass spectral studies were consistant with the two isomeric forms. The mass spectra showed extensive fragmentation and decomposition typical for aluminum derivatives including the lack of observation of the parent ion. These studies did confirm trimeric species in the vapor state however.

Thermal decomposition yielded two crystaline compounds thought to be $(Me_2AlNHMe)_3(MeAlNMe)_4$ and $(MeAlMMe)_8$, but definitive structural information has so far not been obtainable. These compounds are thought to have cage structures composed of aluminum and nitrogen atoms.

In another study the structure of the trimeric form $[H_2Al(NMe_2)]_3$ was examined.[12] The colorless, needlelike crystals are elongated along the axis with the unit-cell parameters a, 6.52 ± 0.03; b, 25.70 ± 0.02; c, 8.85 ± 0.01Å and $\gamma = 92.4$ $z = 12$ space group P2/b. The coordinates of all of the constituent Al and N atoms are given. The trimeric molecule has the chair conformation with a mean Al-N bond distance of 1.93 ± 0.03Å. The coordination of the aluminum atom is distorted tetrahedral with a mean interatomic distance N-C of 1.54. The valance angles are Al-N-Al $115 \pm 2^\circ$, N-Al-N $108 \pm 2^\circ$, C-N-C $110 \pm 3^\circ$. The trimeric molecule forms a six-membered ring similar to that of cyclohexane and is formed by alternating AlH_2 and NMe_2 groups.

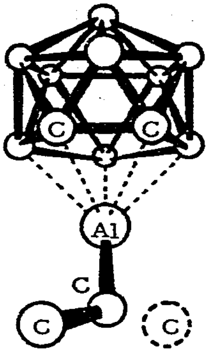
Brauer and Stucky[13] have reported the structure of $[Na(THF)_2][Al\text{-}Me_2C_{14}H_{10}]_2$ determined by the three-dimensional X-ray techniques. The observed structure is indicated in figure **XIII**. This indicates the interaction of the aluminum atoms with the 1,4-dihydro-1,4-anthrylene and shows that the Me_2Al groups serve as bridges between the two ring systems. Further, it shows the position and coordination about the sodium ions in this solid contact ion pair. Speculations were presented concerning the implications of these findings, particularly the association of only 2 THF molecules per sodium, on the nature of contact ion pairs in solution.



XIII

Muetterties and Guggenberger[14] have reported the crystal structure of tris(tropolonato)aluminum. They suggest from their studies and previous work reported in the literature, that the tropolonate ligand is inflexible, therefore, non rigid behavior associated with this molecule is the result of motion of the entire ligand.

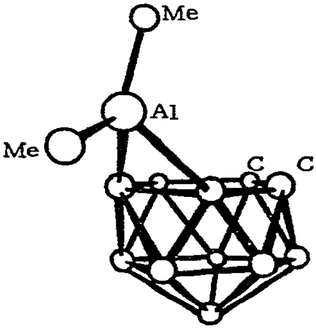
Churchill and Reis[15] have reported the structure of 3-ethyl-3-alumina-1, 2-dicarba-closo-dodecaborane-(12) as indicated in **XIV**. The structure



XIV

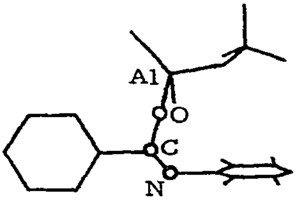
has been interpreted in terms of interaction of the aluminum atom with the two carbon atoms and three boron atoms from the cage in a "π bonded" fashion. In addition, the ethyl group is held to the aluminum by a σ bond.

These same workers have also determined the crystal structure of 7, 8-μ-dimethylaluminum-1, 2-dicarba-nido-undecarborane(13) at -100°.[16] In this structure it was shown that the aluminum is bound to the framework by what appear to be two σ bonds to two boron atoms on the open face of the cage. In addition, the two methyl groups are attached to the aluminum in a normal fashion. This is shown in XV.

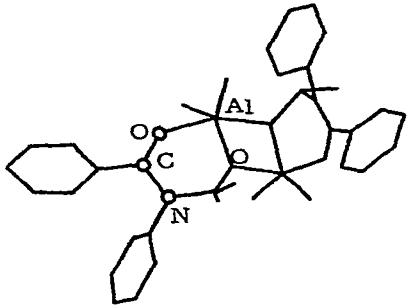


XV

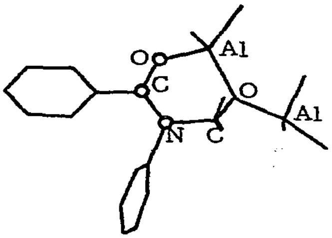
Kai et. al. have determined the crystal structures of three polymerization catalysts by three-dimentional X-ray diffraction techniques. The compounds examined were $Me_2AlOCPh{:}NPh{\cdot}ONMe_3$,[17] $[Me_2AlOCPh{:}NPh{\cdot}MeCHO]_2$[18] and $Me_2AlO{\cdot}CPh = NPh{\cdot}MeCHO{\cdot}AlMe_3$.[19] Drawings showing the geometry around the aluminum in each case are given in **XVI**, **XVII** and **XVIII**.



XVI



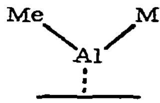
XVII



XVIII

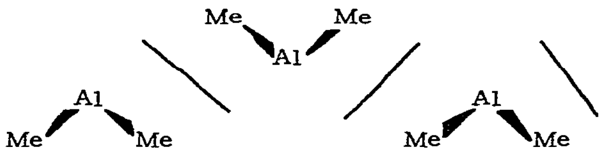
In both **XVI** and **XVIII** the aluminum is in approximately tetrahedral surroundings while in **XVII** it is penta coordinate. These species are discussed in terms of their interconventability and their function as catalysts. The structures are also compared with other known structures of organoaluminum complexes.

The ir and Raman spectra of solid dimethyl(cyclopentadienyl)aluminum has been determined and interpreted in terms of pentahapto-cyclopentadienyl rings of approximately D_{5h} symmetry.[20] The structure indicated in XIX



XIX

was suggested for the monomer while that in XX was proposed for the polymeric



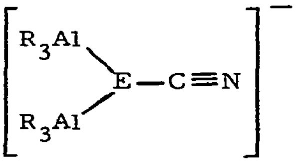
XX

material with bridging cyclopentadienyl rings.

Muller et al.[21] have studied the ir, Raman and ^{1}H nmr spectra of dicyclopropylaluminum and -gallium ethyleneimide. They suggested, on the basis of these studies, that the compounds form six-membered, nonplanar metal nitrogen rings which is in accord with the observed dipole moments of 2.0D. They also reported the vibrational spectra of tricycloproylaluminum dimer in both the solid and liquid phases.

Ir studies of the products from the condensation of aluminum atoms with CO at 20K in a krypton matrix indicates the formation of an aluminum carbonyl species.[22] It was suggested from isotope studies that the species is $Al(CO)_2$ with bands at 1987 and 1889 cm^{-1}, but species containing more than one aluminum atom $Al_x(CO)_2$ could not be ruled out.

The trimethylaluminum complexes $[Me_3AlSCN]^-$, $[(Me_3Al)_2SeCN]^-$ and $[(Me_3Al)_2CN]^-$ have been prepared by the reaction of NMe_4X and Me_6Al_2.[23] The vibrational spectra of these derivatives have been carefully examined using both ir and Raman techniques. The results have been interpreted in terms of two types of coordination, one associated with the S and Se atoms in SCN^- and $SeCN^-$ while the other results in equal bonding to the C and N in CN^-. These are indicated in XXI and XXII.

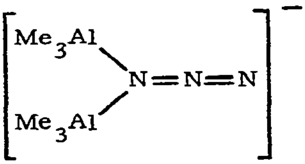


XXI

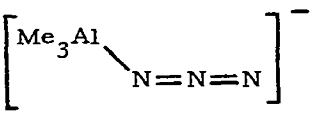
$[R_3Al{-}C{\equiv}N{-}AlR_3]^-$

XXII

Weller and Dehnicke[24] have shown that an excess of Me_3Al reacts with $(NMe_4)N_3$ to yield the complex $NMe_4[(Me_3Al)_2N_3]$. This complex releases Me_3Al thermally to yield $NMe_4[Me_3AlN_3]$. A study of the ir and Raman spectra of both derivatives was reported. On the basis of these studies, the structures indicated in XXIII and XXIV were proposed with C_s symmetry.

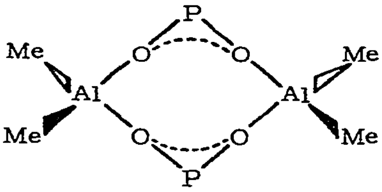


XXIII



XXIV

Another ir and Raman spectral study has been reported by Olapenski et al.[25] on the dimethyl metal dimethylphosphinates and arsinates of aluminum, gallium and indium and concluded that these derivatives contain a puckered eight-membered ring with C_{2h} symmetry as indicated in XXV.

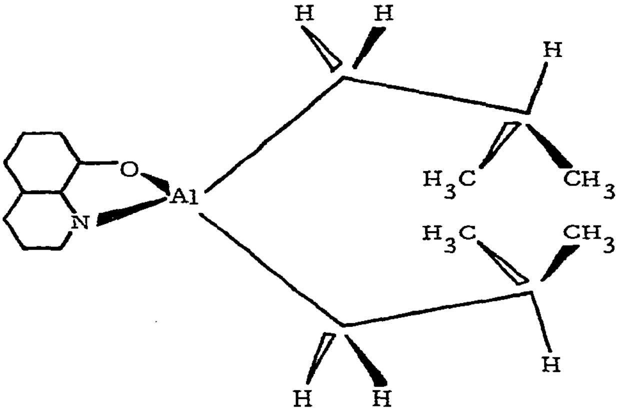


XXV

A number of reports have appeared dealing primarily with the nmr spectra of aluminum derivatives. Westmoreland et al.[26] investigated the pmr spectra of $NaAlEt_4$ in several solvents and have observed $^3J_{Al}$ in the anion when solvents able to coordinate with the cation sufficiently to yield solvent separated ion pairs are used. Studies were also carried out on $NaAlEt_3H$ in DME solvent which give no evidence for resolvable Al-H coupling, thus indicating that T_d symmetry is required for Al-H coupling in these derivatives. The solvating ability of different solvents, as well as the contact-solvent separated ion pair equilibria involved in these systems were discussed.

In another study Visser and Oliver[27] reported the nmr spectra of a variety of metal vinyl derivatives including $(C_2H_3)_3AlNMe_3$ and the gallium and indium analogous.

Sen et al.[28] have reported the nmr spectra of a series of quinolato-complexes of aluminum, gallium and indium dialkyls. They have attributed the variations in the chemical shifts of the alkyl protons to two opposing effects, the first being the inductive redistribution of electron density and the second the diamagnetic anisotropy of the π-electron system in the quinolate ligand. The latter effect causes the diastereotopic protons of the isobutyl groups in $(i\text{-}Bu)_2AlQ$ to be magnetically nonequivalent. The structure is shown in XXVI for the isobutyl derivative. The methyl and ethyl derivatives were also studied.



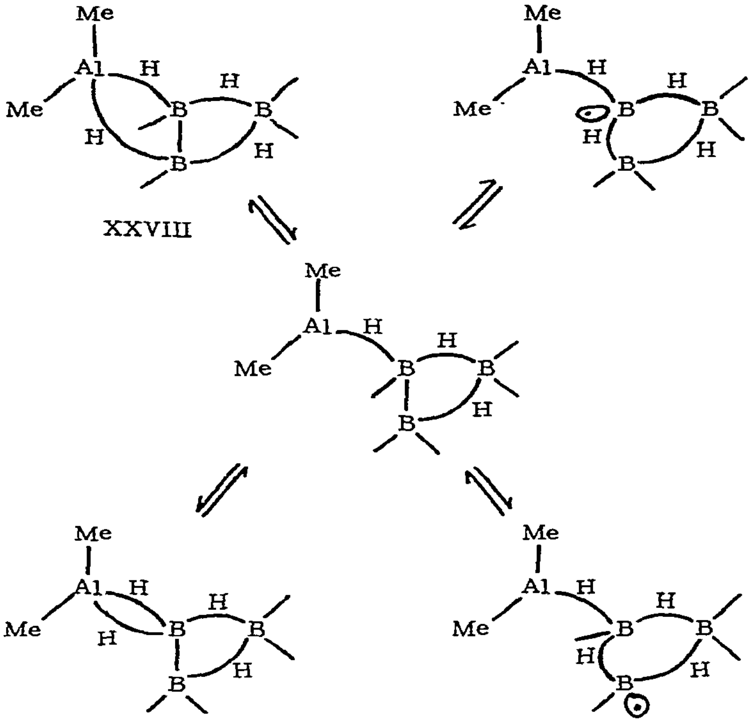
XXVI

Thermodynamic and Kinetic Studies

The first paper delt with under this heading is the preparation and the intramolecular exchange of dimethylaluminum triborane(8) and dimethylgallium triborane(8).[29] These compounds were prepared by reaction 3. Both

$$NaB_3H_8 + Me_2GaCl \longrightarrow NaCl + Me_2GaB_3H_8 \qquad (3)$$

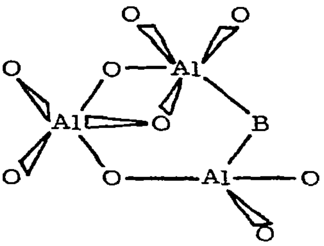
compounds are liquid at room temperature and may be distilled under high vacuum with the reported vapor pressures of 13 and 4 torr respectively at 0^o. The compounds were characterized by ir and mass spectral studies and by both ^1H and ^{11}B nmr studies. The temperature dependence of the nmr spectra led to the proposed exchange reactions indicated in 4. **XXVIII** is the



(4)

low temperature form analogous to known structure for metal triborane derivatives. The other forms and exchange steps occur as the temperature increases above 0°.

Brown and Murrell[30] have presented some additional data and an extensive discussion concerning the exchange reactions of Me_6Al_2 and a variety of its adducts and have also discussed the exchange of Me_6Al_2 with Me_3Ga as well as the self exchange of Me_6Al_2. In addition to a discussion and some modification of the earlier mechanism proposed by Brown for these exchange processes, the mechanism for exchange between Me_6Al_2 and $Me_6Al_2 \cdot B$ systems was suggested. This proposal involves a base assisted associative exchange mechanism with an intermediate as indicated in **XXVII** involved in



XXVII

the exchange process.

Smith has reported several studies on the dissociation of alkylaluminum derivatives which bear on the above exchange processes. In one of these studies he has re-evaluated the heat of dimerization of Me_3Al and reports a value of 19.4 ± 0.3 kcal/mole of dimer in a saturated hydrocarbon solution.[31] The value for Et_3Al was also carefully re-evaluated and $\Delta H^o_d = 16.9 \pm 0.2$ kcal/mole of dimer was obtained. These results were carefully evaluated from measurements by calculation and were tested for consistency as best as possible and appear to represent the best available values for the heats of dissociation of the simple methyl and ethylaluminum dimers.

He has also calculated similar values using a hydrocarbon simulation approach which he suggested should be generally applicable for the determination of dissociation energies of aluminum alkyls.[32]

Smith[33] has also studied the monomer-dimer equilibrium of Et_3Al and Me_3Al in mesitylene solution by measurement of the heats of dillution in this solvent. He has established that the heat of dissociation of Et_3Al dimer in mesitylene is 13.3 kcal/mole which is significantly less than that observed in n-hexadecane (16.9 kcal/mole) the 3.6 kcal/difference is attributed to the interaction of Et_3Al with the mesitylene. A similar finding was also made for Me_3Al which gives a dissociation energy of 15.6 ± 1.4 kcal/mole in toluene solution and 19.4 kcal/mole in cyclopentane. The latter result was based on estimates of the relative complexing ability of aromatic derivatives.

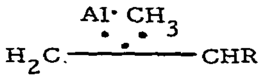
These results were discussed in terms of their implications on the kinetics of the bridge terminal exchange of trimethylaluminum. It was suggested that the mechanism in toluene and in cyclopentane may differ since the activation energy appears to be about the same, approximately 15.6 kcal/mole in the two cases, but the heats of dissociation are substantially different.

Several studies have appeared on the gas phase addition and elimination reactions of aluminum alkyls. Egger and Cocks[34] have investigated the gas phase reaction of excess C_2H_4 with Me_3Al and have shown that this reaction proceeds with addition of ethylene followed by a fast elimination of propene yielding Me_2AlH. This in turn adds C_2H_4 yielding Me_2AlEt. This sequence of steps is illustrated in the following reactions. The rate determining step

$$\left.\begin{array}{c} Al - Me + C_2H_4 \rightleftharpoons AlC_3H_7 \\ AlC_3H_7 \rightleftharpoons AlH + C_3H_6 \\ AlH + C_2H_4 \rightleftharpoons AlC_2H_5 \end{array}\right\} \qquad (5)$$

$$AlMe + 2C_2H_4 \rightleftharpoons AlC_2H_5 + C_3H_7 \qquad (6)$$

appears to be the initial formation of propene and appears to proceed through a concerted addition of the Al-Me species to the double bond. The observation that the addition of trimethylaluminum to ethylene is 10 times faster than the addition of triethylaluminum led these authors to conclude that this step does not go through a polar transition state since this would lead to the opposite relative rate of addition but in fact involved initial complex formation between the olefin and the monomeric aluminum species as shown in XXIX which then



$$H_2C \overset{Al \cdot CH_3}{\cdots\cdots\cdots} CHR$$

XXIX

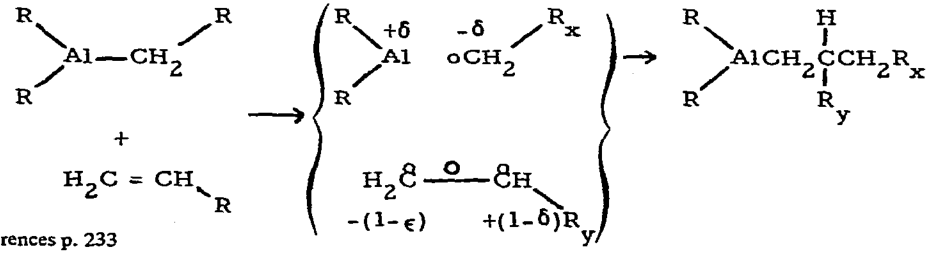
collapses to the final product.

Cocks and Egger have continued their studies on the homogeneous gas phase elimination of olefins from group III derivatives with a study of the elimination of ethylene from triethylaluminum.[35] From their findings on this system they concluded that the activation parameters are compatible with the 4-center polar transition state proposed for olefin elimination from other group III metal alkyls. They also concluded that the effect of β-substitution on the rate of elimination is additive. The activation parameters for the elimination are $E_a = 30.1 \pm 0.3$ and $\Delta G + = 35.2$ kcal/mole and for the addition of Et_2AlH to ethylene was estimated to be 4.9 kcal/mole.

In another study Egger[36] has investigated the kinetics of the reaction indicated in 7. In addition to providing more detailed data on the kinetics

$$Me_3Al + 2C_3H_6 \longrightarrow Me_{3-x}AlPr_x + xCH_2CMe_2 \qquad (7)$$

of these reactions, he proposed that the rate controlling step was not initial π-metal complex formation as had been suggested earlier, but could better be formulated in terms of a concerted four-centered addition as indicated in 8.



(8)

In a subsequent paper[37] he reported additional details on the addition of diisobutylaluminum hydride produced in situ from (i-Bu)$_3$Al to ethylene, propene and 2-methylbut-1-ene. He concluded these data further supported the concerted quadropolar four-centered transition state and did not require formation of an intermediate metal-π complex.

Allen et al.[38] have investigated the kinetics of the reaction between triethylaluminum with oct-1-ene in diphenyl ether and have measured the equilibrium constant for the formation of the complex $Et_3Al \cdot OPh_2$. Parameters for the equilibrium reaction have been estimated by the nmr method

$$1/2\ Et_6Al_2 + Ph_2O \rightleftharpoons Et_3AlOPh_2 \qquad (9)$$

to be $\Delta H^o = -16.3 \pm 1.3$ kJ/mole and $\Delta S^o = -42.7 \pm 1.7$ J/mole^{o}k.

The kinetic data for this reaction were best interpreted in terms of reaction between free Et_3Al and oct-1-ene in the rate determining step. They also suggested that the complex was completely inert toward addition to the double bond. Further, the lack of a solvent effect, other than in removal of Et_3Al was interpreted in terms of an essentially nonpolar mechanism. It was suggested that the low A factor results from the loss of entropy associated with the formation of a compact, rigid transition state. The lack of reactivity of the $Et_3Al \cdot OPh_2$ adduct was associated with its four coordinate nature and therefore reduced ability to form a π-complex with the olefin.

The kinetics of the reactions of $(Me_2CHCH_2)_3Al$ with 1,5-heptadiene, 1,5-hexadiene, 4-vinylcyclohexene, 1-heptene, 1,4-hexadiene and methyl-1,4-hexadiene were studied and a mechanism was proposed.[39] The rate depends on the dissociation rate of triisobutylaluminum and not on the nature of the olefin. Kinetic equations were derived which agreed well with the experimental data. Alkylaluminums had different reactivities, depending on the nature and position of unsaturation in the alkynyl radical.

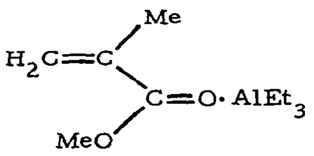
Tsuji et. al.[40] have investigated the photolysis of Et_3Al and several $Et_{3-n}AlCl_n$ derivatives at -196°. The observed formation of ethyl radicals which appear to be produced via **10.** They further noted a substantial solvent

$$Et_3AlCl_3 \xrightarrow{h\nu} 2Et^o + Al_2EtCl_3 \text{ (non paramagnetic)} \qquad (10)$$

effect on the production of the radicals. The effect of the solvents and various complexing agents on the photolysis experiments was discussed.

Allen et. al.[41] have reported on the kinetics of the photochemically initiated polymerization of methylmethacrylate: Et_3Al complex. They concluded that the initiation step occurs following excitation of the complex in a slow step such as that indicated in **XXX** where **XXXI** represents the complex

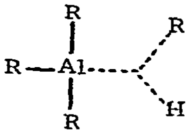
$$\begin{tikzcd}(XXX)^* + (XXXI) \arrow[r, shift left, "k_1"] & (I)^*(XXX) \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_d"] \arrow[d, "k_2"'] & \text{radicals} \\ & 2(XXX) & \end{tikzcd} \qquad (11)$$



XXX

indicated. A detailed discussion of the reaction mechanism was reported.

Olah et al.[42] have discussed the protolysis of boron and aluminum derivatives and have postulated a five-coordinate transition state shown in **XXXII** which may lead to H-D exchange and/or cleavage.

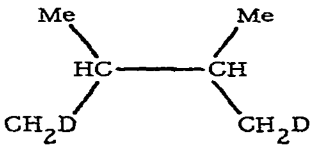


XXXII

The kinetics of the oxidation of $(C_6H_{13})_3Al$ and $(C_{14}H_{29})_3Al$ by oxygen were studied at 0 - 60° in heptane.[43] The reaction rate obeys the equation for consecutive reactions and is first order with respect to R_3Al. The rate constant and activation energies of the addition of the first and second molecules of oxygen were calculated. Aluminum alcoholates are formed by isomerization of the peroxy compounds. Activation energy increases with increased length of the alkyl chain. The amount of peroxy compound formed at -60° was determined.

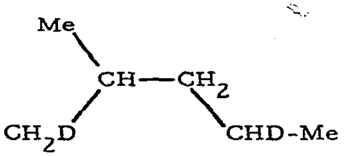
Syntheses of Aluminum Compounds

A number of new organoaluminum derivatives have been prepared and a number of new reactions have been reported. Of these among the most interesting is the direct reaction of aluminum atoms with olefins and acetylenes reported by Skell and Wolf.[44] These reactions were carried out by evaporation of aluminum and co-condensation of these atoms with the organic substrate on a cold trap. It was shown by additional studies that the reaction only took place as described and did not occur when the organic substrate was condensed onto a freshly prepared aluminum surface. When aluminum was reacted with propene, the major product obtained on deuterolysis of the organoaluminum compounds was CH_3CHDCH_2D with significant amounts of XXXIII and XXXIV also obtained showing that the major products were formed



XXXIII

and



XXXIV

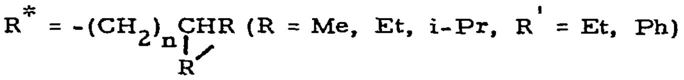
by addition of aluminum(s) to the double bond yielding 1, 2-dialuminoalkanes with the C_6 fragments formed by coupling of 1-alumino-2-propyl radicals or 2-alumino-1-propyl radicals.

Other studies were also carried out in which 1, 3-butadiene was reacted with aluminum yielding on deuterolysis, 3, 4-dideuterio-1-butene as the major product.[38] With propyne the major products were 1-aluminopropyne and 1, 2-dialuminopropene as indicated by deuterolysis while reaction with 2-butyne yielded only cis and trans-2-butene derivatives in a 2:1 ratio.

Another study which is novel is that of Stefani and Pino[45] who have investigated the formation of 1, 3-dialumina alkanes and have demonstrated their existance in solution by deuterolysis. They noted that the compounds were very unstable, undergoing decomposition either by a 1-2 aluminum hydride elimination, or by a 1,3-aluminum shift with olefin elimination. The second process is apparently the reverse of the addition of Al-C to a double bond and occurs readily when a quarternary carbon is present in the 2-position.

Lardicci et al.[46] have shown that optically active aluminum derivatives can be readily prepared via the exchange indicated in 12 where the exchange

$$BR^*_3 + AlEt_3 \longrightarrow BEt_3 + AlR^*_3 \qquad (12)$$



$R^* = -(CH_2)_n\underset{R}{C}HR'$ (R = Me, Et, i-Pr, R' = Et, Ph) between aluminum and zinc derivatives was also shown to go without appreciable racimization.

The preparation of allyl and methylallyl groups by exchange of Me_3Al with R_3B has been reported where R = allyl, methylallyl and crotyl.[47] The methylallyl(dimethyl)aluminum $Me_2AlCH_2C(Me) = CH_2$ is a stable crystaline compound which melts at 72 - 73°. The other derivatives are much less stable, undergoing decomposition at or below room temperature.

All compounds were characterized by their nmr spectra. The variable temperature studies indicated that the species were normally bound allyl groups at low temperature but were involved in dynamic equilibria at high temperatures.

Dickson and Sutcliffe[48] have studied the reaction of $LiAlH_4$ with fluoroalkyl iodides. They have reconfirmed that reaction **13** occur yielding a

$$LiAlH_4 + CF_3CF_2CF_2I \longrightarrow LiAl(CF_2CF_2CF_3)H_2I + H_2 \qquad (13)$$

moderately stable perfluoroalkyl aluminum derivative. This derivative has been characterized by ^{19}F nmr spectra and by its decomposition reactions which leads to several products including fluoroalkenes. Evidence has also been reported for the transient existance of other derivatives including $LiAl(CH_2CF_2CF_3)H_2I$ and $LiAl[CF(CF_3)_2]H_2I$. Both of these species are quite unstable undergoing rapid decomposition either by fluorine elimination or proton abstraction from the solvent.

Labeling and Exchange Reactions Catalyzed by Aluminum Derivatives

Garnett et al.[49] have shown that hydrogen exchange is catalyzed between aromatic moieties by $RAlX_2$ species. This provides a convenient, fast way for deuteration of aromatic compounds by exchange of benzene d_6 with other molecules. Equilibration was attained in 30 minutes at room temperature with C_6H_5Cl, C_6H_5Br, C_6H_5Et, $C_6H_5(t\text{-}Bu)$, p-xylene, mesitylene, allylbenzene, diphenyl, dibenzyl, p-terphenyl and naphthalene. Exchange was also effected with anthracene, chrysene and pyrene but in these three cases, heating for one week at 90^o was required. In all cases only the protons on the aromatic ring underwent exchange.

In a subsequent paper, it was shown that tritium labeled species could also be obtained very rapidly by use of the same catalyst with addition of the tritium as T_2O.[50] This resulted in hydrolysis of some catalyst and provided for rapid incorporation of sufficient tritium into the aromatic moiety. Lower percentages of tritium could also be incorporated into nonaromatic hydrocarbons by this technique to serve as a label. This procedure was not satisfactory for deutereium labeling since complete substitution of D for H was not readily achieved.

Khachaturov et al.[51] have investigated the exchange between alkylaluminum and titanium derivatives by reaction of Me_6Al_2 with $Ti(CD_3)_4$ in the mixed solvent system hexane-toluene-ether 10/5/1. The exchange was followed by ^2D nmr and shown to occur slowly at -75^o showing 25% exchange after 20 minutes in this solvent system in which the etherates are present. At room temperature it was noted that rapid decomposition occurred yielding titanium metal and titanium carbides.

Syntheses of Alkyllead Derivatives From Aluminum Species

Three studies have been reported dealing with the production of lead derivatives from aluminum alkyls. Fleischmann et. al.[52] studied the oxidation of ethylmagnesium halide and tetraethylaluminate at a lead anode in THF solution. The oxidations have been shown to give i/E curves with well-formed waves and conveniently long limiting current plateauxs, but the limiting currents are, however, inconvenient for preparative scale electrolysis due to the slow and rate controlling formation of alkylead compounds as seen in the following equations. A study of the oxidation potentials of the EtMgX and

$$\mathrm{PbEt} + \mathrm{AlEt_4}^- \xrightarrow[\text{high potential}]{\text{r.d.s.}} \mathrm{PbEt_2}^- + \mathrm{AlEt_3} \qquad (14)$$

$$\mathrm{PbEt_2}^- - e^- \xrightarrow[\text{low potential}]{\text{r.d.s.}} \mathrm{PbEt_2} \qquad (15)$$

$$\mathrm{PbEt_2} \xrightarrow[\text{fast}]{\mathrm{Pb} - pe^- + q\mathrm{AlEt_4}^-} \mathrm{PbEt_4} + \mathrm{PbEt} \qquad (16)$$

$\mathrm{AlEt_4}^-$ show the Mg-C bond to be much weaker than the corresponding Al-C bond. Indeed, the $\mathrm{Et_3Al}$ does not oxidize within the potential range accessible on a lead electrode.

The reaction between $\mathrm{Me_3Al}$ and yellow lead oxide has been studied and shown to react as indicated in **17** at elevated temperatures.[53] As indicated,

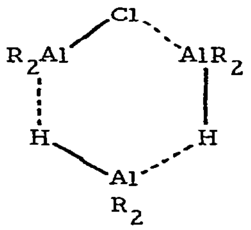
$$4\mathrm{Me_3Al} + 2\mathrm{PbO} \longrightarrow \mathrm{Me_4Pb} + \mathrm{Pb} + 2(\mathrm{Me_2Al})_2\mathrm{O} \qquad (17)$$

this reaction does not lead to complete conversion of the aluminum methyl groups to tetramethyllead. Under the most favorable conditions only 25 to 28% is converted to the lead species with most of the remainder in the form of bis(dimethylaluminum)oxide. The reaction mechanism with PbO was discussed and it was also shown that the reaction was inhibited by the presence of Lewis bases.

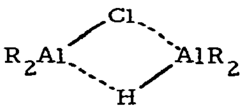
$PbMe_4$ was formed from Me_2AlCl and PbS in the presence of Lewis bases whose activity decreased in the order KCl >dioxane > KBr >NaF.[54] The influence of solvent (xylene, n-decane, tetraline) temperature (80 - 135°) and the molar ratios of the reactants on the yield of $PbMe_4$ was determined. The maximum yield of 39% was obtained at 110° with a reaction time of 1 -2 hours with 2:1:1 Me_2AlCl:PbS:KCl.

Bridged and Complex Organoaluminum Derivatives

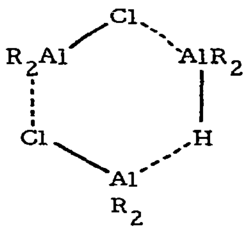
Eisch and Rhee[55] have reported nmr data which supports the formation of mixed bridged systems and have proposed the structures indicated in **XXXV**, **XXXVI** and **XXXVII** for the species formed when diisobutylaluminum hydride



XXXV



XXXVI



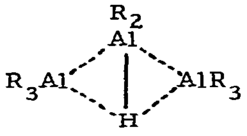
XXXVII

and chloride are mixed. All three species appear to be present in the mixture but **XXXV** appears to be the most stable form.

They[56] also examined the formation of the mixed i-BuAl-AlH systems by study of the nmr resonance of the hydride and by study of the Al-H stretching frequency. They have shown that the dimer $(i\text{-}Bu)_5Al_2H$ and the trimers $(i\text{-}Bu)_8Al_3H$ and $(i\text{-}Bu)_7Al_3H_2$ exist. In addition to the normally postulated ring structures which are found for systems of this type, they have proposed structures **XXXVIII** and **XXXIX** which have open bridge bonds and possibly Al-Al bonding. Support for these structures was based on the unusually low Al-H

$R_2Al{-}H\text{----}AlR_3$

XXXVIII



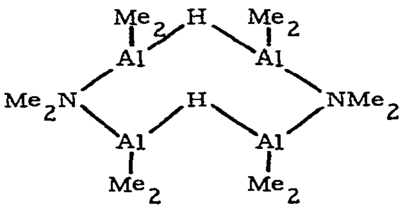
XXXIX

stretching frequency (1350 - 1450 cm^{-1}) as opposed to the normal range of 1675 - 1925 cm^{-1} observed for hydride bridged aluminum species.

The reaction of dimethylaminoborane and trimethylaluminum has been studied and shown to yield a variety of products as indicated in 18.[57] Various

$$6Al_2Me_6 + 2(Me_2NBH_2)_2 \longrightarrow Al_4Me_8(NMe_2)_2H_2 + (Me_2NAlMe_2)_2 + 2(Me_2AlH)_3 + 4BMe_3 \quad (18)$$

reaction paths leading to these products have been considered with a proposed reaction sequence leading to the formation of $Al_4Me_8(NMe_2)_2H_2$. The latter compound has been extensively studied and both the ir spectrum and preliminary X-ray data have been reported. The proposed structure is indicated in XL



XL

which contains 4 Al, 2 N and 2 H atoms forming an eight-membered ring.

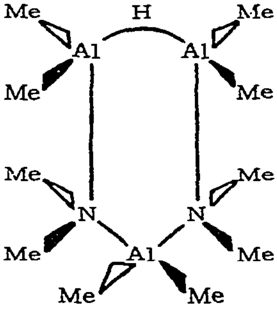
The exact nature of this structure awaits the report of the complete X-ray structural determination.

In a subsequent paper Glore and Schram[58] have investigated the reactions of $Al_4Me_8(NMe_2)_2H_2$ with NMe_3 and found that the reaction occurs in two ways as indicated in 19 and 20. The structure of $Al_3Me_6(NMe_2)_2H$ shown

$$Al_4Me_8(NMe_2)_2H_2 + 2NMe_3 \longrightarrow (Me_2AlNMe_2)_2 + 2Me_2AlHNMe_3 \qquad (19)$$

$$Al_4Me_8(NMe_2)_2H_2 + NMe_3 \longrightarrow Al_3Me_6(NMe_2)_2H + Me_2AlHNMe_3 \qquad (20)$$

in XLI was proposed on the basis of the physical and spectroscopic properties



XLI

of the molecule. Reaction with NH_3 led to Me_2AlNH_2 and other products while reaction with Me_2O also led to cleavage of the ether and production of $(Me_2AlOMe)_3$. PMe_3 did not appear to react or cause rearrangement of $Al_4Me_8(NMe_2)_2H_2$. The stability and decomposition of this derivative were discussed in some detail.

Ashby and Shwartz[59] have examined the reaction of $LiAlH_4$ with n-BuMgBr and have found that this reaction proceeds according to the following sequence of steps. They also studied the stability of these derivatives and found that

$$LiAlH_4 + 6n\text{-}BuMgBr \longrightarrow 2n\text{-}BuMgBr + 2MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}Bu)_4 \quad (21)$$

$$LiAlH_4 + 4n\text{-}BuMgBr \longrightarrow 2MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}Bu)_4 \quad (22)$$

$$LiAlH_4 + 3n\text{-}BuMgBr \longrightarrow MgH_2 + LiBr + 1/2MgBr_2 + BrMgAl(n\text{-}Bu)_3 \quad (23)$$

$$LiAlH_4 + 2n\text{-}BuMgBr \longrightarrow MgH_2 + BrMgAlH_2(n\text{-}Bu)_2 + LiBr \quad (24)$$

$$MgH_2 + BrMgAlH_2(n\text{-}Bu)_2 \longrightarrow BrMg_2AlH_4(n\text{-}Bu)_2 \quad (25)$$

$$LiAlH_4 + n\text{-}BuMgBr \longrightarrow n\text{-}BuMgAlH_4 + LiBr \quad (26)$$

$$n\text{-}BuMgAlH_4 \longrightarrow HMgAlH_3(n\text{-}Bu) \quad (27)$$

for $HMgAlH_3R$ the derivatives are stable if R = Et or n-Bu, but for R = Me, Ph or sec-Bu it disproportionates to yield MgH_2 and $Mg(AlH_3R)_2$.

In a subsequent paper, they showed that the following reactions occurred.[60]

$$RMgAlH_4 \xrightarrow[\Delta]{} HMgAlH_4 + \text{olefin} \quad (28)$$

$$RMgAlH_4 + H_2 \xrightarrow[\Delta]{} HMgAlH_4 + RH \quad (29)$$

$$RMgAlH_4 + MH \longrightarrow MR + HMgAlH_4 \quad (30)$$

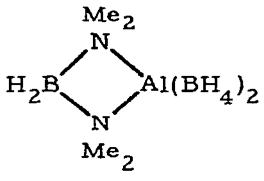
Keller[61] has studied the reaction of B_2H_6 with trimethylaminealane and with dimethylaminealane. The reactions proceed as indicated in **31** and **32.**

$$Me_3N\cdot AlH_3 + 1.5\ B_2H_6 \longrightarrow Me_3N\cdot Al(BH_4)_3 \quad (31)$$

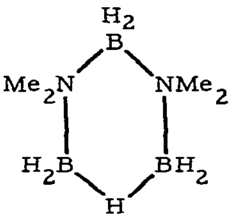
$$Me_2NAlH_2 + B_2H_6 \longrightarrow Me_2NAl(BH_4)_2 \quad (32)$$

The various equilibria possible were discussed and the influence of solvents and added Lewis bases on the reaction were discussed.

In a subsequent paper it was shown that diborane reacts with tris(dimethylamino)alane to yield a variety of products including two new materials with the structures proposed in **XLII** and **XLIII**.[62] The compounds were characterized by nmr, ir and mass spectral data, all of which were consistent with the above structure.



XLII

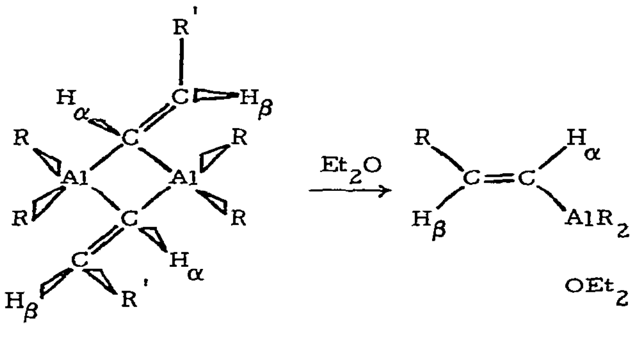


XLIII

In studies on the reactions of aluminum hydroborate [$Al(BH_4)_3$] with ethers, amines and the lithium salts LiH, LiD, LiCl and $LiBH_4$, Davies and Wallbridge[63] have shown that formation of both 1:1 and 1:2 complexes occur. These products have been characterized by ir and nmr studies and various reactions as well as the stabilities of products formed have been considered. Of particular interest are the formation of the species $HAl(BH_4)_2$ which shows rapid interchange of all hydrogen atoms.

Unsaturated Organoaluminum Compounds

A number of studies have been carried out which involve the interaction of metal atoms or M-X bonds with unsaturated groups. In one of these studies Zweifel and Clark[64] have examined the nmr spectra of a variety of vinyl alanes with trans substituents including n-butyl, cyclohexyl, t-butyl, phenyl, isopropyl and 1-cyclohexenyl. They concluded, on the basis of the change in chemical shift of the β-protons between the dimer and the etherated monomer, that extensive interaction occurred between the metal and the π system in the bridged dimer. This conclusion was further supported by the low frequency of the C = C stretch (approximately 1550 cm^{-1}) observed in vinyl alanes, and supports the structures indicated in XLIV and XLV. These findings were

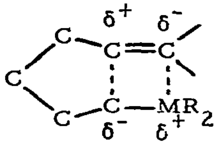


(33)

XLIV XLV

suggested as support for the generalization of the stabilization of vinyl bridged systems as initially proposed by Visser and Oliver for the vinyl gallium systems.

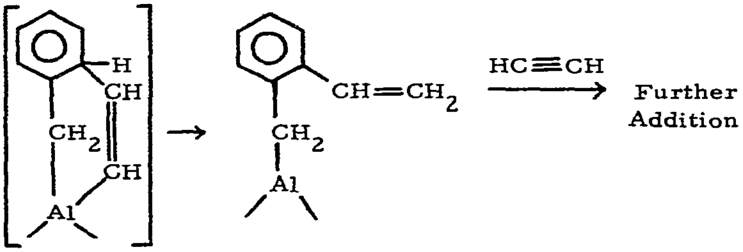
In another study, St. Denis et al.[65] have investigated the cyclization of 1-aluminahex-5-ene along with that of a number of other organometallic species to produce the corresponding methylenecyclopentane metal derivatives. It was proposed that the reaction goes through the internal addition as indicated in XLVI with a semi-polar interaction as well as a metal-π-electron interaction operating in a synergestic fashion to increase the ease of addition.



XLVI

Eisch and Amtmann[66] have reported a detailed examination of the hydroalumination and subsequent reductive oligomerization of t-butyl(phenyl)acetylene with diisobutylaluminum hydride. An examination of the products obtained under a variety of conditions led them to the conclusion that the regiochemistry of the hydrolumination observed was consistent with a polar mechanism, while that of the carbalumination requires a steric explanation. The nature of activated complexes and the possible role of π-complex intermediates in the reductive oligomerization of alkynes are discussed.

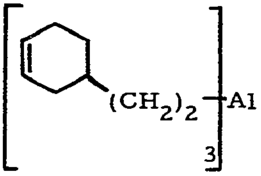
In more conventional investigations, tribenzylaluminum has been shown to react with acetylene via two routes, by normal addition to the Al-C bond and by substitution in the ortho position. These products may undergo further addition.[67] The predominant mode of reaction is by ortho addition as shown in 34.

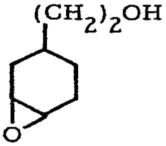


(34)

(i-Bu)$_3$Al reacts with 4-vinylcyclohexene to form 100% Me$_2$C = CH$_2$ and tris[2-(3-cyclohexene-1-yl)ethyl]aluminum (XLVII) which with H$_2$O gave 4-

ethylcyclohexene.[68] Oxidation of XLVII with oxygen gave approximately 100% 2-(3-cyclohexene-1-yl)ethanol (XLIX). Epoxidation of XLIX by $EtMe_2COOH$ in the presence of $MoCl_5$ gave 70% epoxide (XLVIII). Hydrogenation of XLIX over Pd gave 2-cycloxytetranol.


XLVII

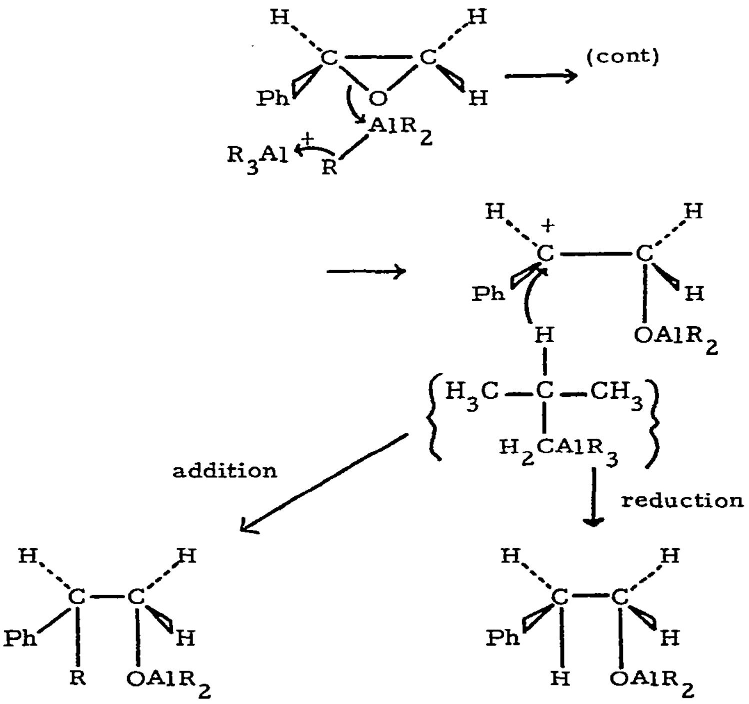

XLVIII

3-Methyl-1, 4, 6-heptatriene and (i-Bu)$_2$)$_3$Al formed 100% tris-3-methyl-4, 6-heptadien-1-yl-aluminum (nmr spectrum shown).[69] This was converted into 3-methyl-4, 6-heptadiene by acid hydrolysis, while aeration at 50 - 60° and hydrolysis gave 3-methyl-4, 6-heptadienol, characterized by its acetate, and by oxidation to the aldehyde. Similar reactions of 3-methyl-2, 5, 7-nonatriene gave 80% tris-4-methyl-5, 7-nonadien-1-ylaluminum, which gave 4-methyl-5, 7-nonadienol and the corresponding aldehyde.

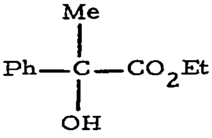
Reactions of Aluminum Derivatives with Carbon-Oxygen Bonds

A number of studies have appeared dealing with the reaction of organoaluminum derivatives with carbon-oxygen bonds. Namy and co-workers have presented a number of studies on epoxides. Triisobutylaluminum was shown to react with epoxides to give addition and reduction products.[70] Thus, styrene oxide was treated with two equivalents of $(i\text{-}Bu)_3Al$ at 35° to give 65% $PhCH(CH_2CHMe_2)CH_2OH$ and 24% $PhCH_2CH_2OH$; 3-phenyl-1, 2-epoxypropane gave 29% $PhCH_2CH(CH_2CHMe_2)CH_2OH$, 15% $Ph(CH_2)_3OH$ and 4% $PhCH_2CH(OH)Me$. Other reactions were also studied.

The reaction between trialkylaluminum compounds containing a hydrogen in the β position with respect to the metal and expoxides has been investigated.[71] It has been shown that these species are capable of reducing the epoxide or adding to it across the C - O bond. The ratio of addition/reduction is largely dependent on the epoxide considered and is essentially independent of the contact time; the ratio of the reactants, the temperature and the substitution on the aromatic part of the expoxide. The following mechanism has been suggested to account for this reaction.

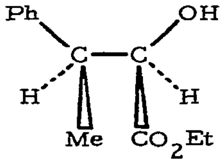


Abenhaim and Namy[72] have studied the product distribution for the reaction of Me_3Al with the epoxide $PhCH\underset{O}{-}CH - CO_2Et$. They examined both the cis and trans isomers and determined the effect of varrying the ratio of aluminum to expoxide. They observed 19% of L for reaction with the cis epoxide and none for the trans derivative. Both LI and LII were produced in all reactions in varying amounts.



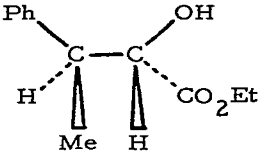
$$Ph-\overset{Me}{\underset{OH}{C}}-CO_2Et$$

L



Erthro

LI

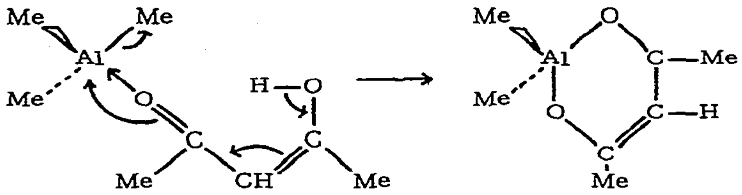


Threo

LII

$NaAlH_2[O(CH_2)_2OMe]_2$ in THF was shown more stereospecific, especially in dilute solutions, than in Et_2O, C_6H_6 or MePh,[75] probably because of the solvation effects of THF. A mechanism was proposed. Similar reduction of 3, 3, 5-trimethylcyclohexanone with $NaAlH(OR)[O(CH_2)_2OMe]_2$ (R = Me, Et i-Pr, Bu, sec-Bu, t-Bu, cyclohexyl and $-(CH_2)_2OMe$) in THF gave 76 - 81% of the trans 3, 3, 5-trimethylcyclohexanol.

Pasynkiewicz and Dowbor[76] have studied the reaction of Me_nAlCl_{3-n} with acetylacetone and have suggested that the reaction proceeds through initial formation of an adduct followed by elimination of methane or HCl as indicated in 38. One, two or three acetylacetonates are added to the aluminum depending on the initial ratio of Me_3Al/acetylacetone. In the mixed methylaluminum chlorides methane is eliminated first. If additional acetylacetone is present, then HCl is eliminated yielding the di- or trisubstituted product.

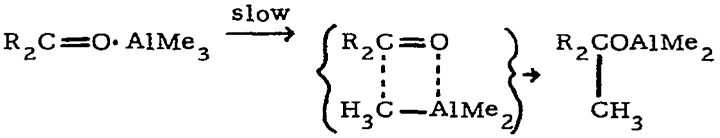


+ MeH↑ (38)

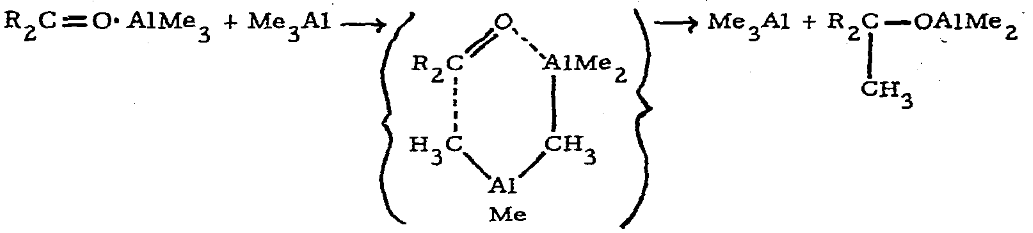
The effects of tetrabutylammonium halides on the reaction of Et_3Al with benzaldehyde have been investigated.[77] It was found that they increased the ratio of addition/reduction in the order Cl > Br > I while lowering the reactivity of the organoaluminum compound. This was interpreted in terms of complex

The trans-glycidic ester (LIII) was treated with $Me_3Al(1/2)$ to give 66% erythro-$PhCHMeC(OC)HCO_2Et$ (LI) and 22% threo-$PhCHMeC(OC)HCO_2Et$ (LII).[73] LIII and $Me_3Al(1/1)$ gave 41% LI and 37% LII. The cis-ester and $Me_3Al(1/2)$ gave 19% $PhCMe(OH)CO_2Et$, 27% LI and 8% LII.

Ashby et al.[74] have investigated the stereoselectivity of Me_3Al (and Grignard reagents) to 4-t-butylcyclohexanone. When the reaction was carried out in ether or THF predominantly equitorial attack occurred with formation of the axial alcohol (73%). When the reaction was carried out in hydrocarbon solvent with a Me_3Al:ketone ratio of 1:1, similar results were obtained. When the ratio is 2:1 or greater, a drastic reversal of the stereochemistry was observed with axial attach yielding approximately 90% of the equitorial alcohol. These differences were discussed in terms of the two reaction paths 36 and 37 and the effect of the solvent on the accessability of the organometallic



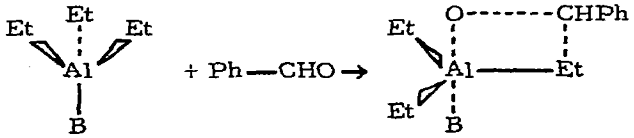
$$R_2C{=}O\cdot AlMe_3 \xrightarrow{\text{slow}} \left\{\begin{matrix} R_2C & = & O \\ \vdots & & \vdots \\ H_3C & — & AlMe_2 \end{matrix}\right\} \rightarrow \begin{matrix} R_2COAlMe_2 \\ | \\ CH_3 \end{matrix} \qquad (36)$$



(37

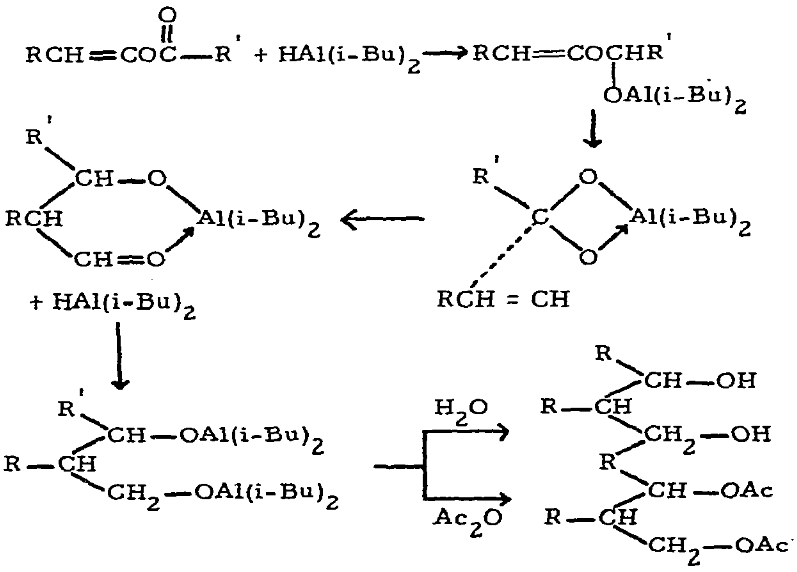
species.

In another study the reduction of 3, 3, 5-trimethylcyclohexanone with formation and its influence on the transition state as indicated in 39.

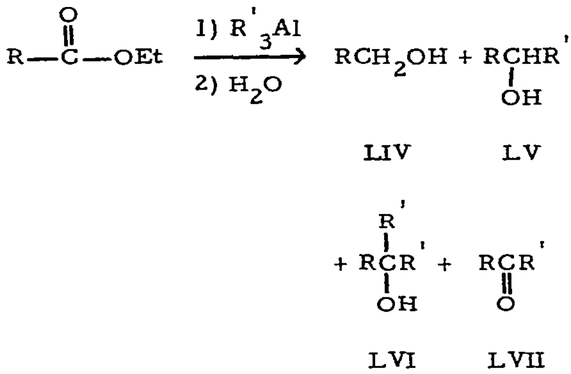


(39)

Warrell et al.[78] have shown that $HAl(i\text{-}Bu)_2$ react with aldoenol esters to yield aluminum compounds which on hydrolysis give 1, 3-diols. Acetolysis gave rise to the 1, 3-diacetates in about 50% yield. The proposed reaction scheme for these processes is indicated in 40.



Abenhaim and Namy[79] have studied the reaction of Me_3Al, Et_3Al and $(i\text{-}Bu)_3Al$ with esters and have shown that the products formed are a function of both the ester to aluminum ratio and the alkyl group on the aluminum. The products formed are indicated in **41**. **LV** and **LVI** were predominate for $R' =$ Me, Et while **LIV** and **LV** were the major products for $(i\text{-}Bu)_3Al$.

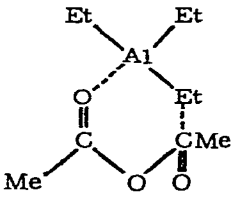


$$R{-}C({=}O){-}OEt \xrightarrow[2)\ H_2O]{1)\ R'_3Al} RCH_2OH + RCH(OH)R' + RC(R')_2OH + RC({=}O)R'$$

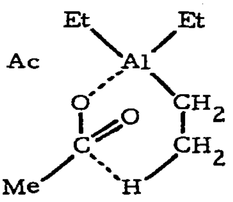
LIV LV

LVI LVII

The reaction products from Et_3Al and Ac_2O were tabulated as C_2H_4, C_2H_6, EtOAc, MeEtCHOAc, MeEtC = CHMe, as well as hydrolysis products including $Al(OH)_3$, AcOH, Et_2MeCOH and C_2H_6 from several runs of equimolar mixtures of these reactants.[80] The reaction was exothermic when started at room temperature in hexane or benzene and developed a color indicative of complex formation. Similar reaction results were tabulated for Et_2AlOR (R = Me, Et, i-Pr, <u>sec</u>-Bu, t-Bu, Me_2EtC). The results indicated formation of a complex (**LVIII**) which decomposes hetrolytically into MeCOEt



LVIII



LIX

or AcH and C_2H_4. The carbonyl compounds then enter further reactions with R_3Al. R_2AlOR and Ac_2O react at the OR groups and form AcOR and Et_2AlOAc. Et_2AlOR forms a 2/1 complex with Bz_2O_2 which decomposes homolytically and forms but 20 - 30% AcOR.

Meisters and Mole[81] have reported that exhaustive methylation of tertiary alcohols to alkanes, ketones to gem-dimethyl and carboxylic acids to t-butyl compounds can be effected by treatment with Me_3Al at approximately 120° for prolonged periods. The reactions may lead to rearrangement and are unsatisfactory for higher alkylaluminum compounds due to the side reactions which occur. Details of the methylation reaction were discussed.

Inoue and Yokoo[82] have investigated the reaction of CO_2 with $(i\text{-}Bu)_6Al_2$ and with $(Et_2AlNEt_2)_2$ in toluene solution. They noted that addition of bases reduced the rate of reaction with $(i\text{-}Bu)_6Al_2$ while these bases accelerated the addition of the Al-N bond to CO_2. The factors influencing these reactions were discussed.

Formation and Reactions of Compounds Containing Al-X Bonds ($X = -NR_2$, $-SR$, $-SiR_3$, -I, -Cl, etc.)

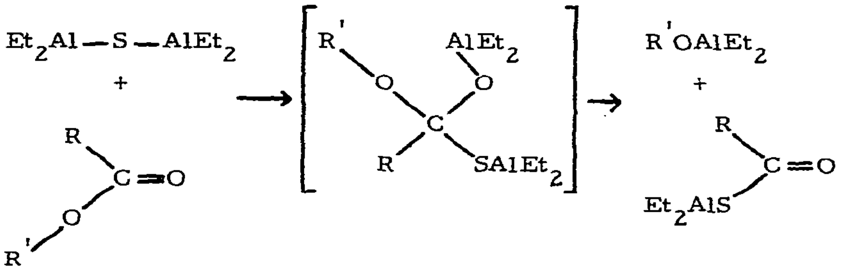
The dimethyl amine adducts of Et_2AlI were prepared as indicated in 42.[83]

$$Et_3Al + Me_2NH_2I \longrightarrow C_2H_6 + Et_2IAl{:}NHMe_2 \qquad (42)$$

Pyrolysis of the adduct led to the elimination of ethane and the isolation of bis-μ-dimethylamido-bis(ethyliodoaluminum). The compounds were studied by nmr, ir, mass spectroscopy and the molecular weights were determined indicating the monomeric and dimeric degrees of aggregation.

$$Et_2IAl{:}NHMe_2 \xrightarrow{140^{\circ}} [EtIAlNMe_2]_2 \qquad (43)$$

Hirabayashi et. al.[84] have investigated the reaction of bis(diethylaluminum)sulfide with organic esters and have observed the formation of stable 1/1 adducts. Elimination of diethylaluminum alcoholate was observed when large substituents were present in the ester. The reaction is best described by equation 44. A similar elimination of the alcoholate was observed on reaction of Et_2AlX ($X = SEt, NMe_2$) with esters to give the corresponding thioesters or amides. The 1/1 adducts were characterized by nmr, ir and boiling points.


(44)

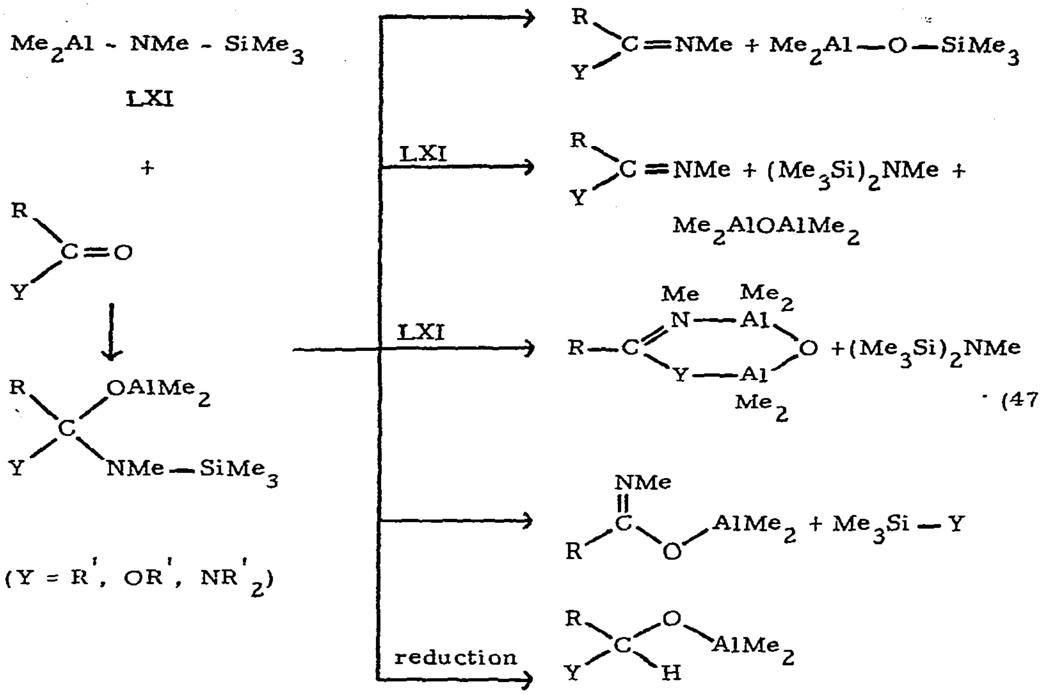
LX

A series of derivatives of the type $R_2Al\text{-}X\text{-}SiMe_3$ have been prepared by the reactions indicated in 45 and 46.[85] These derivatives have been characterized by their spectra and by other physical measurements.

$$Me_3SiCl + H_2X \xrightarrow[\text{in ether}]{\text{amine}} Me_3SiXH + \text{amine}\cdot HCl \qquad (45)$$

$$Me_3SiXH + R_3Al \xrightarrow[\text{benzene}]{0 - 80^{\circ}} R_2Al - X - SiMe_3 + RH \qquad (46)$$

Their reactions with a variety of ketones, esters, amides and isocyanates have been examined and have been classified according to the five reaction types indicated in 47.



(47)

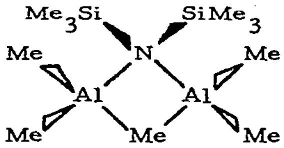
It has been shown that reaction of phenyl isocyanate (PhNCO) and Et_2AlOR (R = Me, Et, i-Pr, t-Bu and benzyl) in either equimolar or 3:1 ratios gave mainly Et_2Al derivatives of N-phenyl carbamate esters, in contrast to the corresponding reactions with Et_2AlNMe_2 or Et_2AlSEt which gave primarily trimeric products.[86]

The diethylaluminum allophanate, $[PhN(AlEt_2)COHPhCO_2R]$ was found to be unstable, decomposing to the carbamate and isocyanate. The mechanisms for these reactions were discussed.

Wiberg et. al.[87] have investigated the reactions of Me_2AlY (Y = Me, Cl, I) with bis(triorganosilyl)amines $(R_3Si)_2NX$ (X = H, Cl, Na) and have shown that initially Lewis acid-base adducts are formed. These decompose on heating with elimination of the XY molecule to yield either $(Me_3Si)_2NAl_2Me_5$

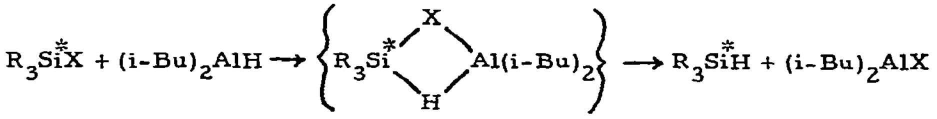
or $(Et_3Si)_2NAlMe_2$. If the temperature is increased, $(Me_3Si)_2NAl_2Me_5$ reacts with $(Me_3Si)_2NH$ to yield $[(Me_3Si)_2N]_2AlMe$. The reaction can be reversed by addition of Me_3Al but cannot be driven to yield $Al[N(SiMe_3)_2]_3$. The compounds were characterized by their melting points, molecular weights and nmr spectra.

Wiberg and Baumeister[88] have studied the nmr and mass spectra of $(Me_3Si)_2NAl_2Me_5$ and concluded from these studies that the mixed bridged species shown in LXII is the stable form. This was said to represent the most stable mixed bridged species so far observed showing stability on the nmr time scale until approximately 100°.



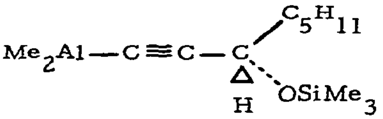
LXII

A variety of potentially useful reactions have been developed either for the production of optically active compounds or for stereospecific introduction of groups into optically active systems. Sommer et. al.[89] have investigated the use of $(i\text{-}Bu)_2AlH$ for the reduction of optically active silicon derivatives and have shown retention occurs for a large number of cases, including cases where inversion normally occurs with $LiAlH_4$. On this basis they proposed the reaction proceeds as indicated in 48 with a bridged transition state leading to retention of configuration.



(48)

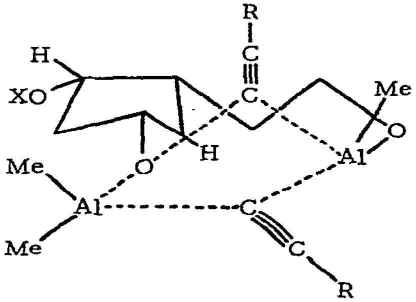
Fried et. al.[90] used (S)-(-)-3-silyloxy-1-octynyldimethylalane (LXIII)



LXIII

in their preparations of the E and F series of prostaglandins as a means of introduction of the optically active eight-carbon side chain.

In a subsequent paper, in an effort to improve the regiospecific epoxide opening with acetylenic alanes in their synthesis of E and F prostaglandins, they reasoned that location of an oxygen donor in a suitable location relative to the epoxide would complex the alane and result in a much higher specificity of the reaction.[91] It was found that the postulate led to the desired result, but only when a strong Al-O bond was produced by reaction with an alcohol rather than simple adduct formation by an acetal. They proposed the following intermediate in the successful synthesis with the desired regiospecificity.



LXIV

Nagata et. al.[92] have developed two methods for hydrocyanation. The first involved the reaction of a mixture ($R_3Al \cdot HCN$), method A, with α, β-

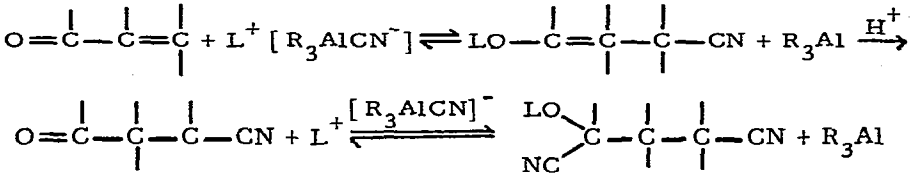
unsaturated ketones and the second, method B, involved the reaction of R_2AlCN with the α-enone. Both of these reactions are carried out at or below room temperature with the first, A, normally run in THF while the second, B, may be run in a wide variety of solvents but preference is given to the reaction in nonpolar media such as benzene.

A veriety of studies were carried out to illucidate the mechanism of these reactions and explore their utility in chemical synthesis. Studies on the factors which influenced the rate of reaction and the fact that the isomer product ratios in method A led to the conclusion that this procedure was a catalytic process with regard to R_3Al, however, reasonable rates and yields required use of much larger quantities of R_3Al. This also suggested that the products formed were kinetically controlled. In method B, it was shown that equal molar quantities of the substrate and R_2AlCN were required and further it was shown that the product ratio was time dependent. This led to the conclusion that the reaction was reversible and one could preferentially obtain the thermodynamically favored product. The two mechanisms proposed are shown in the following schemes. In mechanism A, the first steps appear to be those shown in 49 and 50. In reaction with the α-enone, it appears

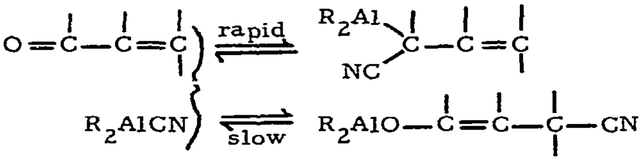
$$2R_3Al \rightleftharpoons [R_2Al]^+ + [R_4Al]^- \qquad (49)$$

$$R_3Al + HCN \rightleftharpoons H^+ + [R_3AlCN]^- \qquad (50)$$

this function is activated by the cationic species R_2Al^+ followed by attack of the $[R_3AlCN]^-$ at the β carbon yielding the enolate which is rapidly protonated. In method B, R_2AlCN initially attacks the carbonyl function of the α-enone in a concerted fashion with rapid formation of the 1, 2-product. The 1, 4-product is formed in the much slower reaction from the α-enone as indicated. All steps appear to be reversible.

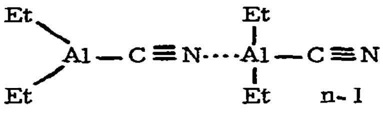


(51)



(52)

Further studies have also been carried out on these two hydrocyanation reactions which support the mechanisms outlined.[93] In these studies the structure of the reagent R_2AlCN was investigated and it was shown by equilioscopic molecular weight measurements that the average degree of aggregation of Et_2AlCN is 1.86 at 66° (0.038 and 0.076 M) in 13:1:THF/i-Pr_2O, 4.7 in benzene at 80° and 5.0 in i-Pr_2O at 68°. From these data and the observed ir C≡N stretching frequency (2211 cm^{-1}) the linear bridged structure shown in **LXV** was proposed. It was suggested that the reactive species in the



LXV

hydrocyanation process was monomer and that dimer or higher aggregates first underwent dissociation before reaction.

These two procedures have been extended successfully for hydrocyanation of the following α,β-unsaturated ketones to yield the corresponding β-cyano ketones; mesityl oxide, cyclohexenone, bi- and tricyclic enones, steriodal enones and to a wide variety of other systems including the preparation of α-cyanohydrins from carbonyl compounds of low reactivity.[94]

These workers have also explored the stereochemistry of these hydrocyanation reactions in substantial detail and have proposed reaction sequences which account for the stersochemistry of the products under various conditions.[95]

Hoberg and Kieffer[96] have studied the cyanoethylation of the C_{α}-H bond in the aluminum imides. They noted that the normally slow rate of the ketimine C_{α}-H addition to the C=C bond of the vinyl cyanide was greatly increased by addition of Lewis acids, making this a convenient procedure for the preparation of the mono- and dicyanoethylation products. They also noted a correlation between the chemical shift of the C_{α}-H with reactivity.

Systems Containing Aluminum Bound to Another Metal Either Directly or by Bridging

Several studies have appeared during the year in which aluminum is bound to another metal either directly or through a bridge system.

Of these studies, only two have been reported in which aluminum is directly bound to another main group element. Weibel and Oliver[97] have prepared $Li[Me_3AlSnMe_3]$ by reaction of $LiSnMe_3$ with Me_3Al. The compound is quite unstable decomposing to $LiAlMe_4$, Me_4Sn and $Li[Sn(SnMe_3)_3]$. The parent derivative was identified by the coupling constants $^2J_{SnCH} = 24.5$ Hz and $^3J_{Sn-AlCH} = 17.2$ Hz.

Durkin and Schram[98] have, in their studies on Lewis acid adducts of $(Ph_3P)_3Pt$, studied the reaction of Me_3Al with both the parent platinum derivative and $Ph_2Pt \cdot SiF_4$. They have observed a rather complex reaction yield paramagnetic products as well as simple adducts. They concluded that the adduct $Ph_3P \cdot AlMe_3$ was formed as one product and proved this by comparison with a sample prepared by direct reaction of Ph_3P and Me_3Al. The second product characterized was $Ph_2Pt \cdot 2AlMe_3$. This compound was found to be relatively unstable yielding new products either on standing or on warming to 60°. The decomposition products were not fully characterized.

A general investigation of the interaction of trialkylaluminum derivatives with metal carbonyl compounds has been reported.[99] It has been shown that Et_3Al and $(i\text{-}Bu)_3Al$ form complexes as indicated in Table I with the

TABLE I
R_3Al - Metal Carbonyl Adducts

Metal Carbonyl	R_3Al	Stoichiometry
$[(h^5\text{-}Cp)Fe(CO)_2]_2$	Et_3Al	1:1, 1:2
	$(i\text{-}Bu)_3Al$	1:1, 1:2
$[(h^5\text{-}Cp)Fe(CO)]_4$	Et_3Al	1:4
	$(i\text{-}Bu)_3Al$	1:4
$[(h^5\text{-}Cp)Ru(CO)_2]_2$	Et_3Al	1:1, 1:2
	$(i\text{-}Bu)_3Al$	1:1, 1:2
$[(h^5\text{-}Cp)Ni(CO)_2]_2$	Et_3Al	1:1
	$(i\text{-}Bu)_3Al$	1:1
$(h^5\text{-}Cp)_3Ni_3(CO)_2$	Et_3Al	1:1, 1:2
	$(i\text{-}Bu)_3Al$	1:1, 1:2
$[(h^5\text{-}Cp)Mo(CO)_3]_2$	Et_3Al	not determined
	$(i\text{-}Bu)_3Al$	"

bridging carbonyl groups in the metal carbonyl derivative indicated. It was further suggested that the ir stretching frequency of the complexed carbonyl (approximately 1600 - 1800 cm^{-1}) could be roughly correlated with the basisity of the carbonyl group. It was also noted that two equilibria in these systems were effected by adduct formation. These are the cis - trans ratio of isomers and the ratio of derivatives with and without bridging carbonyls.

Further studies were also reported on the formation of adducts of the form $Mo(phen)(PPh_3)_2(COAlR_3)_2$ where R = Et, i-Bu by addition of the metal alkyl to the transition metal complex.[100] In this study, Shriver and Alich provided information on the electronic and molecular structure of the complexes from studies on the uv spectra of the complexes. They observed a large blue shift in the charge transfer band which they associated with a decrease in energy of the $Mo(CO)_2$ π_{b1} molecular orbital. This resulted in additional $Mo \rightarrow CO$ back bonding and led to a greater separation of the energy state as indicated. They further noted that shifts in the charge transfer spectra may be used to establish the following order of electron pair acceptor strength, $Et_3Al > (i\text{-}Bu)_3Al > Me_3Ga$.

Chatt et. al.[101] have studied the formation of complexes between trimethylaluminum and a variety of bases including metal carbonyls and dinitrogen derivatives. They established the following order of donor strength from changes in the ^1H nmr spectra of various equilibrium mixtures: THF > trans[$Re(N_2)(PMe_2Ph)_4$] > trans-[$Mo(N_2)_2(dpe)_2$] > trans-[$W(N_2)_2(dpe)_2$] > trans-[$ReCl(N_2)(PMe_2Ph)_2\{P(OMe)_3\}_2$] > trans-[$ReCl(CO)(PMe_2Ph)_4$] > Et_2O > mer-[$OsCl_2(N_2)(PEt_2Ph)_3$], (dpe = $Ph_2PCH_2CH_2PPh_2$). They did not find correlation of the base strength with $\nu_{N\equiv N}$ or the ^1H chemical shift.

Aresta[102] has studied the reaction of Et_3Al with cis-$Mo(N_2)_2L_4$, cis-

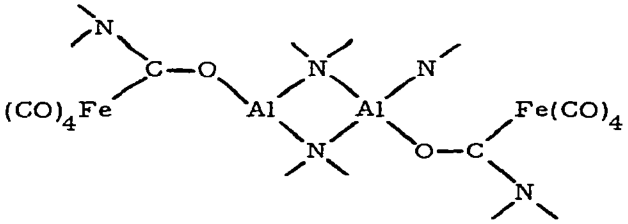
$Mo(CO)_2L_4$ (L = PMe_2Ph); trans-$Mo(N_2)_2L'_4$ (L$'$ = PEt_2Ph); trans-$Mo(N_2)_2dp$, cis- and trans-$Mo(CO)_2dp$ (dp = 1, 2-bis(diphenylphosphino)ethane). These transition metal compounds were reported to form 1:2 adducts with Et_3Al in which the aluminum was complexed to the CO or N_2 groups. The compounds were all relatively unstable, but some could be isolated in crystaline form. All were characterized by their ir spectra which showed a red shift of approximately 100 cm^{-1} for $\nu_{N\equiv N}$ and $\nu_{C\equiv O}$ and were shown by nmr studies to still retain the transition metal phosphine complex. The trans-$Mo(CO)_2dp_2$ complex was isomerized to the cis derivative by catalytic amounts of Et_3Al.

The metal carbonyl halides, $(CO)_5MnX$, $Cp(CO)_2FeX$, $(PMe_3)_2(CO)_2FeX_2$ (X = Cl, Br, I) and $(PMe_3)_2(CO)NiI_2$ react in solution to form adducts with AlX_3.[103] These adducts were characterized by their ir spectra and have been formulated as halogen donor-acceptor complexes $L_n(CO)_mMX \cdot AlX_3$ rather than carbonyl adducts as noted in the previous work.

Petz and Schmid[104] have reported the formation of a metal carbene complex in reaction 53 in which aluminum derivatives may interact with transition metal carbonyl compounds. The nmr, ir and Mossbauer spectra were

$$2Fe(CO)_5 + [(Me_2N)_3Al]_2 \longrightarrow [(CO)_4FeC(NMe_2)OAl(NMe_2)_2]_2 \qquad (53)$$

interpreted in terms of the structure given in **LXVI**. This shows another



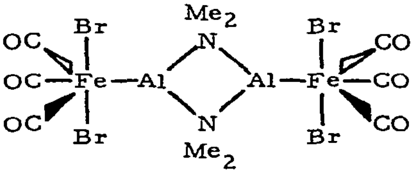
LXVI

manner in which aluminum derivatives may interact with transition metal carbonyl compounds.

Petz and Schmid[105] have also investigated the formation and reactions of compounds which contain the group Al-NMe_2 bonded to iron by aluminum. The preparation was effected as indicated in 54. The structure proposed for

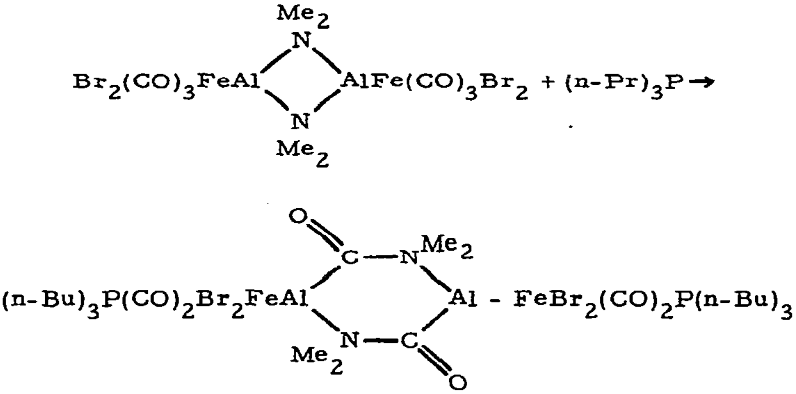
$$Fe_3(CO)_{12} + (Me_2NAlBr_2)_2 \longrightarrow (CO)_3[Me_2NAl]FeBr_2 + CO + Fe(CO)_5 \quad (54)$$

this compound based on mass spectral studies and spectroscopic data is indicated in LXVII. THF reacts with it forming the coordinated compound

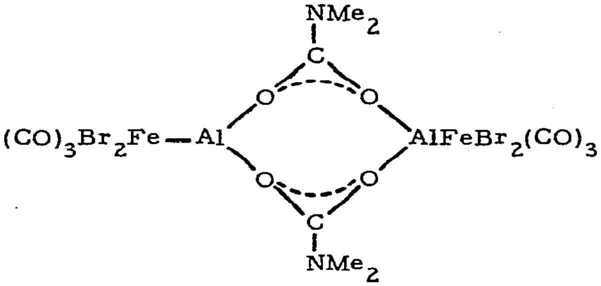


LXVII

$(CO)_3Br_2FeAl(NMe_2)THF$. $(n\text{-}Bu)_3P$ reacts with it to displace a CO molecule which is inserted as seen in 55. Insertion of CO_2 also occurs leading to the product shown in LXVIII.



(55)

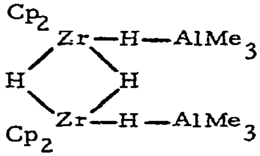


LXVIII

Schmid and Batzel[106] have examined the reaction of $Br_3Al \cdot NEt_3$ and $AlBr_3$ with $Co_2(CO)_8$. These reactions led to the cluster compounds $Co_3(CO)_9COAlBr_2 \cdot NEt_3$ and $Co_3(CO)_9COAl_2Br_5$ respectively. Reaction of $AlBr_3$ via the addition compound $Co_2(CO)_8 \cdot AlBr_3$ allows conclusions to be drawn concerning the mechanism of formation of the cluster derivative.

$$7Co_2(CO)_8 + 4Br_3AlNEt_3 \longrightarrow 4Co_3(CO)_9COAlBr_2NEt_3 + 16CO + 2CoBr_2 \qquad (56)$$

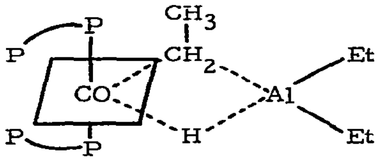
Wailes et. al.[107] have reacted Cp_2ZrH_2 with Me_3Al in benzene at room temperature and have obtained a novel compound with the proposed structure indicated in **LXIX** in which there are Zr-H-Zr and Zr-H-Al bridge bonds. This structure was proposed on the basis of analysis, nmr and ir data and is consistant with the known behavior of zirconium hydride derivatives. The compound is thermally unstable and undergoes decomposition



LXIX

with elimination of methane. The hydrogen is obtained from the hydride ion as shown by dueterium labeling at this position yielding DCH_3.

Another system in which Al-H-M bridging was proposed is the complex catalytic system $CoCl_2$/1, 2-bis(diphenylphosphino)ethane/Et_3Al in dichloroethane.[108] It was found this system shows high activity and selectivity for the production of cis-1, 4-hexadiene from butadiene and ethylene. A mechaism for this was discussed and a structure for the active catalyst was proposed which incorporates an octahedral complex of cobalt bridged to the aluminum as indicated in LXX.



LXX

Lardicci et al.[109] have reported a detailed study and procedure for the displacement reaction between $(i\text{-}Bu)_3Al$ and vinylidene olefins in the presence of Co(II), Ni(II) and Pd(II) complexes, containing dissymmetric ligands, which leads to optically active alkylaluminum derivatives. They have shown that the extent of asymmetric induction is dependent on the structure of the olefin and on the nature of both the ligand and the transition metal in the catalytic complex.

Hirabayashi and Ishii[110] have reported the synthesis of a variety of compounds containing the Al-X-Ni linkage via the reaction indicated in 57.

$$2R_2AlX + Ni(COD)_2 \longrightarrow (R_2AlX)_2Ni(COD) + COD \tag{57}$$

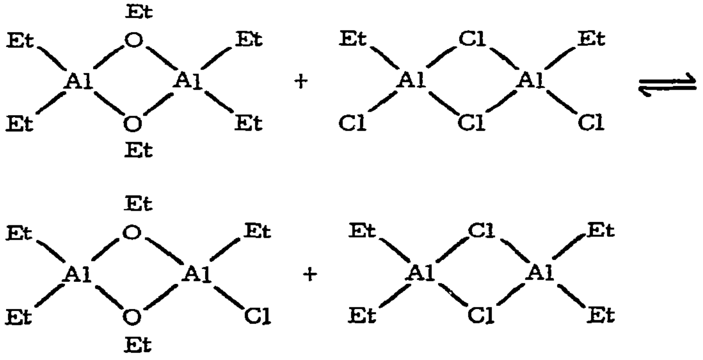
COD = cyclooctadiene

LXXI $R = Me;\ X = SPh$
LXXII $R = Et;\ X = PPh_2$
LXXIII $(R_2AlX)_2 = (Me_2AlSCH_2)_2$

Products **LXXI** and **LXXII** were monomeric in benzene while **LXXIII** was too insoluble to permit measurement.

Reactions between Me_2AlSPh and $Ni(Acac)_2$ or $Ni^{II}(\pi\text{-}Cp)_2$ did not yield products corresponding to those indicated in reaction 57, but gave products with Ni-S bonds.

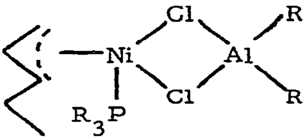
Su and Collette[111] have investigated a three component catalyst system, Al/Ni/P, for the synthesis of *trans*- and *cis*-1,4-hexadiene from ethylene and butadiene. Of particular interest to this review is the role played by the aluminum Co-catalyst. It was shown that the catalylic activity of the system using $Ni^{O}COD_2$ (COD = cyclooctadiene)/Ph_3P/R_nAlCl_{3-n} was enhanced as $n \rightarrow O$ with no effective catalytic activity when n = 2 or 3. This correlates with the Lewis acidity of the aluminum derivatives which decreases in the



(58)

order $AlCl_3 > RAlCl_2 > R_2AlCl > R_3Al$. It was also noted that other effective co-catalysts incorporated lower concentrations of R_2AlOR or R_2AlNR_2 even though these species were ineffective by themselves and also gave rise to increased trans/cis ratios of the products formed. This led to an analysis of the mixture of the aluminum system indicated in 58 by nmr techniques and the proposed equilibrium. Alternately there may also be chloride-alkoxide mixed bridged species present.

These authors also discussed the nature of the catalytic species and proposed structures of the type indicated in LXXIV involving halide bridged complexes and discussed proposed reaction mechanisms for the polymerization process.



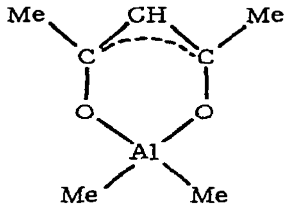
LXXIV

The activity of alkylaluminum catalysts in the alkylation of benzene or substituted benzenes with C_2H_4, $CH_2 = CHMe$, $Me_2C = CH_2$ or 1-octene increased in the order: $Et_3Al < Et_2AlCl < EtAlCl_2$.[112] The addition of $TiCl_4$ (10:1 Al-Ti) increased the yield of Me_2CHPh and the degree of conversion of benzene. The optimum conditions for preparation of Me_2CHPh from $CH_2 = CHMe$ and benzene were determined. Other complex catalyst systems were also studied.

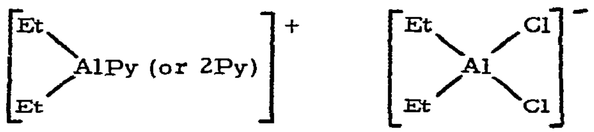
Armstrong et. al.[113] have carried out a theoretical calculation on Ziegler-type catalysts. The calculations on the titanium-aluminum-ethylene system were used to propose a path for the polymerization reaction in which it was unnecessary to have a vacant site on the titanium. It was further suggested that alkyl group could migrate on the surface of the catalyst system and it was proposed that the aluminum served no function other than to occupy coordination sites.

Aluminum Alkyl Complexes and Addition Compounds

Several studies have been reported on the properties and reactions of addition compounds of aluminum derivatives. For example, it has been shown that addition of a Lewis base to Me_2AlAA causes an irreversible disproportionation as indicated in 59.[114]

2  $+ 2Py \rightarrow Al(AA)_3 + 2Me_3AlPy$ (59)

Matsubayashi et. al.[115] have investigated the complexes formed between Et_3Al, Et_2AlCl and $EtAlCl_2$ and 4-methyl, 2, 6-dimethyl-, and 2, 4, 6-trimethylpyridine by nmr and conductometric studies. On this basis they concluded that in the move substituted derivatives ionic species of the form **LXXV** were



LXXV

present in solution along with the normal adducts and the uncomplexed aluminum derivatives when halide was present. For Et_3Al only normal complexes were obtained. Variable temperature nmr studies indicated exchange was occurring but no quantitative data were reported.

The complexes formed between dimethylacetamide, n-methylpyrrolidone, and dimethylpropionamide with Et_3Al, $(i\text{-}Bu)_3Al$ and n-octylaluminum have been investigated by observation of the ir spectral changes of the carbonyl group.[116] A discussion of the equilibrium for these reactions has also been presented.

Kagawa and Hashimoto[117] have presented their results on a brief study of the adducts formed between Et_3Al and Et_2AlCl and the phosphines $Ph_2P(CH_2)_nPPh_2$. Their data on the nmr spectra of these systems indicate that 2:1 complexes are formed except for $Et_3Al/Ph_2PCH_2PPh_2$ which forms both 1/1 and 2/1 complexes. They also discussed the changes in chemical shift and coupling constants in terms of the electronegativity of the groups.

The nmr spectra of the complexes of PhNMe(i-Pr) (LXXVI) and $PhCHMeNMe_2$ with $AlCl_3$, $MeAlCl_2$ and Me_3Al were determined in benzene and toluene.[118] The difference between the chemical shifts in the free amines and in the complexes were given. The diastereotopic methyl groups in the complexes were anisochronous. The complexes of LXXVI with $MeAlCl_2$ and Me_3Al were unstable in solution at room temperature on the nmr time scale, and the rate of topomerization was independent of the inversion rate of N in the free amine.

The nmr spectra of protons and ^{27}Al are reported for $(i\text{-}Bu)_3Al$ complexes of EtOAc, Bu_2O, MeCN, Pyridine and $CH_2{=}CHCH_2OAc$.[119] The 1:1 complexes are very labile and have life times of approximately 10^{-2} seconds. $CH_2{=}CHOAc$ is displaced by the above RCN and RCO_2R from its complex with the R_3Al, but is able, in turn, to displace Bu_2O and $CH_2{=}CMeCO_2Me$.

1:1 adducts were prepared from $(i\text{-}Bu)_3Al$ and R_2O (R = i-Pr, Bu, $Me(CH_2)_4$, C_7H_{15}, $CH_2{=}CHCH_2$) as well as with THF, MeOPh, EtOPh, Ph_2O and $(PhCH_2)_2O$ and with 2 moles $(i\text{-}Bu)_3Al$ per mole of dioxane.[120] The adducts showed conductance in the 10^{-9} to 10^{-10} ohm^{-1} cm^{-1} range. The adducts did not ignite in air and reacted with H_2O smoothly without forming the insoluble residue which are common in hydrolysis of $(i\text{-}Bu)_3Al$. The *in situ* preparation of the adducts by the reaction of 2g atoms of Al and 3g atoms of Mg with 6 moles RX in the desired ether was unsuccessful. Although the reaction of Mg and Al with i-BuI in PhOEt at 80 - 85° did proceed, the product was a mixture of iodo and phenoxy derivatives of aluminum mixed with various Et and i-Bu derivatives. Bu_2O and $[Me(CH_2)_4]_2O$ also failed to yield $(i\text{-}Bu)_3Al$ in reaction of Mg, Al and RI as the reaction stopped at $Bu_2AlI\cdot OR_2$ stage.

Aluminumalkoxides and Related Compounds

$PhAl(OR)_2$ and Ph_2AlOR (R = i-Pr, Bu, t-Bu or C_7H_{15}) were prepared (50-99%) by treating Ph_3Al with ROH in Et_2O, ROLi with Ph_2AlCl or Ph_3Al with $Al(OR)_3$ in benzene.[121]

A variety of mixed group III metal isopropoxides containing aluminum have been prepared via reaction 60.[122] These materials and the corresponding mixed isopropoxides, $Al[Ga(i\text{-}PrO)_4]_3$, $Al[Al(i\text{-}PrO)_4]_3$ and $Ga[Al(i\text{-}Pr)_4]_3$ have also been obtained by heating the pure metal isopropoxides in the appropriate ratios. The compounds were characterized by spectroscopic measurements and by their molecular weights.

$$InCl_3 + KM(i\text{-}PrO)_4 \longrightarrow In[M(i\text{-}PrO)_4]_3 + KCl \qquad (60)$$

$$M = Al,\ Ga$$

Nmr spectra of double isopropoxides $[M'(M''(i\text{-}OPr)_4)_3]$ confirm a structure similar to that of tetrameric aluminum isopropoxide and show magnetic non-equivalence of methyl protons in the bridging as well as terminal isopropoxy groups.[123] Nmr parameters for the compounds study, $[Sc(Al(i\text{-}OPr)_4)_3]$ and $[In(Al(OPr)_4)_3]$, were reported.

In another study the preparation of sodium dihydro-bis(2-methoxyethoxy)-aluminate was described starting from Na, Al, H_2 and aluminum 2-methoxyethoxide or sodium tetrakis(2-methoxyethoxy)aluminate.[124]

Under anhydrous conditions, reaction of CF_3CO_2H with Al_2Cl_6, Ga_2Cl_6 and $InCl_3$ yielded $M(OCOCF_3)_3 \cdot 3Q$ (Q = pyridine, DMF, Me_2SO) and $M(OCOCF_3)_3 \cdot THF$.[125]

Ph_3SiOH reacted in benzene with Et_3Al to give $Ph_3SiOAlEt_2$.[126] Pyrolysis of this material at 250° gave C_2H_4, C_2H_6, C_6H_6, EtPh, $AlEt_3$, and C_4H_{10} while hydrolysis gave C_6H_6, $EtPh_2SiOH$, $PhSiEt_2OH$ and $Al(OH)_3$.

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