

## ALUMINUM

## ANNUAL SURVEY COVERING THE YEAR 1973

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1.	Introduction, Reviews and Books	264
2.	Structural and Spectroscopic Studies	264
3.	Fast Exchange Reactions and Related Mechanistic Studies	273
4.	Syntheses and Simple Reactions of Aluminum Compounds	275
5.	Bond Strengths and Stabilities of Complexes	278
6.	Alkylaluminum-Multiple Bond Reactions	279
7.	Reactions of Organoaluminum Derivatives with Ketones, Aldehydes and Related Species	285
	A. Reactions with Ketones	285
	B. Reactions with Aldehydes	291
8.	Reactions of Organonitrogen Compounds	298
9.	Oxygen and Mixed Bridged Species	301
10.	Physical and Chemical Properties and Reactions of Selected Aluminum Hydride Derivatives	303
11.	Syntheses, Properties and Reactions of $[AlR_4]^-$ Derivatives	305
12.	Transition Metal-Organoaluminum Derivatives	307
	A. Spectroscopic Studies	307
	B. Preparation and Characterization of Compounds	308
	C. $N_2$ and $O_2$ -Aluminum-Transition-Metal Complexes	312
13.	Aluminum Coordination Compounds	314
14.	Aluminum-Tin Bonded Compounds	317
15.	Miscellaneous Reactions	

## 1. Introduction, Reviews and Books

The literature on organoaluminum chemistry for 1973 is again extensive and in the present survey an effort has been made to cover all of the periodicals, but not the patent literature. The emphasis on the chemistry in the literature has changed to some extent with more work reported on compounds containing transition metals and with extensive studies reported on reactions of aluminum species with aldehydes and ketones. Again, extensive structural studies have appeared, but other areas are less well represented.

Special note should be taken of the book by Mole and Jeffery<sup>1</sup> which provides the most extensive review of organoaluminum chemistry available. This volume should serve as an excellent guide to the literature appearing up to 1971. The Chemical Society also has started an annual review series which covers aluminum chemistry with the first survey by Maher<sup>2</sup> having appeared in 1972.

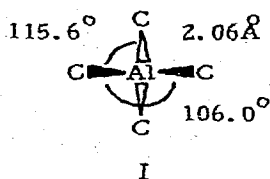
In addition to these surveys it might be noted that Mason<sup>3</sup> has dealt with the bonding in organoaluminum compounds in his review on metal-organic bonding and finally a review by Weidlein<sup>4</sup> has provided a survey of the species formed by  $\text{SO}_2$ ,  $\text{CO}_2$ , etc. which yield dimers containing 8-membered rings.

## 2. Structural and Spectroscopic Studies

The determination of the structures of organoaluminum compounds by X-ray diffraction techniques and the related spectroscopic studies have played a major role in the development of our understanding of the chemistry of these species.

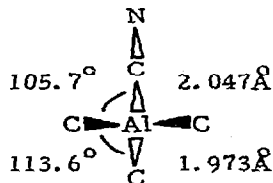
Atwood and co-workers<sup>5-8</sup> have reported a number of related studies which provide details of the environment around a pseudo-tetrahedral aluminum atom. The structures determined include that of  $\text{Rb}[\text{AlMe}_4]$ .<sup>5</sup> A diagram

the  $[\text{AlMe}_4]^-$  ion in this compound, determined from three dimensional X-ray crystallographic studies, is shown in I. It was found that the anion was a slightly



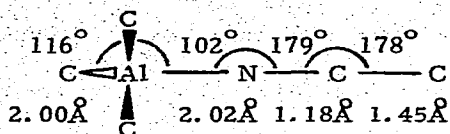
distorted tetrahedron with two independent angles of  $106.0(2)^\circ$  and  $115.6(3)^\circ$  and with carbon-aluminum bond lengths of  $2.006(8)\text{Å}$ . The  $\text{Rb}[\text{AlMe}_4]$  for this study was prepared by the thermolytic or photochemical decomposition of  $\text{M}[\text{Al}_2\text{Me}_6\text{N}_3]$  in an aromatic solvent which was said to yield the product quantitatively.

In a related study<sup>6</sup> the structure of  $\text{K}[\text{Me}_3\text{AlCN}]$  was determined from single crystal X-ray studies. A diagram of this anion is shown in II.



The monomeric unit  $[\text{Me}_3\text{AlCN}]^-$  has no crystallographic symmetry and the packing in the unit cell is such that the nitrogen atoms on three units approach the potassium atom to within  $3.11\text{Å}$ . The average aluminum-methyl carbon distance is  $1.971(7)\text{Å}$  while the Al-CN distance is  $2.047(7)\text{Å}$ . This lengthening was attributed to partial electron deficiency in the Al-CN carbon bond.

Atwood, Seale and Roberts<sup>7</sup> determined the structure of the acetonitrile adduct of trimethylaluminum,  $\text{Me}_3\text{Al}\cdot\text{NCMe}$ , from three dimensional X-ray diffraction studies. The structural features of the complex are shown in III.



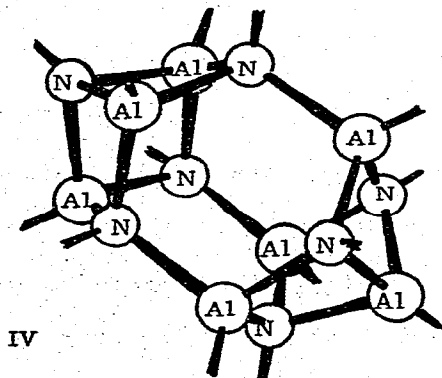
## III

Additional information also has appeared on the Al-N bond distance observed in  $\text{Cl}_3\text{Al}\cdot\text{NH}_3$  which was determined from gas phase electron diffraction studies. The value obtained for the Al-N bond distance is  $1.996\text{\AA}$  which is similar to the reported in the crystalline adduct. The Al-Cl distance is  $2.10\text{\AA}$  and the  $\text{AlCl}_3$  unit is nearly planar with the Cl-Al-Cl angle equal to  $118 \pm 1.5^\circ$ .

A full discussion of the previously reported structure of iododimethylaluminum trimethyl amine adduct has also appeared<sup>8</sup> (see Annual Survey, *J. Organometal. Chem.*, **62** (1973) 179).

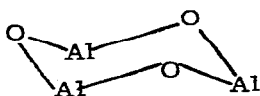
In all of these structures, it was found that the Al-C bonds were between  $1.95$  and  $2.02\text{\AA}$  and that the aluminum atom occupied a distorted tetrahedral environment in the molecule. Clearly these findings will be of use in future studies on the spectra and structures of these systems.

A wide variety of other structures also has been recorded. One of the more interesting of these is of the compound  $(\text{MeAlNMe})_7$  which was shown to exist in a cage form as determined by X-ray studies.<sup>10</sup> This is shown in IV.



All of the aluminum and nitrogen atoms are four coordinate with each bound to three sites in the cage and to one methyl group.

Another interesting sequence of structural studies which has appeared is that reported by Haaland, et al.<sup>11-13</sup> In the first of these they determined the structure of the trimeric molecule  $(\text{Me}_2\text{AlOMe})_3$  in the gas phase from electron diffraction studies.<sup>11</sup> The structure which they proposed, based on these investigations, is shown in V. It contains a non-planar ring of aluminum



V

and oxygen atoms with reported parameters of  $\text{Al-C} = 1.957$ ,  $\text{Al-O} = 1.851$ ,  $\text{O-C} = 1.436\text{\AA}$ ;  $\angle \text{Al-C-Al} = 117.3^\circ$ ,  $\angle \text{O-Al-O} = 103.2^\circ$  and  $\angle \text{Al-O-Al} = 125.8^\circ$ .

A related study on the infrared and Raman spectra of the  $[\text{Me}_2\text{AlOMe}]_3$  and of the deuteromethoxide also has been reported and assigned.<sup>12</sup> The results are in accord with those of the electron diffraction study. In the same paper, it was noted that the structure of the methylmethoxyaluminum could not be determined definitively from spectroscopic data.

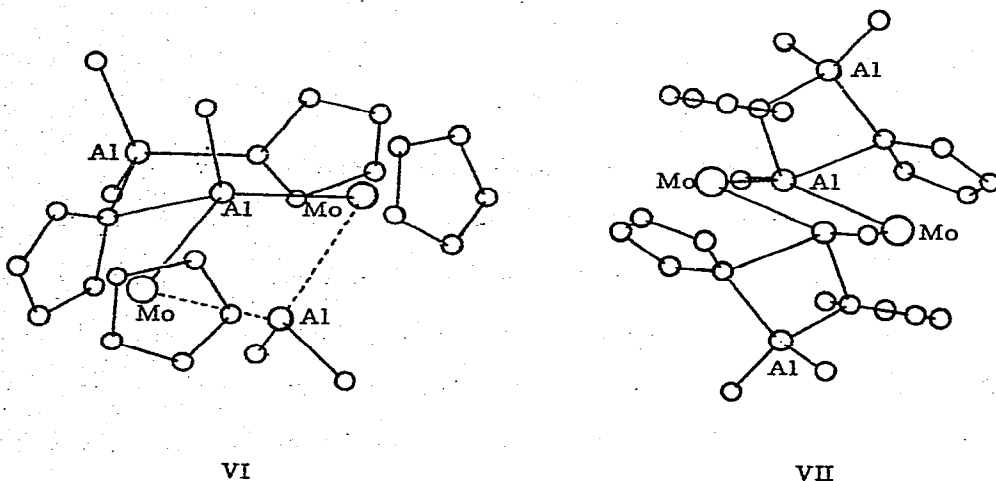
The report of the crystal structure of tris(acetylacetonato)aluminum(III) provides additional information concerning the Al-O bond distances observed in a nearly octahedral environment for comparison with the bridged Al-O distances in the alkoxides and related systems.<sup>14</sup>

Haaland, et al.,<sup>13</sup> also have determined the structure of the tetrameric molecule  $[\text{Me}_2\text{AlF}]_4$  in the gas phase by electron diffraction techniques and reported that the molecule has an eight-membered  $[\text{AlF}]_4$  ring of low symmetry. The parameters reported for this molecule are  $\text{Al-C} = 1.947(4)\text{\AA}$ ,  $\text{Al-F} =$

1.810(3) Å,  $\angle C-Al-C = 131.2(1.9)^\circ$ ,  $\angle F-Al-F = 92.3(1.2)^\circ$  and  $\angle Al-F-Al = 146.1(2.6)^\circ$  with the  $(AlF)_4$  ring puckered.

In this article they also gave a discussion of the factors which they felt affected the degree of association of compounds of the type  $R_2AlX$  ( $X = F, -OR, -NR_2, Cl, -SR$  and  $-PR_2$ ).

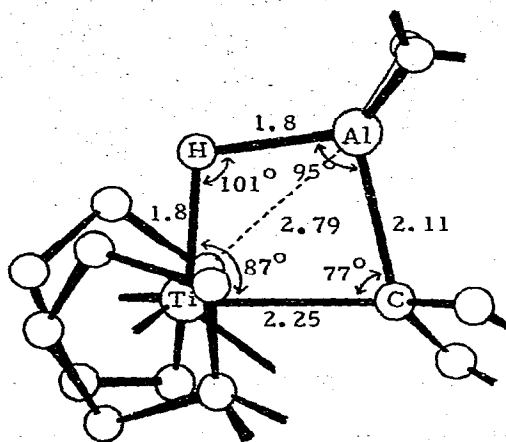
X-ray crystal structure determinations also have been reported for several compounds which contain both aluminum and a transition metal. Two of these are the novel molybdenum compounds shown in VI and VII prepared by



reaction of  $Cp_2MoH_2$  with  $Me_6Al_2$ .<sup>15</sup> These same authors also reported that a single compound was obtained on reaction of  $Me_6Al_2$  with  $Cp_2WH_2$ .

In both molecules the aluminum methyl systems have pairs of aluminum atoms with  $C_5$  rings which were formulated as  $C_5H_4$  by these authors. In each case there are two types of aluminum, one bound to two  $C_5$  rings and two methyl groups, while the other is bound to the same two  $C_5$  rings but to two Mo atoms and one methyl group giving rise to a 5 coordinate aluminum atom in each case.

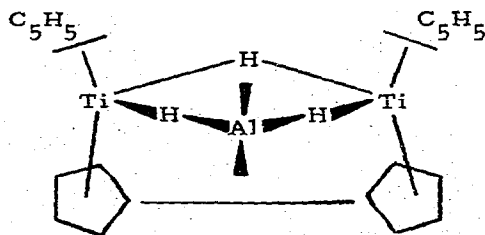
Another rather interesting compound is that reported by Tebbe and Guggenberger<sup>16</sup> which is shown in VIII. In this instance the aluminum is bound to the titanium by



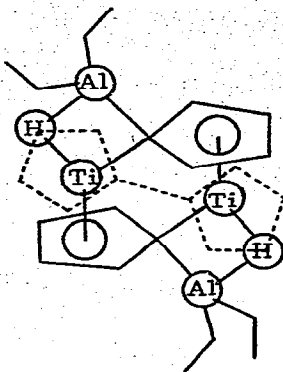
VIII

a hydride and by a  $C_5H_4$  bridge group. The location of the hydride bridge in this olefin polymerization catalyst was suggested from the observed locations of the other groups.

Guggenberger and Tebbe<sup>17</sup> also have determined the structures of two other complex species,  $[(\pi-C_5H_5)Ti]_2(H)(H_2AlEt_2)(C_{10}H_8)$  and  $[(C_5H_4)TiH-AlEt_2]_2(C_{10}H_8)$ . Diagrams of the essential features of these are shown in IX and X. Details of the reactions are given in Section 12.



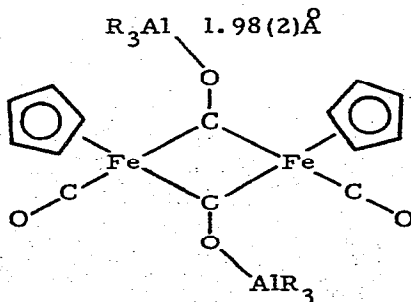
IX



X

Another class of compounds involving both transition metals and aluminum is clearly shown in the studies of Kim, et al.,<sup>18</sup> in their investigation of the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{-Al}_2\text{Et}_6$  system. They observed formation of a 1/1 adduct which could be isolated as a red air-sensitive crystalline material. The asymmetric stretching frequency of the bridging carbonyl was shifted  $112\text{ cm}^{-1}$  to lower energy. Infrared, molecular weight and NMR data all indicate that the adduct is partially dissociated in hydrocarbon solution.

A diagram of the structure determined from single crystal X-ray diffraction studies is given in XI and shows that in this instance the aluminum is bound to the transition metal moiety via coordination to the bridging carbonyl oxygen.

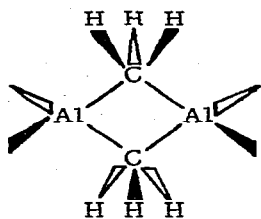


XI

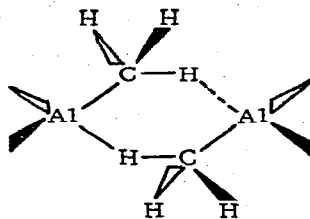


A wide variety of spectroscopic and theoretical studies have appeared which deal with the structure, bonding and equilibria for aluminum species.

In a continuation of the argument provoked by the suggestion that trimethylaluminum dimer was bonded through C-H bridging units, an infrared and Raman study of  $\text{Me}_6\text{Al}_2$  was reported<sup>19</sup> and it was stated that this study supported structure XII rather than XIII.



XII



XIII

In a discussion of the bonding in both electron deficient and electron precise compounds, Mason and Mingos<sup>20</sup> have suggested that metal-metal interaction plays an important role in the stability of the systems. They suggest, that for the electron deficient species, this interaction is bonding while for the electron precise compounds it is anti-bonding.

From CNDO/2 calculations, carried out by Grompen and Haaland<sup>21</sup> on  $\text{H}_3\text{Al}\cdot\text{NMe}_3$  and  $\text{Cl}_3\text{Al}\cdot\text{NMe}_3$  as well as on other species, it was found that charge transfer from the donor to acceptor increased as the substituents on the acceptor became more electronegative. The resulting net negative charge on the acceptor was carried by the substituents, while the resulting net positive charge on the donor was said to be carried by the methyl groups.

For aluminum both (sp) and (spd) basis sets were used. The (sp) set underestimated the stability of the aluminum complexes indicating them to be

unstable. The (spd) set grossly overestimated these values. Other parameters such as rotational barriers, dipole moments, bond distances and charge distributions were estimated.

Several experimental studies on the spectra of the simple alkylaluminum adducts have been reported. Mennier and Forel<sup>22</sup> reported the infrared and Raman spectra of the dimethylsulfoxide complexes  $\text{Me}_3\text{Al}\cdot\text{DMSO}$ ,  $\text{Et}_3\text{Al}\cdot\text{DMSO}$  and  $\text{Et}_2\text{AlCl}\cdot\text{DMSO}$  and of their deuterated homologues. Most of the fundamental vibrations were assigned and discussed. The compounds are all typical adducts with bonding of the DMSO to aluminum through oxygen.

Two studies on the NQR of complexes have been reported. The first by Dewar, et al.,<sup>23</sup> who reported the  $^{27}\text{Al}$  NQR spectra of a wide range of mono and dimeric aluminum complexes of the type  $\text{Me}_3\text{AlX}$  and  $(\text{R}'\text{R}''\text{AlX})_2$ . Measurements were interpreted in terms of the simple treatment of Townes and Dail which has been shown to account well for the observed trends.  $^{35}\text{Cl}$ ,  $^{75}\text{As}$ , and  $^{123}\text{Sb}$  NQR spectra for the appropriate complexes were reported.

For the species  $\text{Me}_3\text{Al}\cdot\text{B}$  adducts they observed a correlation of the bond strength with the quadrupole coupling constant and suggested that their observations indicated back donation for the ether complexes due to the far larger coupling constants observed for these adducts than predicted from their correlation based on the relative stability of these complexes.

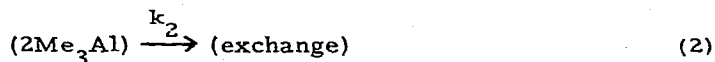
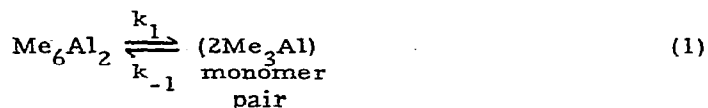
These arguments were extended to the bridged systems with  $\text{OMe}$ ,  $\text{OEt}$ ,  $\text{NMe}_2$ ,  $\text{R}$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{Ph}$  and  $-\text{C}\equiv\text{CPh}$  and it was suggested that little back donation between  $\text{Ph}$  or  $\text{Ph-C}\equiv\text{C-}$  and the aluminum atoms occurred.

Müller<sup>24</sup> gave a brief report on the  $^{14}\text{N}$  NQR spectra of a number of alkyl metal azides including those of aluminum. He discussed the results in terms of the inductive and association effects. He also noted that the three resonance peaks expected for the covalent azides were not always observed.

Other spectroscopic studies on transition-metal-organoaluminum derivatives are presented in Section 12 along with the chemistry of these species.

### 3. Fast Exchange Reactions and Related Mechanistic Studies

Investigation of fast exchange reactions involving organoaluminum derivatives has been quite limited during the past year, however, the work which has appeared provides some new insight into these reactions. Jeffery and Mole have restated their position regarding the self exchange of trimethylaluminum and its exchange with other organometallic species.<sup>25</sup> The mechanism for exchange which they support differs from that of Williams and Brown and of Matteson [Annual Surveys, J. Organometal. Chem., 62 (1973) 190] in that rapid self exchange is said to occur in a solvent caged monomer pair of trimethylaluminum and that intramolecular exchange occurs between this monomer pair and other species in solution such as  $\text{Me}_2\text{Zn}$  or  $\text{Me}_3\text{Ga}$  without complete separation as indicated in 1 and 2. It is in this latter step that the mechanisms proposed



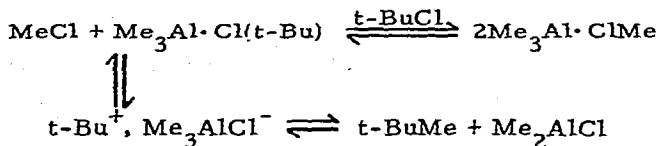
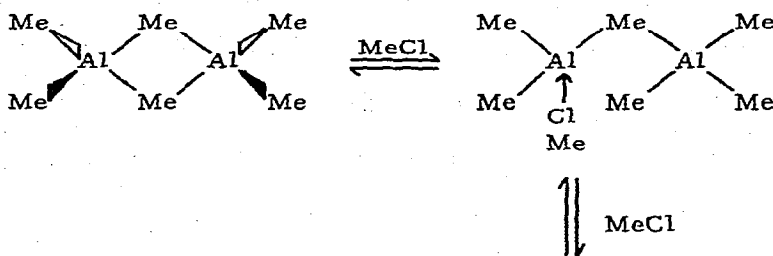
by Jeffery and Mole differ from that of Brown and of Matteson, i. e., the use of the solvent caged monomer pair as opposed to the discrete monomers used in the other treatment.

Mole and Jeffery have reevaluated the data in the literature using their proposed mechanism and have provided additional data on the exchange of  $\text{Me}_6\text{Al}_2$  with both  $\text{Me}_2\text{Zn}$  and  $\text{Me}_3\text{Ga}$ . All of these data appear to fit in the solvent caged monomer pair mechanism well. They provided an extensive discussion of the

relative merits of both mechanisms and compared rate constants derived use of both mechanisms from the same sets of experimental data.

Kennedy, et al.,<sup>26</sup> have provided some additional data which is of in both to the alkyl exchange systems and in their studies on polymerization. They observed that the rate of bridge-terminal methyl group exchange in aluminum is altered in the solvents MeCl, MeBr and MeI with the rate of exchange decreasing in that order, but faster in all cases than the self exchange reported in hydrocarbon solvents.

The mechanism proposed for the alkylation of the tert-butyl halides trimethylaluminum is shown in scheme 3. This mechanistic scheme accou



for the observed kinetics. Pseudo second-order rate constants were determined for the alkylation reaction of t-BuCl, t-BuBr and t-BuI in each of the solvents. It was found that the rates of alkylation decreased from MeCl to cyclopentane and also decreased in the order t-BuCl > t-BuBr > t-BuI. The activation energies also were determined and found to be approximately 10 kcal/mole for all reactions in the halogenated solvents and approximately 16 kcal/mole for all reactions in cyclopentane. These results were interpreted in terms of the scheme shown in 3 with the solvent assisted dissociation of the dimeric trimethylaluminum

playing a crucial role in the alkylation reaction. It was suggested, in fact, that the alkylation occurred in cyclopentane due to the limited ability of the *t*-Butyl halide to cause dissociation of the aluminum dimer.

The stereochemistry of the reaction also was investigated by study of the alkylation of optically active  $\alpha$ -phenylethylchloride. The results showed that the reaction proceeded with predominant racemization as expected for a reaction involving carbenium ions as suggested.

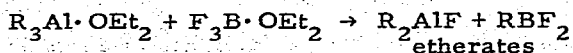
In the last paper in which fast exchange studies are reported, Wakatsuki, et al.,<sup>27</sup> have reported their investigation of the interaction of  $\text{Me}_3\text{Al}$  and  $\text{Me}_2\text{AlCl}$  with methyl substituted pyridines in  $\text{CH}_2\text{Cl}_2$ . Their variable temperature PMR studies indicated that 4-methylpyridine formed a 1/1 addition complex with  $\text{Me}_3\text{Al}$  and  $\text{Me}_2\text{AlCl}$ , while 2,6-dimethyl and 2,4,6-trimethylpyridines produced three types of complex with  $\text{Me}_2\text{AlCl}$  but only one type with  $\text{Me}_3\text{Al}$ . The configurations of the complexes in solution and exchange equilibria between the methylaluminum compounds and 2,6-dimethylpyridine were studied.

#### 4. Syntheses and Simple Reactions of Organoaluminum Compounds

A number of papers have reported preparation of organoaluminum species via new or previously unreported procedures or suggesting improved procedures for preparations of compounds. Thus, Sonnek and Reinheckel<sup>28</sup> have reported the preparation of the partially deuterated species  $\text{CD}_3\text{CH}_2\text{AlBr}_2$  (71%) and  $\text{CH}_3\text{CD}_2\text{AlBr}_2$  (69%) and of  $\text{EtAlBr}_2$  (83%) by treatment of excess aluminum powder with the corresponding alkylbromide at 45-60° for 30 minutes followed by reaction with  $\text{AlBr}_3$  and distillation. A preparation for  $^{14}\text{C}$  labeled  $\text{Et}_3\text{Al}$  from the catalyzed exchange of ethylene- $^{14}\text{C}$  with  $\text{Et}_3\text{Al}$ <sup>29</sup> has been reported.

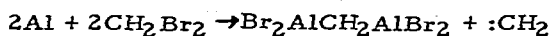
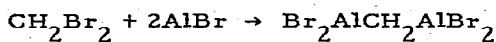
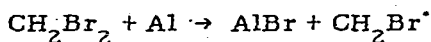
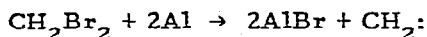
Lehmkuhl, et al.,<sup>30</sup> have reported that tri-*t*-butylaluminum and tri-*i*-propylaluminum can be obtained free from isomers in 60-90% yield by reaction of the corresponding dialkylaluminum fluoride or  $\text{AlCl}_3$  with the appropriate

alkyllithium reagent. The dialkylaluminum fluoride species can be obtained via reaction 4. The tert-butyl- and isopropylaluminum chlorides can be prepared



by reaction of the trialkylaluminum and  $AlCl_3$  in 1/2 or 2/1 ratio. Methylene bis(aluminum dichloride) and methylene bis(aluminum dibromide) have been synthesized in essentially quantitative yields.<sup>31</sup> It is postulated that the reaction sequence which leads to these compounds requires aluminum monohalide as a transitory intermediate.

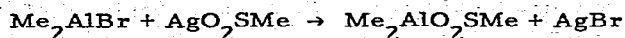
The initial reactions shown in 5 and 6 have been proposed with a secondary reaction shown in 7 following. The overall reaction with carbene formation is then given in 8. The carbenes (or radicals) formed couple or undergo addition



reactions to yield a variety of products including  $\nabla$ ,  $BrCH_2CH_2Br$  and  $H_2C=CH_2$ . Methylene chloride does not undergo direct reaction because it is not reduced by aluminum, but the chloride may be formed by the exchange reaction shown in 9.



Gaiser and Weidlein<sup>32</sup> have prepared  $Me_2AlO_2SR$  via the reaction given in 10 and have characterized this compound by chemical analysis, infrared



Raman spectra. The product cannot be obtained readily via the direct reaction of  $R_3Al$  and  $SO_2$  which instead normally yields only  $Al(O_2SR)_3$ .

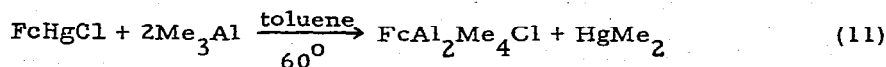
In n-heptane it has been shown that  $Et_3Al$  reacts at room temperature with ethyl silicate to give diethyl(ethoxy)aluminum and  $Et_{n+1}Si(OEt)_{3-n}$  ( $n = 0-3$ ).<sup>33</sup>  $Et_2AlOEt$  did not react with ethylsilicate indicating that the  $Et_3Al$  was the active species in the reaction.

The system  $KF \cdot AlEt_3 - AlEt_3$  was studied by DTA techniques for 12-100 mole %  $KF \cdot AlEt_3$  between 40 and 125°. <sup>34</sup> A new compound,  $KF \cdot 2AlEt_3$ , was observed which melts at 122-123°; it was shown to form a eutectic mixture with  $KFAlEt_3$ .

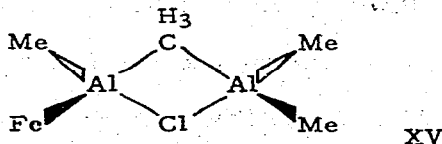
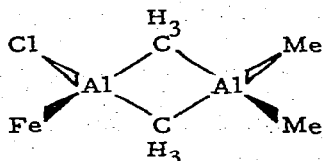
In another study Popov, et al.,<sup>35</sup> reported the preparation and properties of  $Et_3Al$ ,  $Bu_3Al$  and  $Et_2AlCl$ -etherates (ether =  $Et_2O$ ,  $(n-Pr)_2O$ ,  $(n-Bu)_2O$ ,  $(i-C_5H_{11})_2O$ , anisole, phenetole,  $Ph_2O$  and dioxane). They stated that the replacement of the aromatic ether with an aliphatic ether substantially affected the properties of the complex.

Moore and Wilkinson<sup>36</sup> reported the preparation of  $(Me_3SiCH_2)_3Al \cdot OEt_2$  as well as the corresponding zinc analogue and gave some reaction of these species with  $NbCl_5$  and  $TlCl_5$ .

Atwood, et al.,<sup>37</sup> reported the preparation of ferrocenylalane via the reaction shown in 11. This compound was characterized by means of X-ray



diffraction, NMR and mass spectral studies. The NMR studies indicate fluctational behavior in solution which can be slowed at  $-40^\circ$  permitting observation of complex patterns. Two structures, XIV and XV, were suggested as possible.



Clearly the latter is most likely correct with rapid intramolecular exchange between bridge and terminal positions occurring.

### 5. Bond Strengths and Stability of Complexes

Several studies have appeared which deal with the stabilities of the Al-C or with the various bridged systems. Glockling and Irwin<sup>38</sup> have studied the n spectra of Group III phenyl derivatives and have noted that only the metals derived from the  $\text{Ph}_3\text{Al}$  and  $\text{Ph}_3\text{Ga}$  produce ions derived from the dimers  $\text{Ph}_6\text{M}_2$  under electron impact. The fragmentation patterns reported reflect the progressive weakening of the Ph-M bond as the series is descended. They also reported the appearance potentials for the metal containing ions and evaluated  $D(\text{Ph}_2\text{M}^+-\text{Ph})$

In other studies Owens<sup>39</sup> provided some additional data on the degree of association of a series of saturated aluminum alkyls and alkoxides derived from ebullioscopic data. He stated that intramolecular association of these material occurs to an extent consistent with the steric limitations of the alkyl and alkoxy groups bound to aluminum and he presented some generalizations concerning steric limitations and their relationship to intermolecular association of organoaluminum compounds. He noted that the predominant effect determining the degree of association was the steric bulk of the alkyl group either in the trialkylaluminum or for the aluminum alkoxide. Some of the data are collected in Table I.

It should be noted that his discussion is only valid for normal saturated alkyl derivatives and does not apply to unsaturated species or to species which have unusual bonding such as that observed in tricyclopropylaluminum dimer.

Other data obtained which provide information concerning monomer-dimer equilibria and related thermodynamic properties include the study reported on the  $\text{Me}_3\text{Al}$  and  $\text{Me}_2\text{AlCl}$  in  $n\text{-C}_7\text{H}_{16}$ .<sup>40</sup> These studies included information on the vapor pressure equations, heats of vaporization and trouton constants.



TABLE I

Degree of Aggregation of Some Aluminumalkyls  
Determined Ebullioscopically in n-Pentane

alkyl	i at infinite dilution
$\text{Et}_3\text{Al}$	2.0
$(n\text{-Bu})_3\text{Al}$	1.97
$(n\text{-C}_6\text{H}_{13})_3\text{Al}$	1.89
$(\text{neo-C}_5\text{H}_{11})_3\text{Al}$	1.92
$[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2]_3\text{Al}$	0.93
$(n\text{-C}_8\text{H}_{17})_3\text{Al}$	1.77

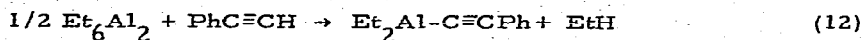
Related data of some interest, particularly for comparison with alkyl-aluminum halides, are the heats of formation of the aluminum halides,  $\text{AlX}_3$ , and their polymeric forms  $(\text{AlX}_3)_n$  reported by Anthony, et al.,<sup>41</sup> and for the heats of formation of the triphenylphosphine adducts of  $\text{AlBr}_3$  and  $\text{GaCl}_3$ .<sup>42</sup>

Pinnavaia, et al.,<sup>43</sup> have examined the redistribution equilibria for six-coordinated aluminum and eight-coordinated zirconium diketonates in solution in order to assess the factors influencing the stabilization of mixed-ligand  $d^0$  metal complexes which contain  $\text{MO}_6$  and  $\text{MO}_8$  cores. These factors are discussed in terms of entropy and enthalpy changes which occur when the diketones are distinguishable and were shown not to be greatly influenced by solvation of the species involved.

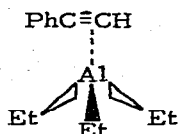
## 6. Alkylaluminum-Multiple Bond Reactions

A number of studies have appeared which deal with the interaction of the vacant orbital on an aluminum alkyl with a multiple bond. Some of these studies have established fairly clearly that the initial interaction is to form a complex between the multiple bond and the metal center.

This has been illustrated very well by the studies of Allen and Laugh<sup>44</sup> who have examined the rate of reaction of  $\text{Et}_3\text{Al}$  with  $\text{PhC}\equiv\text{CH}$  in cyclohexane solvent over the temperature range of 313-333<sup>o</sup>K. Two reactions were shown to occur, the first, metalation, which proceeds by a bimolecular reaction of  $\text{Et}_6\text{Al}_2$  with  $\text{PhC}\equiv\text{CH}$  as shown in Equation 12.

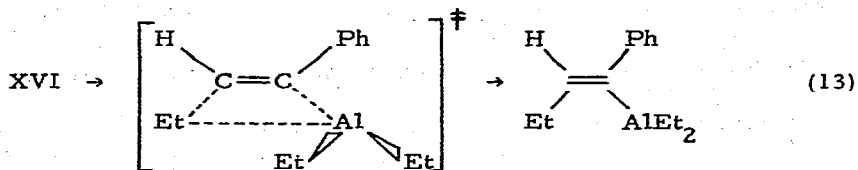


The second reaction, addition across the triple bond, was shown to proceed through initial formation of the complex shown in XVI. The existence of



XVI

this complex was established from examination of the NMR spectra of mixtures of  $\text{PhC}\equiv\text{CH}$  and  $\text{Et}_6\text{Al}_2$ . Then it was proposed that this complex formed the cyclization transition state XVII which collapsed to products as shown in 13. The rate and



XVII

activation energy for this reaction were reported. In a subsequent paper the importance of this type of interaction was implied from the influence of coordinating solvents on the addition reactions of trialkylaluminum species which

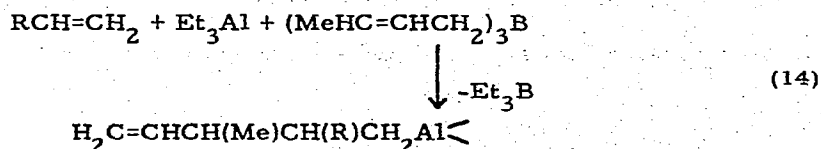
are slowed on addition of coordinating solvents.<sup>45</sup> It was noted in this paper that the influence of solvent on reaction rates is dependent on the mechanism and that other addition reactions, for example of alkyllithium derivatives to multiple bonds, proceeded by different paths, thus accounting for the differing solvent effects.

Another reaction in which it is presumed that the same intermediate occurs is the addition of  $R_3Al$  to  $C_2H_4$ . A set of conditions to effect this reaction in solution of  $R_3Al$  has recently been described.<sup>46</sup>

It is also likely that the isomerization processes described by Lehmkuhl and Olbrysch proceed through elimination and addition.<sup>47</sup> They observed the isomerization of  $R_3Al$  ( $R = CHMe_2$  or  $t-Bu$ ) at  $120-140^\circ$  to give  $R'_3Al$  ( $R' = Pr$  or  $iso-Bu$  respectively) by NMR techniques and found that the kinetics of these reactions obey second order rate laws. The activation parameters for the isopropyl reaction were  $\Delta H^\ddagger = 26.2$  kcal/mole and  $\Delta S^\ddagger = 13$  cal/mole deg. and for tert-butyl  $\Delta H^\ddagger = 29.8$  kcal/mole and  $\Delta S^\ddagger = -5$  cal/mole deg. The kinetics for  $(t-Bu)_2AlMe$  indicated that the isomerization, to give isobutyl compounds, proceeded via an equilibrium in which  $(t-Bu)_3Al$  was formed.

In another study Warwel and Hemmerich<sup>48</sup> observed that the irradiation of *n*-octenes containing internal double bonds and cis- and trans-2-undecene gave the thermodynamic equilibrium mixture of cis-trans isomers in the presence of a 4-fold excess of triisobutylaluminum at  $60^\circ$ . Double bond migration was not observed in this isomerization process. The isomerization did not occur either in the absence of light or in the absence of the aluminum compounds.

Stefani<sup>49</sup> studied the reaction of crotylaluminum derivatives with olefins, as noted in reaction 14 in which the crotylaluminum species are produced in situ



under very mild conditions ( $-10$  to  $+25^{\circ}$ ). It was noted that the reaction high stereospecificity which increased with the bulkiness of the R group. Further, it was shown that olefins with more than one substituent did not undergo this reaction under the same set of conditions.

A mechanism involving a cyclic transition state was proposed to account for the observed products and stereoselectivity.

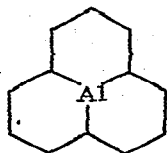
In another study on the reactions of crotyl derivatives, Lehmkuhl and Nehl<sup>50</sup> noted that dicrotylzinc reacts more selectively to give products derived from 1-methyl-2-propenyl form than either crotylmagnesium or crotylaluminum in the temperature range  $20-60^{\circ}$ .

It also has been reported that reaction of the 3-methylaluminacyclopropene moiety with  $\text{CH}_2=\text{CHCH}_2\text{Br}$  in dioxane, followed by hydrolysis, gave 1-alkyl-2,2-dimethylcyclopropane, a small amount of 1-alkyl-1,2-dimethylcyclopropane, 15%  $\text{CH}_2=\text{CMeCHMeCH}_2\text{CH}=\text{CH}_2$  and 5%  $\text{CH}_2=\text{CHCMe}_2\text{CH}_2\text{C}$ . Substitution of  $\text{CH}_2=\text{CHCH}_2\text{Cl}$ ,  $\text{PhCH}_2\text{Cl}$  or  $\text{PhCH}_2\text{Br}$  for the alkyl bromide decreased the yield of cyclopropyl products to 25% or less.

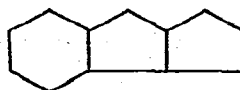
Unsaturated hydrocarbons of high electron affinity were shown by Li et al.,<sup>52</sup> to react with  $\text{R}_3\text{Al}$  and alkali metals in ether to give equimolar mixtures of  $\text{MAlR}_4$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ;  $\text{R} = \text{alkyl}$ ) and alkali metal(dialkylaluminum)dihydroalkenes. The tendency to form complexes increased with the electron affinity of the olefins. Moreover, the reaction was influenced by the solvation strength of the solvent and the ionization potential of the alkali metal. In the "ate" derivatives are not dissociated into ions. It was shown that magnesium could be used instead of an alkali metal by reaction with isoprene, 2-methylbutadiene and butadiene.

1,3-Diolefins were hydrogenated in a fairly selective manner by reaction with alkali metal and  $\text{R}_3\text{Al}$  and subsequent protolysis in  $\text{Et}_3\text{N}$  without isolation

the necessary aluminum complex. The major product from isoprene was 2-methyl-1-butene, from 1,3-pentadiene it was 2-pentene and from 1,3-dimethylbutadiene it was 2,3-dimethyl-1-butene. It was reported that bonds from aluminum to secondary carbon atoms were more readily cleaved than bonds to primary carbon atoms. Equimolar amounts of  $(i\text{-Bu})_3\text{Al}$  and trans, trans, cis- or trans, trans, trans-1,5,9-cyclododecatrienes were shown to react to give perhydro-9-aluminophenylene, XVIII; the hydrolysis and oxidation of this product by intramolecular cyclization gave derivatives of [6.4.0.0.<sup>3,7</sup>] dodecane, XIX. A number of other reactions were reported for XVIII which gave rise to a variety of polycyclic derivatives.

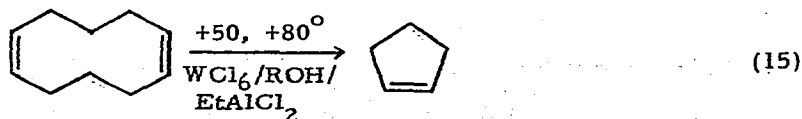


XVIII



XIX

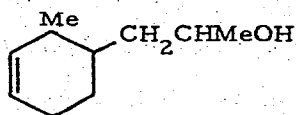
It was shown by Küpper and Streck<sup>54</sup> that reaction of 1,6-cyclodecadiene in the presence of a homogeneous catalyst, did not give rise to ring expansion or formation of a stable aluminum intermediate, but instead resulted in cleavage as shown in 15.



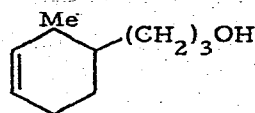
(15)

Reactions of the thermally equilibrated dimer of piperylene showed that aliphatic trans-substituted olefins are quantitatively trans-alkylated by  $(i\text{-Bu})_3\text{Al}$  with almost no shift of the double bond to the  $\alpha$  position.<sup>55</sup> From piperylene containing 40% cis form this reaction gave, in 10 hours at  $190^\circ$ , 3-methyl-4- (and 5-) propenylcyclohexenes along with 1,7-dimethyl-1,5-cyclooctadiene. Heating

$(i\text{-Bu})_3\text{Al}$  1 hour at  $140^\circ$  ( $\text{Me}_2\text{C}=\text{CH}_2$  evolution) followed by treatment at  $100^\circ$  with 3-methyl-4-propenylcyclohexene and completion of the reaction at  $140^\circ$  gave tris[2-(2-methyl-3-cyclohexenyl)propyl]aluminum which, blown with air and treated with aq HCl, gave 92:8 XX/XXI. Similar reactions were performed with 3-methyl-5-propenylcyclohexene.

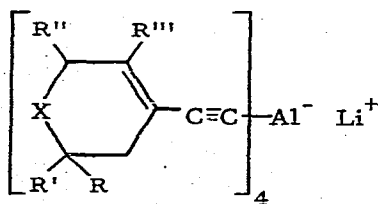


XX



XXI

In another study it was shown that condensing the appropriate enyne with  $\text{LiAlH}_4$  in THF, diglyme or pyridine gave derivatives or the type shown in XXII



$\text{R} = \text{H}, \text{Alkyl}, \text{Ph}; \text{X} = \text{O}, \text{NMe}$

XXII

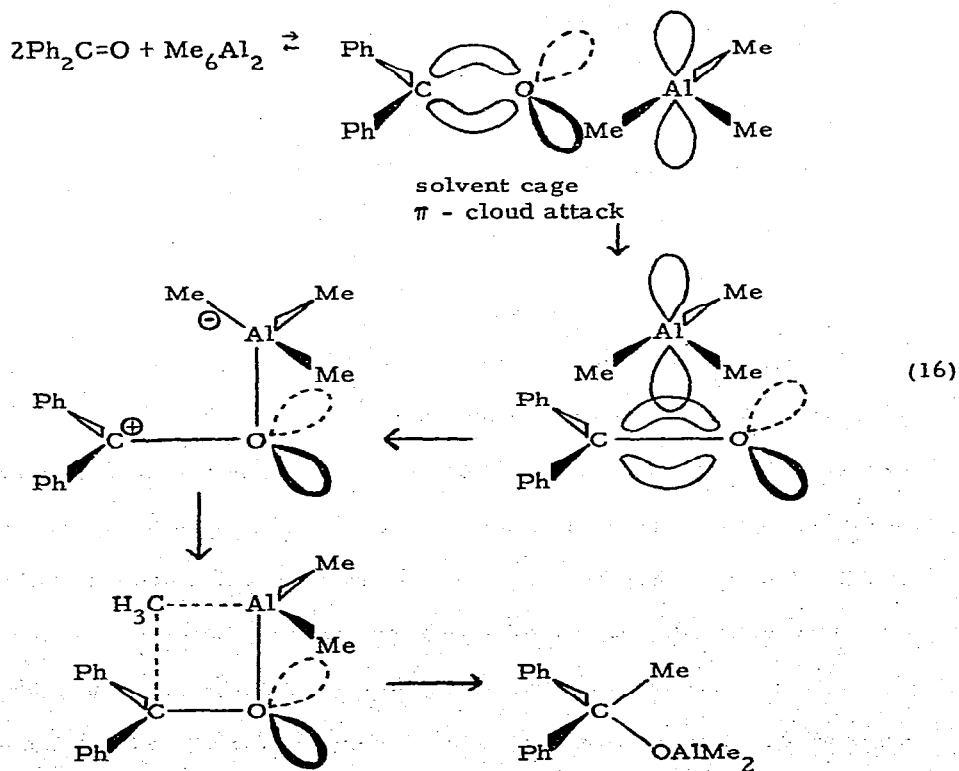
in which reaction of the hydride with the acidic proton on the acetylinic group occurred rather than addition to a multiple bond.<sup>56</sup> Reactions of the aluminum compound were reported and shown to be typical for reaction at the Al-C bond.

In a final report on the reactions of unsaturated aluminum compounds, it was shown that  $(\text{CH}_2=\text{CHCH}=\text{CHCHMeCH}_2\text{CH}_2)_3\text{Al}$  reacted with  $\text{CO}_2$  on heating in xylene solution, to give the carboxylic acid and the tertiary alcohol  $\text{R}_3\text{COH}$  on hydrolysis.<sup>57</sup>

## 7. Reaction of Organoaluminum Derivatives with Ketones, Aldehydes and Related Species

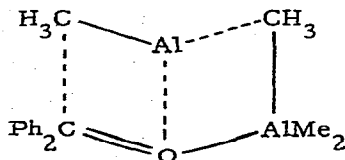
A. Reactions with Ketones. A large number of papers have appeared during the past year dealing specifically with the reactions of organoaluminum species with ketones and have provided a great amount of information concerning the mechanisms and steric control observed in these reactions.

Neumann, et al.,<sup>57</sup> have investigated the reaction of  $\text{Me}_3\text{Al}$  with benzophenone in detail. They first established that the 1/1 complex formed between  $\text{Me}_3\text{Al}$  and benzophenone was a  $\sigma$  complex rather than a  $\pi$  complex. This was accomplished primarily via spectroscopic studies of the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions. Little effect was observed on the  $\pi \rightarrow \pi^*$  transition but loss of the normal  $n \rightarrow \pi^*$  transition was observed. These findings are consistent with the formation of a  $\sigma$  complex between the ketone and aluminum alkyl.



They then discussed the mechanism of addition of the Al-C bond to the ketone under two sets of conditions and in two solvent systems. They conclude that the addition occurs via the following reaction sequence for the 1/1 complex in benzene and in the reaction in diethyl ether solvent in which the transition state is a solvent caged but non-complexed species, i. e., it does not have the Al-O ketone complex present. These conclusions were drawn from a rather lengthy and involved argument concerning the energetics of the reactions and provides a plausible mechanism consistent with the experimental rate law.

When the reaction was carried out in benzene with excess  $\text{Me}_3\text{Al}$  present the reaction proceeded much more rapidly and by a different mechanism. It was suggested that a possible transition state for the reaction is that shown in XXIII on the basis of the large negative entropy of activation which would be associated with the fairly rigid structure, however, other possible transition states were also considered.



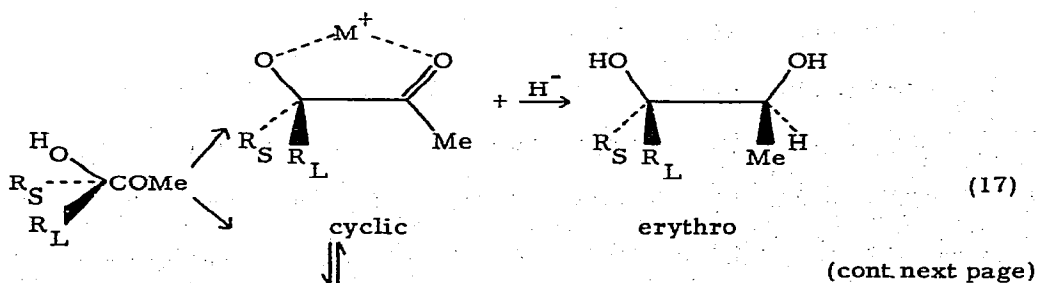
XXIII

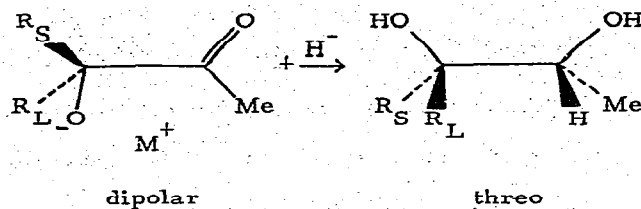
Further studies on the stereochemistry of the reaction of organoaluminum compounds with ketones also were reported.<sup>58</sup> In the latter investigation an extensive investigation of the factors governing the stereochemistry of the products was made. These results clearly show that several factors are involved and the authors concluded that in those cases in which product ratios are dependent on reaction ratios, a "compression effect" opposes the "steric approach factor". Several other possibilities were considered for the control of the stereochemistry and rejected as not accounting for all of the observations.



The reduction of 3,3,5-trimethylcyclohexanone and 4-tert-butylcyclohexanone with diisobutylaluminum hydride and with triisobutylaluminum have been also studied in benzene and ether.<sup>59</sup> The mechanism was discussed in terms similar to those for the  $\text{Me}_3\text{Al}$  reduction. The isomer ratio of the products mixture was found to be essentially independent of the solvent, but dependent on the reactant stoichiometry and the initial concentration of the  $(i\text{-Bu})_3\text{Al}$ . Evidence was reported which indicates that the epimeric ratio of alcohol produced was influenced by several factors including the degree of association of  $(i\text{-Bu})_3\text{Al}$ , the complex formed between  $(i\text{-Bu})_3\text{Al}$  and the aluminum alkoxide formed and by isomer equilibration by a Meerwein-Ponndorf-Verley pathway.

In another study Katzenellenbogen and Bowlus<sup>60</sup> have examined the stereoselective reduction of six  $\alpha$ -ketols with different patterns of substitution and size of substituents with a variety of aluminum hydride reagents in order to determine what factors govern the stereoselectivity in these systems. They found that the predominant diol produced was the one predicted by Cram's cyclic model. They also found that the degree of stereoselectivity correlates well with the  $\alpha$ -ketol structure only with one reagent (triisobutylaluminum) while with all other reagents, selectivity is related only in an irregular manner to the  $\alpha$ -ketol structure. They discussed several explanations for these observations and suggested the competing paths shown in 17 as one possibility to account for the observed results.



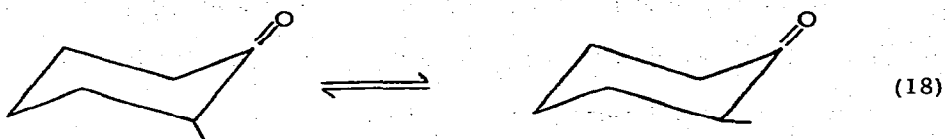


Giacomelli, et al.,<sup>61</sup> also have studied the mechanism for the asymmetric reduction of a series of phenyl ketones by optically active organoaluminum compounds which have  $\beta$ -branched alkyl groups. The reactions which have been carried out at 0° afforded (S)-alkylphenylcarbinole in good yield. The extent of the asymmetric reduction was found to depend on the structure of a donor ligand to the aluminum atom. Moreover, the reduction of isopropyl phenyl ketone by chiral solvates of triisobutylaluminum occurs with low but definite asymmetric induction. The overall results, which are consistent with a  $\beta$ -hydride transfer from the alkyl group of the organoaluminum compound to the carbonyl atom, are interpreted as indicating that in the presence of ethers the reaction occurs without prior dissociation of the ligand from the aluminum atom in cyclic six-membered transition states. The stereoselectivity of the reduction process is rationalized in terms of steric and electronic interactions in competing transition states for the hydrogen-transfer step.

This same research group<sup>62</sup> also reinvestigated the ability of tris[(2-methylbutoxy)aluminum to bring about asymmetric reduction of methyl ethyl ketone and they observed only a low stereoselectivity for this reaction.

In other studies Ashby, et al.,<sup>63</sup> have reported results from stereochemical studies which demonstrate that complexation of the carbonyl group by a metal cation occurs in the reduction of ketones by complex metal hydrides and has shown that the stereochemical outcome is affected by this complex formation as in the case for trialkylaluminum species. They suggested that this occurs in this case by shifts in the equilibria on formation of the metal-ketone complex.

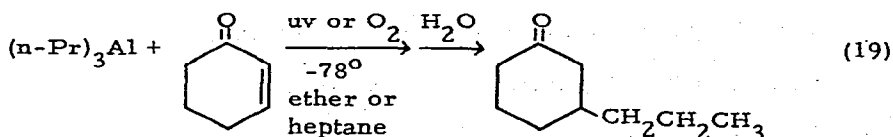
followed by reduction with the hydride. Hydrides studied were  $\text{LiAlH}_4$ ,  $\text{ClMgAlH}_4$  and  $\text{Mg}(\text{AlH}_4)_2$ .



Ashby and Heinsohn<sup>64</sup> also have studied the reduction of the ketones 4-tert-butylcyclohexanone and 3,3,5-trimethylcyclohexanone with  $(i\text{-Bu})_3(n\text{-Bu})\text{Al}$  ion. In these reactions they observed that the stereoselectivity was quite good (47% for the first case and approximately 97% for the second) and further that the ratio of products was independent of the ratio of ketone to aluminate.

In other studies<sup>65</sup> it has been shown that the aluminum derivative of  $\text{PhCH}=\text{CHCH}_2\text{Cl}$  reacted with ketones to give only products such as  $\text{CH}_2=\text{CHCHPh}-\text{CRR}'\text{OH}$  after hydrolysis, and the aluminum derivative of  $\text{CH}_2=\text{CHCH}=\text{CHCH}_2\text{Cl}$  gave  $\text{CH}_2=\text{CHCH}(\text{CH}_2=\text{CH})_2\text{CRR}'\text{OH}$  on reaction with ketones,  $\text{RCOR}'$ , followed by hydrolysis.

In a rather interesting investigation, Kabalka and Daley<sup>66</sup> have reported the first clear example of a radical 1,4-addition of an aluminum compound to an  $\alpha,\beta$ -unsaturated ketone. This is illustrated in 19. The reaction was shown to

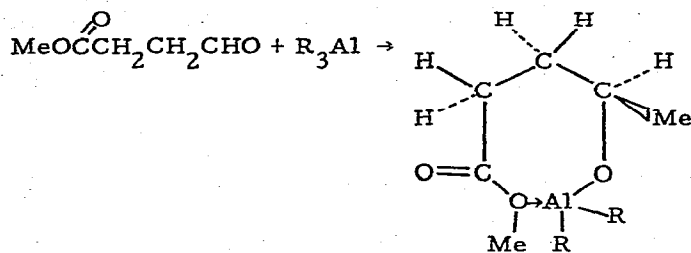


be initiated by uv radiation or by addition of a small amount of oxygen and was stopped by addition of an effective radical scavenger. The reaction was shown to occur with 2-cyclohexenone, 3-penten-2-one and methylvinylketone.

Kritz, et al.,<sup>67,68</sup> have studied the reduction of a number of compounds with complex metal hydrides. In their studies with  $\text{NaAl}_2\text{H}_4(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ <sup>67</sup>

they examined the reduction of aldehydes, ketones, esters, unsaturated esters,  $\text{BzCl}$ ,  $p\text{-MeC}_6\text{H}_4\text{CN}$ , and dehalogenations of 1-chloroheptane, 1-bromoheptane,  $\text{PhCl}$ ,  $\text{PhBr}$  and  $\text{PhI}$ . The results were compared with those obtained by similar reactions using  $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ . Similar studies<sup>68</sup> were carried out using benzene solutions of  $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OR})_2$  ( $\text{R} = \text{Me}, \text{Pr}, i\text{-Pr}$  or  $\text{Bu}$ ),  $\text{NaAlH}_2(\text{OCHMeCH}_2\text{OMe})_2$ ,  $\text{NaAlH}_2(\text{OCMe}_2\text{CH}_2\text{OMe})_2$ ,  $\text{NaAlH}(\text{OCMe}_2\text{CH}_2\text{OMe})_2$ ,  $\text{NaAlH}[\text{O}(\text{CH}_2)_n\text{OMe}]_3$  ( $n = 2, 3, 4$ ) and  $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{CHMeOMe})_3$ . The effect of the alkoxy group on the reductions was discussed.

Kobayashi, et al.,<sup>69</sup> have shown that on reaction of  $\beta$ -carbomethoxypropionaldehyde in methylene chloride or benzene with a 1/1 or 1/2 ratio of  $\text{Me}_3\text{Al}$  or  $\text{Et}_3\text{Al}$  the aldehyde group is reduced and the product is the unusual coordination compound shown in XXIV. The structure with intramolecular coordination to

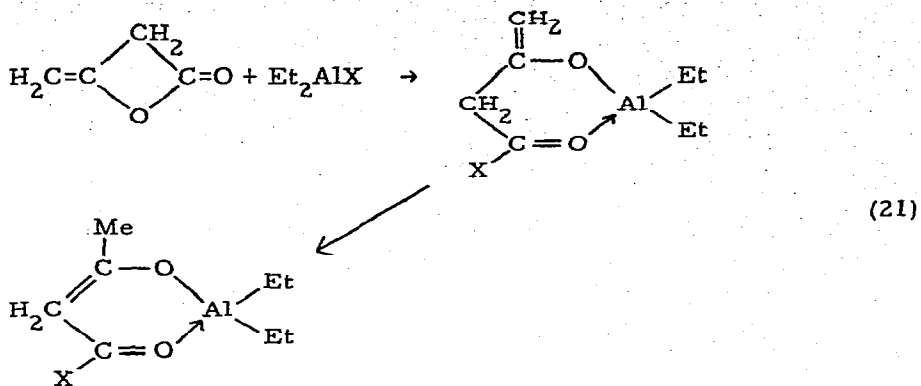


XXIV

the carbonyl oxygen and the methoxy group was suggested on the monomeric nature of the molecule and confirmed by infrared and NMR spectroscopic studies.

Somewhat different coordination compounds were obtained on the reaction indicated by equation 21 in which diethylaluminum dimethylamide and diethylaluminum ethanethiolate,  $\text{Et}_2\text{AlX}$ , ( $\text{X} = \text{NMe}_2, \text{SEt}$ ) were reacted with diketene. It was suggested that initially acyl-oxygen bond cleavage occurred followed by a 1,3-hydrogen shift to give the corresponding diethylaluminum acetic acid dimethylamide or acetothiolacetic ethyl acid ester. Both products had the character

structure as indicated which was consistent with NMR and infrared spectral studies and molecular weight of the product.

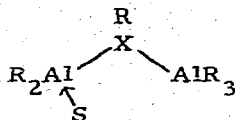


Complexes also have been reportedly formed on addition of  $\text{Me}_2\text{AlCl}$  to  $\text{PhC}(\text{O})\text{Me}$ .<sup>71</sup> In these studies, it was concluded from infrared, NMR and cryoscopic molecular weight measurements that two complexes were formed, a 1/1 complex of the type  $\text{PhC}(\text{OMe})\text{OAlMe}_2\text{Cl}$  and a 1/2 complex in which two moles of the aluminum derivative were associated with one mole of  $\text{PhC}(\text{OMe})\text{O}$ . Low temperature and room temperature NMR studies indicated that rapid exchange in the latter system occurred. Several suggestions were made concerning the nature of the 2/1 complex.

B. Reactions with Aldehydes. Tani and coworkers,<sup>72-79</sup> in a series of papers, have explored the nature and catalytic activity of a variety of complex organoaluminum derivatives in the polymerization of aldehydes. In the first of these papers the structures of complexes of the type  $\text{R}_5\text{Al}_2\text{ZM}$  in aromatic hydrocarbon solutions were explored by extensive NMR studies. The observed spectra could be explained on the basis of binuclear complexes of the type  $[\text{R}_2\text{AlZM}][\text{AlR}_3]$  with nonequivalent aluminum atoms where  $\text{R} = \text{Et}; i\text{-Bu}; \text{Z} = \text{O}; \text{M} = \text{Na}, \text{K}$ , at the temperatures studied. It was suggested that this type of structure was also predominant for  $\text{R} = \text{Et}; \text{Z} = \text{O}; \text{NPh}; \text{M} = \text{Li}$ ; for  $\text{R} = \text{Et};$

Z = S; M = Na; for R = Et; Z = O; M = Cs and for R = i-Bu; Z = O; M = Cs.

The structure proposed for this type of complex is shown in XXV in which one mole of aromatic solvent is complexed with the aluminum atom. At higher temperatures

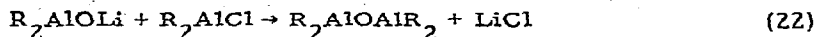


S = benzene, toluene, THF

XXV

peratures rapid intramolecular alkyl group exchange occurs, presumably by loss of the solvent molecule, which is very weakly bound and then by alkyl bridge formation. Addition of one mole of THF per mole of dimer displaced the aromatic solvent to give the same type of structure. A fairly lengthy discussion of the factors which determine the structures was presented and it was concluded that one of the factors appeared to depend upon the ionization energy and ionic radius of the alkali metal ion.

In a subsequent paper<sup>73</sup> the formation of dialkylaluminum oxides, their physical properties and some of their reactions were explored. The compounds were prepared by the reaction shown in 22. The products obtained from this

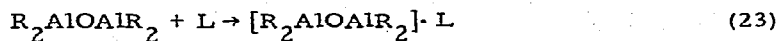


R = Me, Et, i-Bu

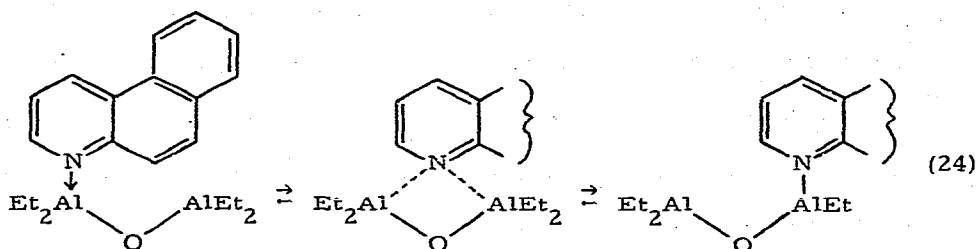
reaction were shown to have properties similar to the compounds obtained by hydrolysis of  $\text{R}_3\text{Al}$ . The bis(dialkylaluminum)oxides were characterized by their infrared and NMR spectra and by conductometric studies. They were shown to be associated, with the degree of association dependent on the bulk of the alkyl group and on the concentration with observed degrees of association ranging from

tetramer for the diethylaluminum species to approximately 1.5 for the iso-butyl derivative.

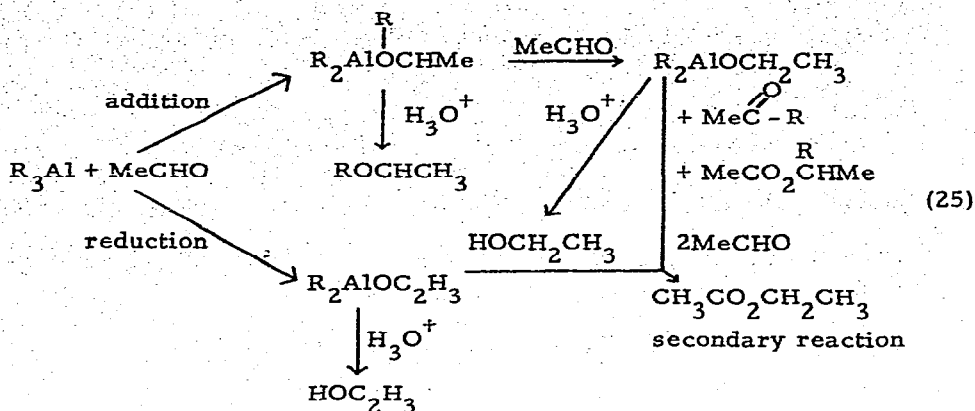
It also was shown that these derivatives form stable 1/1 complexes as indicated in equation 23 with a number of donors including THF, PhOMe and 5,6-benzoquinolate. The latter also forms an unstable 2/1 complex. It was



suggested that the 1/1 complex was undergoing rapid fluctuation of the nitrogen as shown in 24, however, this was not established unequivocally.

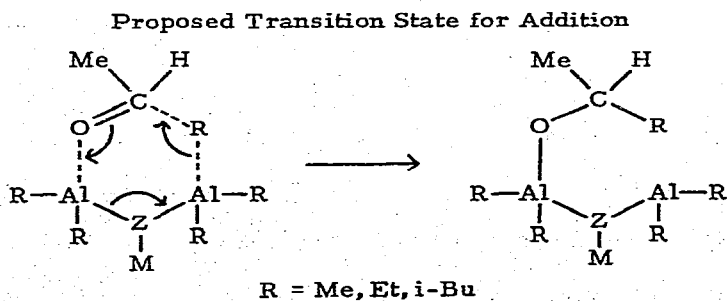


Compounds of the type  $[R_2AlZM][AlR_3]$  ( $M =$  alkali metal;  $Z = O, NR^1,$  or  $S$ ;  $R$  and  $R^1 =$  alkyl groups) have been prepared by the reaction of trialkylaluminum compounds in a molar ratio of 2/1 with alkali metal hydroxides (for  $Z = O$ ), lithium  $N$ -substituted amides (for  $Z = NR^1$ ) and sodium hydrosulfide (for  $Z = S$ ).<sup>74</sup> In most cases the complexes were isolated in crystalline form. The reaction was shown to involve two steps,  $AlR_3 + MZH \rightarrow R_2AlZM + RH$ , followed by  $R_2AlZM + AlR_3 \rightleftharpoons [R_2AlZM][AlR_3]$ , since the intermediate products  $R_2AlZM$  have been isolated and shown to react with  $AlR_3$  to give the complex. The latter is considered to be a bimolecular donor-acceptor complex, in which  $R_2AlZM$  acts as an electron donor and  $R_3Al$  as an acceptor. Infrared spectra of the oxygen complex  $[Et_2AlOM][AlEt_3]$  where  $M = Li, Na, K$  or  $Cs$  show that they have closely similar structures.



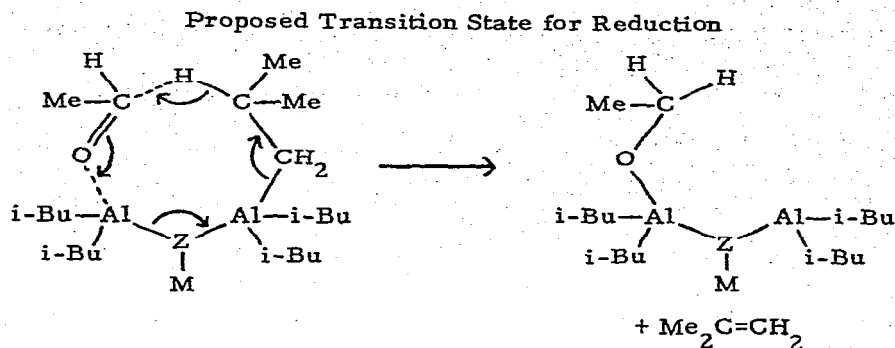
Studies of the reactions of the pentaalkylaluminum alkali metal oxides and of the related sulfur and nitrogen analogs with acetaldehyde have been reported and compared with the results obtained when  $\text{R}_3\text{Al}$  or  $\text{R}_3\text{Al} \cdot \text{L}$  were used.<sup>75</sup> The reaction scheme for  $\text{R}_3\text{Al}$  is outlined in 25 and shows addition and reduction as the primary reactions. Secondary reactions also occur as indicated, especially with increases in the strength of the complexes which are formed.

The pentaalkyldialuminum complexes have been shown to have high reactivity in the primary process, but little secondary reaction occurs when they are used. The results can be understood by invoking a bimetallic cyclic transition state as shown in 26. With  $[\text{R}_2\text{AlZLi}] \cdot [\text{AlR}'_3]$ , R and R' addition occurred simultaneously, indicating an alkyl exchange process occurred in the complex.

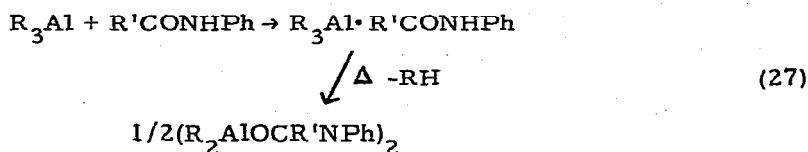


(26)



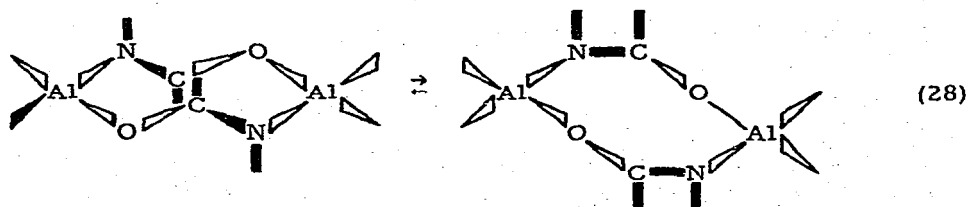


Yasuda, et al.,<sup>76</sup> also have prepared and separated the polymerization catalysts of the general form  $[\text{R}_2\text{AlOCR}'\text{NPh}]_2$  by the reaction shown in 27



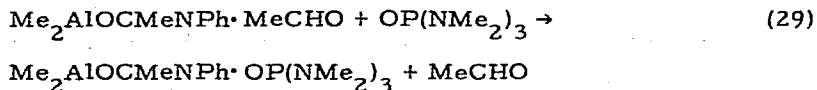
which is said to be the superior method for this preparation. The chemical behavior of these species toward Lewis acids and bases was interpreted in terms of the structure of  $[\text{Me}_2\text{AlOCPHNPPh}]_2$  and its trimethylamine oxide adduct  $\text{Me}_3\text{NO} \cdot \text{AlMe}_2\text{OCPhNPPh}$  which had been previously reported [Annual Surveys, J. Organometal. Chem., 62 (1973) 185].

Variable temperature NMR studies were reported which were interpreted in terms of isomeric forms which underwent rapid interconversion in solution as shown in 28.

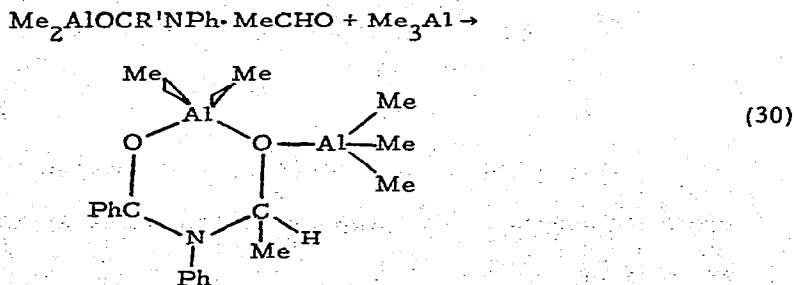


Yasuda, et al.,<sup>77</sup> have examined the reaction between aliphatic aldehydes (acetaldehyde, propionaldehyde and butyraldehyde) and the stereo-

specific polymerization catalysts of the type just described,  $R_2AlOCR'NPh$ . These studies were carried out in an attempt to elucidate the initiation mechanism of the polymerization reaction. The 1/1 monomer/catalyst complexes obtained from these aldehydes and  $R_2AlOCR'NPh$  showed excellent catalytic activity toward the stereospecific polymerization. The structure of these complexes in solution has been proposed on the basis of NMR and infrared studies and the previously reported crystal structures which provided evidence for five coordinate aluminum, [Annual Surveys, J. Organometal. Chem., 62 (1973) 185]. The structure of the aromatic monoaldehyde complex also has been studied and shown to be identical with that of the aliphatic derivative. The chemical behavior of these aldehyde complexes towards Lewis bases and acids has been investigated. The aldehyde moiety of the  $R_2AlOCR'NPh \cdot MeCHO$  complex is liberated by the action of strong Lewis bases such as trimethylamine oxide or HMPA as shown in equation 29 and is exchanged easily for another kind of aldehyde.

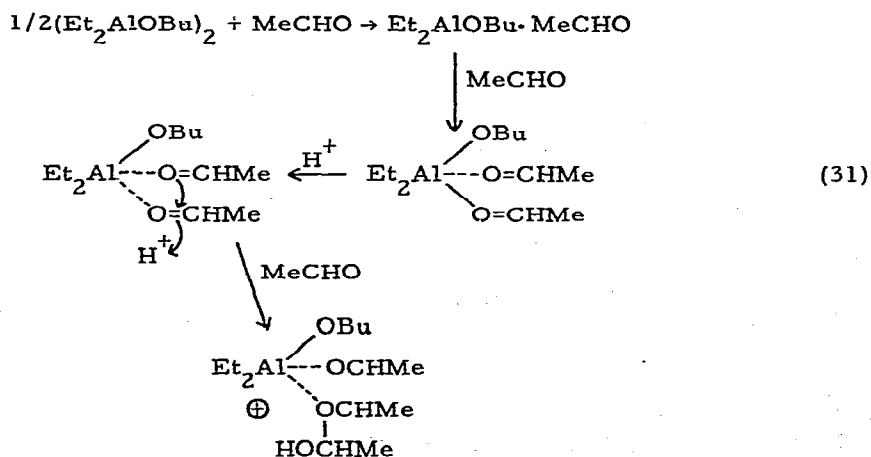


The trimethylaluminum complex  $Me_2AlOCPhNPhMeCHO \cdot AlMe_3$  leads only to the formation of amorphous polyacetaldehyde in contrast to the simple aldehyde complex already discussed. The  $Me_3Al$  adduct is formed as indicated in 30. The structure has been established in the solid state by X-ray studies and in solution by studies of the infrared and NMR spectra.



Extensive discussions on the various equilibria and exchanges phenomena possible in solution were presented.

In another article Yasuda, et al.,<sup>78</sup> have reported their results on the stereospecific polymerization of acetaldehyde using four different purified diethylaluminum butoxides,  $(Et_2Al-O-Bu)_2$  (Bu = n-Bu, i-Bu, sec-Bu or t-Bu) as catalysts. These catalysts gave isotactic polyacetaldehyde quantitatively irrespective of the degree of branching of the butyl group, only when an optimum amount of water (about 0.03 mole/mole of catalyst) was added to the purified acetaldehyde monomer. Quite similar results were obtained for organozinc systems. These results indicate that water is an indispensable cocatalyst in the polymerization reaction with organoaluminum and zinc systems. They proposed the following scheme based on the above information and the fact that the catalysts are deactivated on addition of a strong Lewis base.

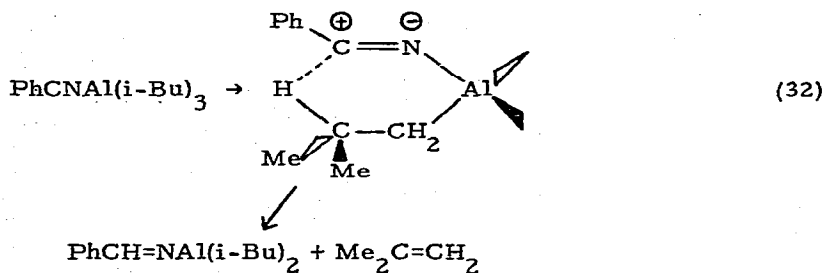


Finally, the catalytic activity of  $Et_3Al/H_2O$  systems for the polymerization of acetaldehyde were investigated in which inorganic bases were reacted with  $Et_3Al$  instead of pure water in toluene/ether media.<sup>79</sup> A uniform soft gel-like product was obtained. This material gave high stereoregularity in the

polymerization of acetaldehyde. The system was compared with others obtained using pure water and the influence of the inorganic base was discussed.

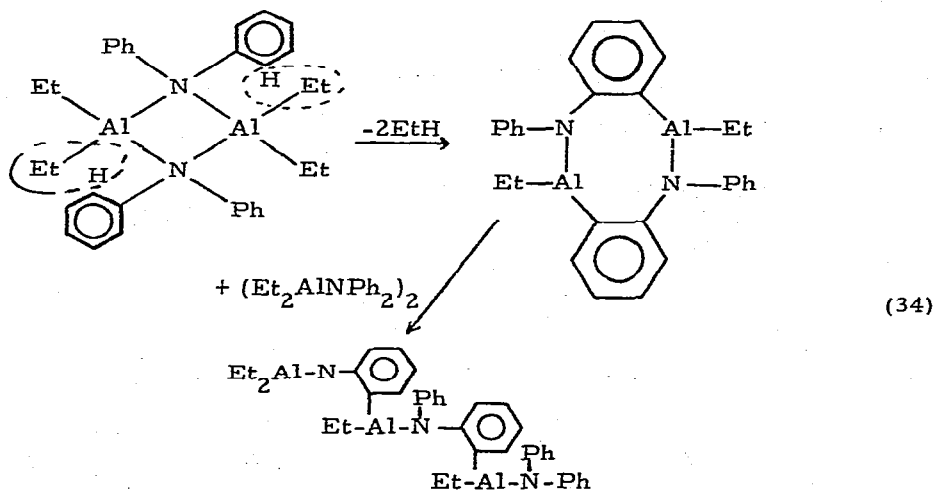
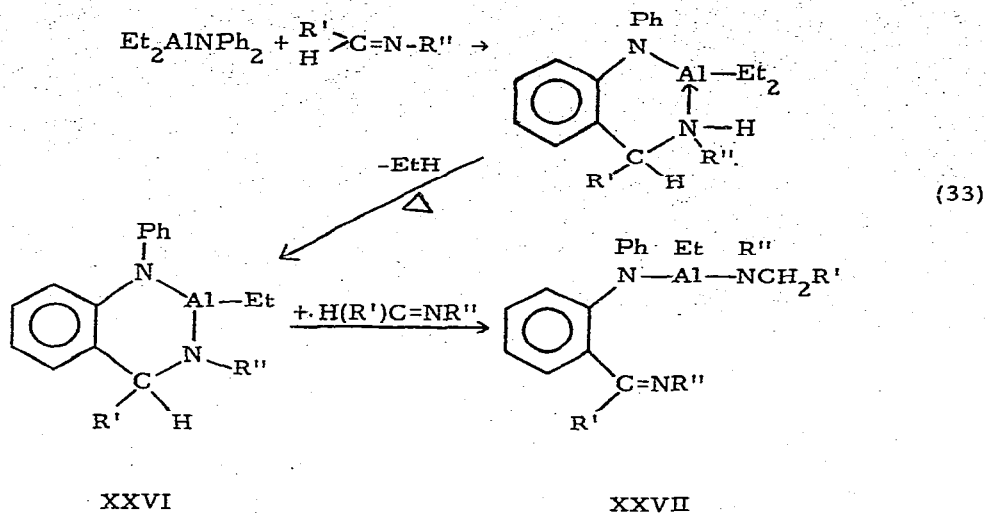
### 8. Reactions of Organonitrogen Compounds

Several reactions have been reported between aluminum derivatives and a variety of nitrogen compounds. Giacomelli and Lardicci<sup>80</sup> have investigated the thermal decomposition of  $(i\text{-Bu})_3\text{AlNCPH}$  and have reported the first order rate constants for its unimolecular decomposition to benzylideneamino(diisobutyl)aluminum at several temperatures. The rate of reduction was shown to be independent of toluene as solvent. The activation parameters determined for the reaction are  $E_a = 25.0 \pm 1$  kcal/mole and  $A = 10^{12}$  sec<sup>-1</sup>; all of the data obtained are consistent with the hypothesis that the reduction proceeds through a six-centered transition state as shown in 32. In the presence of excess  $(i\text{-Bu})_3\text{Al}$ ,



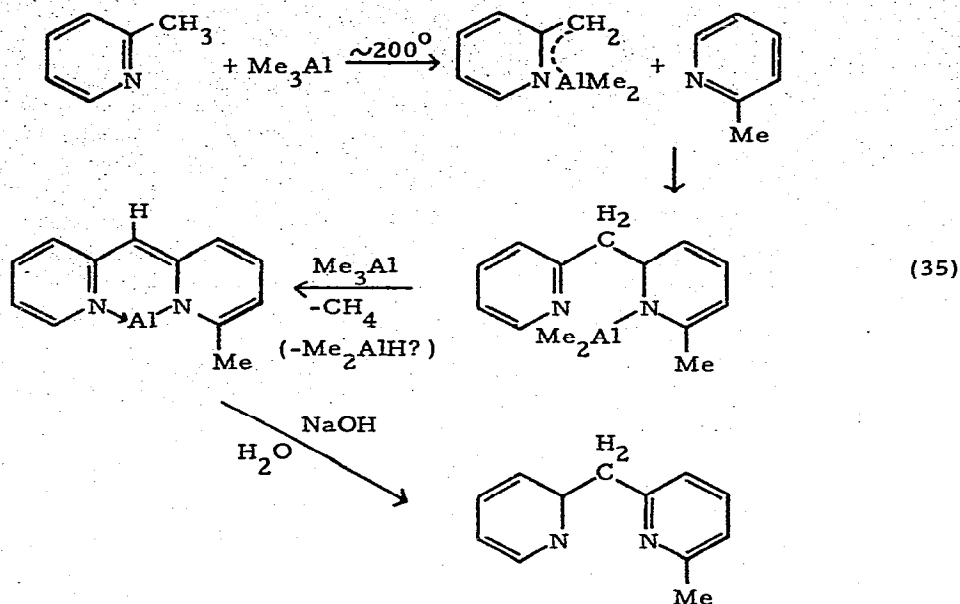
diisobutyl( $\alpha$ -isobutylbenzylideneamino)aluminum is formed by addition. On the basis of these results, possible mechanisms for addition are discussed.

Hoberg and Milchereit<sup>81</sup> have investigated the reaction of N-diethylaluminum N,N-diphenylamide with aldehydes and have shown that they produce the aluminum heterocycles shown in XXVI which yields XXVII on hydrogen transfer. XXVII yields the o-anilinoketamine on hydrolysis. Hoberg has shown that



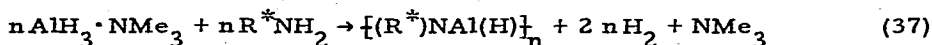
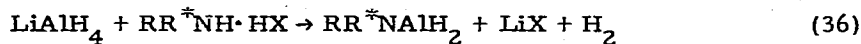
ethane is eliminated by heating of diethylaluminum N,N-diphenylamide at  $110^\circ$  and the crystalline trimeric amide is produced.<sup>82</sup> The mechanism shown in 34 was proposed for this reaction.

Meister and Mole<sup>83</sup> have shown that 6-methyl-2,2'-methylenedipyridine is formed in 60% yield from  $\alpha$ -picoline. The reaction is thought to proceed as shown in 35. A similar product also was reported on initial reaction of 2,6-



lutidine with  $\text{Me}_3\text{Al}$  followed by treatment with pyridine. This reaction may prove to be a generally useful laboratory synthesis for methylenedipyridienes.

Giongo, et al.,<sup>84</sup> have examined the formation of optically active aluminum species via the reactions shown in equations 36 and 37 and their subsequent use as reducing agents for several asymmetric ketones. Their results showed



that optical activity is retained in the products. The influence of solvent and temperature on the optical activity of the product was examined.

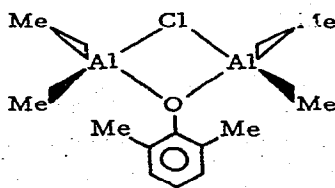
Studies also have been reported on the reaction of  $\text{Ca}(\text{AlH}_4)_2$  and  $\text{Mg}(\text{AlH}_4)_2$  with primary amines or nitriles.<sup>85</sup> For amine or nitrile/aluminate ratios of 3/1 mixed polyamino compounds which contained  $-\text{AlH}-\text{NR}-$  and  $-\text{Ca}-\text{NR}-$  (or  $-\text{Mg}-\text{NR}-$ ) units were formed with lower ratios definite compounds were not isolated, except in the reaction of  $\text{Ca}(\text{AlH}_4)_2$  with aniline which gave crystals of calcium 1-phenyliminodialane.

Wagner<sup>86</sup> has studied the reaction of aluminum azide with a variety of unsaturated  $\beta$ -cyano esters. Both cis- and trans-3-cyanacrylates gave trans-3-tetrazole-5-acrylate. trans-3-Cyanocrotonate produced trans-3-methyl-terazole-5-acrylate, while cis-3-cyanocrotonate gave a mixture consisting mainly of 1-(2-cyanopropenyl)tetrazolin-5(4H)one and tetrazolo[1,5-c]pyrimidin-5(6H)-one. The reaction of  $\text{Al}(\text{N}_3)_3$  with ethyl o-cyanobenzoate gave a variety of products. The possible mechanisms of reaction were discussed.

### 9. Oxygen and Mixed-Bridged Species

Dimethyl-(2,6-dimethylphenoxy)chloroaluminum, methyl-(2,6-dimethylphenoxy)chloroaluminum and methyl-(2,6-dimethylphenoxy)iodoaluminum have been prepared, their molecular weights determined and their infrared and NMR spectra recorded. These data have been used as a basis for determining the chemical constitution of these compounds in benzene solution. All of the compounds were shown to be dimeric in benzene and those which contain halogens were shown to coordinate preferentially with the halogen atom.

On the basis of the NMR studies, it was suggested that at room temperature in benzene solution methyl-(2,6-dimethylphenoxy)chloroaluminum exists as a mixture of cis and trans isomers and it also was suggested that mixed bridged species such as that shown in XXVIII were formed on addition of  $\text{Me}_6\text{Al}_2$  to  $\text{Me}_2(\text{Me}_2\text{PhO})_2\text{Al}_2\text{Cl}_2$ .

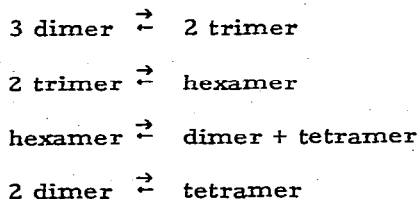


XXVIII

In other studies, it was found that aluminum isopropoxide reacts with  $\text{Me}_6\text{Al}_2$  irreversibly in aromatic solutions to produce three kinds of tetrameric

and two kinds of dimeric complexes.<sup>88</sup> The terminal isopropoxyl groups aluminum isopropoxide can be substituted successively by the methyl group  $\text{Me}_6\text{Al}_2$  forming mixed ligand complexes. After all of the terminal isopropoxyl groups have been replaced by methyl groups, the resultant tetrameric complex undergoes decomposition reactions leading to dimeric complexes. In the species isopropoxyl groups form stable bridge bonds while methyl groups occupy the terminal sites. Studies of the relaxation times of the methyl groups indicated that the local mobility of the ligands in the bridge positions is less than that at the terminal sites and that the mobility of the ligands varies as the size of the complex is varied.

Finally it should be noted that the interconversion of dimeric, trimeric and tetrameric aluminum isopropoxide have been investigated by cryoscopic and NMR techniques.<sup>89</sup> Starting from pure dimer, the first step is rapid reaction with trimer, after which the tetramer is formed very much more slowly. Starting from pure tetramer, a mixture of all three species is slowly formed. These reactions are treated by the scheme shown in 38 which appears to fit the kinetic and equilibrium requirements of the reactions. Rate coefficients



individual steps of the interconversion process were suggested on the basis of the fit of the overall kinetic results by computer simulation of the NMR spectra obtained. The hexamer was proposed on this basis, although not observed. It was suggested that 5-coordinate aluminum was involved in the transition state of some of the exchange steps.



## 10. Physical and Chemical Properties and Reactions of Selected Aluminum Hydride Derivatives

Ashby, et al.,<sup>90</sup> have examined the equivalent conductance of THF solutions of  $\text{LiAlH}_4$ ,  $\text{NaAlH}_4$ ,  $\text{Bu}_4\text{NAlH}_4$  and  $\text{LiBH}_4$ . Their data are consistent with the presence of free ions and ion pairs in dilute solutions and with the formation of triple ions as the concentration is increased. The application of the Fuoss treatment to the data for dilute solutions permit the evaluation of the equivalent conductance ( $\Lambda_0$ ) at infinite dilution and the ion pair dissociation constant ( $K_a$ ) for each hydride. Utilizing a sphere in a continuum model, the center to center distance between the ions in the ion pair calculated from the experimental  $K_a$  values indicated that the ion pairs of  $\text{Bu}_4\text{NAlH}_4$  and  $\text{LiBH}_4$  are in intimate contact, whereas the  $\text{LiAlH}_4$  and  $\text{NaAlH}_4$  species are solvent-separated ion pairs. The thermodynamic parameters also suggest that  $\text{LiAlH}_4$  ion pairs are predominantly solvent separated. In contrast to this, a substantial fraction of the  $\text{NaAlH}_4$  ion pairs are in intimate contact at  $25^\circ$ , thus it would appear that for the aluminum series the contact ion-pair formation is strongly dependent on solvent-cation interactions. In the more concentrated solutions where ion pairs and triple ions are present, the Fuoss treatment also has been used to evaluate  $K_t$ , the triple ion dissociation constant.

NMR studies confirmed strong solvent-cation interactions indicating formation of  $\text{LiAlH}_4 \cdot 4\text{THF}$  and  $\text{LiBH}_4 \cdot 2\text{THF}$  complexes, but showing no complex formation with  $\text{Bu}_4\text{NAlH}_4$ . Infrared spectral studies were used to confirm the solvation of the cation.

In a separate study Shirk and Shriver<sup>91</sup> examined the infrared and Raman spectra of  $\text{MH}_4^-$  ( $M = \text{Ga}, \text{Al}$ ) with  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{Et}_4\text{N}^+$  counter ions for aluminum and  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  for gallium. They interpreted their data in terms of three forms of species, tight complexes, loose aggregates and less tightly bound

ion pairs and again suggested that there was no evidence for solvent- $\text{AlH}_4^-$  coordination.

Somewhat in contrast to this, Kadlecova, et al.,<sup>92</sup> studied the apparent degrees of association of  $\text{Na}[\text{MeO}(\text{CH}_2)_2\text{O}]_2\text{AlH}_2$  as a function of concentration in benzene and THF. In this study they observed that 2/1 and 1/1 complexes of solvent/ $\text{Na}[\text{H}_2\text{Al}(\text{O}(\text{CH}_2)_2\text{OMe})_2]$  were formed and that benzene could not be displaced from these complexes, even by strong donors such as pyridine or THF, suggesting an unusual interaction between benzene and the aluminum complex.

They also noted that in solution the degree of association of the hydride complexes was a function of the  $n$ , the number of hydrogen atoms present in  $\text{Na}[\text{H}_n\text{Al}(\text{O}(\text{CH}_2)_2\text{OMe})_{4-n}]$ .

The Raman and infrared spectra of  $\text{Al}(\text{BH}_4)_3$  have been reported and interpreted as indicating that no significant changes in structure occur in going from gas to liquid to solid.<sup>93</sup> The data were consistent with a  $D_{3h}$  prismatic structure and all 23 of the optically allowed fundamental transitions were assigned for each molecular isotope. A number of modifications in earlier assignment have been made. Finally, some correlated NMR - Raman spectral studies were made over the temperature range  $-60$  to  $+80^\circ$  and the results suggest that traces of decomposition products may act in a catalytic manner to profoundly change the NMR spectra of  $\text{Al}(\text{BH}_4)_3$ .

In another study of  $\text{Al}(\text{BH}_4)_3$ , 1/1  $\pi$ -complexes with  $\text{C}_6\text{H}_6$ , PhMe, *o*- $\text{Me}_2\text{C}_6\text{H}_4$ , *p*- $\text{Me}_2\text{C}_6\text{H}_4$  and durene were observed by low temperature thermographic methods.<sup>94</sup> Complexes with nonpolar hydrocarbons exhibited non-congruent m. p. The dissociation pressure of the durene complex was determined as a function of temperature over the range  $-35$  to  $+12^\circ$ .  $\Delta H^\circ$  and  $\Delta G_{285}$  of this

complex were  $-6.50$  and  $2.72$  kcal/mole respectively. Infrared spectral studies indicated a weak interaction at room temperature.

In an attempt to examine the compound  $\text{Be}(\text{AlH}_4)_2$  Ashby, et al.,<sup>95</sup> reacted  $\text{NaAlH}_4$  and  $\text{LiAlH}_4$  with  $\text{BeCl}_2$  but obtained no evidence for the  $\text{Be}(\text{AlH}_4)_2$  species. They did observe production of  $\text{BeH}_2$ ,  $\text{AlH}_3$  and the rather interesting complexes  $\text{Li}_2\text{BeCl}_2\text{H}_2$  and  $\text{LiBeH}_2\text{Cl}$ .

In studies on other hydride derivatives, Beachley and Bernstein<sup>96</sup> have reinvestigated the nature of trimethylamine-dimethylalane ( $\text{Me}_3\text{NAlMe}_2\text{H}$ ) in an effort to resolve the controversy concerning its structure. Their data are consistent with the hypothesis that  $\text{Me}_3\text{NAlMe}_2\text{H}$  is a discrete compound which exists as an equilibrium mixture of monomeric and more associated species. Tensimetric titrations between pure dimethylalane and  $\text{NMe}_3$  established that only a 1/1 adduct is formed. The reaction between  $\text{Me}_3\text{NAlMe}_2\text{H}$  and  $\text{NMe}_2\text{H}$  provides additional evidence that  $\text{HMe}_2\text{Al}\cdot\text{NMe}_3$  is a discrete compound since the only aluminum-containing product formed in this reaction is  $[\text{Me}_2\text{AlNMe}_2]_2$ . Solution and gas phase molecular weight studies show that an equilibrium exists between monomeric and more associated species. Furthermore, the  $^1\text{H}$  NMR data are consistent with the existence of an equilibrium between monomer and associated species.

Ashby, et al.,<sup>97</sup> have reported the formation of ether soluble  $\text{AlH}_3$  which is said to be monomeric (and presumably present as the complex) by reaction of  $\text{LiAlH}_4$  with  $\text{BeCl}_2$ ,  $\text{H}_2\text{SO}_4$  or  $\text{ZnCl}_2$ .

## 11. Synthesis, Properties and Reactions of $[\text{AlR}_4]^-$ Derivatives

Several studies have been reported on the properties and reactions of the "ate" derivatives. Lehmkuhl, et al.,<sup>98</sup> in their studies on the electrochemistry of organic ion pairs, have reported the half wave potentials and standard poten-

tials for the alkali and alkaline earth metals using  $\text{AlMe}_4^-$  and  $\text{AlEt}_4^-$  anions as the counter ions in THF solvent.

More direct evidence on the anions of this type was reported by Westmoreland, et al.,<sup>99</sup> who observed the  $^{13}\text{C}$  NMR spectra of  $\text{NaAlEt}_4$  and  $\text{NaAlBu}_4$  in benzene and DMSO solvents ( $^1\text{H}$  noise decoupled). They found that  $^{27}\text{Al}$ - $^{13}\text{C}$  coupling could not be observed in benzene solvent due to quadrupolar relaxation, but in the following coupling constants were obtained for  $\text{AlEt}_4^-$   $^1\text{J} = 73$  Hz and  $^2\text{J} \approx 1.0$  Hz in  $\text{AlBu}_4^-$   $^1\text{J} = 71.6$  and  $^2\text{J} \approx 4.0$  Hz. They commented specifically on the use of  $^{13}\text{C}$  NMR as a tool for studying solvation effects.

A variety of syntheses of "ate" complexes have been reported in other studies. Ivanov, et al.,<sup>100</sup> have reported that  $\text{M}(\text{AlEt}_4)_2$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) were conveniently prepared by reaction of freshly cut metal turnings with excess  $\text{Et}_6\text{Al}_2$  with stirring in the presence of glass balls.  $\text{M}(\text{AlEt}_4)_2 \cdot 2$  diglyme complexes also were prepared by dropwise addition of diglyme to solutions of  $\text{M}(\text{AlEt}_4)_2$  in benzene or hexane solvent.

Dickson and Sutcliffe have investigated the reaction of  $\text{LiAlH}_4$  with polyhalogenated aromatic species.<sup>101, 102</sup> They observed that in THF at  $-45^\circ$  or in ether at  $20^\circ$  the reaction of  $\alpha$ -bromo-2,3,4,5,6-pentafluorotoluene replaced the bromine with hydrogen. The same reaction also occurred initially at  $20^\circ$  in THF, but then was followed by reaction at the para position to yield the complex  $\text{LiAl}(\text{C}_6\text{F}_4\text{Me})\text{H}_2\text{F}$ . The reaction between  $\text{LiAlH}_4$  and  $\text{C}_6\text{F}_5\text{Me}$  was found to be complete after 30 minutes at  $65^\circ$ . It also was found that 2,3,5,6-tetrafluorotoluene reacts with  $\text{LiAlH}_4$  in refluxing THF to form the fluorocarbon-alane complexes,  $\text{LiAl}(\text{C}_6\text{F}_4\text{Me})\text{H}_{n-4-n}$  ( $n = 1 - 3$ ).

In other studies<sup>102</sup> they reported that  $\text{LiAlH}_4$  reacts with chloropentafluorobenzene to yield mainly p-chlorotetrafluorobenzene. They also found that the nature of the solvent influenced the formation of other fluorocarbon deriva-

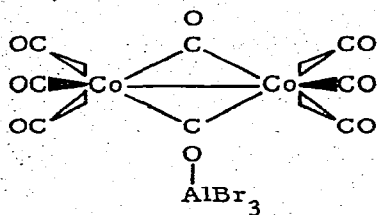
tives in the reaction. *p*-Chlorotetrafluorobenzene reacts further in THF, but not in ether, to give predominantly 1-chloro-2,3,5-trifluorobenzene and 1-chloro-2,3,6-trifluorobenzene. In turn, the trifluorobenzene derivatives reacts with  $\text{LiAlH}_4$  in THF to give mainly 1-chloro-2,5-difluorobenzene. The major products are formed by (i) direct nucleophilic displacement of fluorine by hydride and (ii) by hydrolysis of the compounds  $\text{Li}[\text{Al}(\text{C}_6\text{F}_4\text{Cl})\text{H}_2\text{F}]$ ,  $\text{Li}[\text{Al}(\text{C}_6\text{F}_3\text{HCl})\text{H}_2\text{F}]$  and  $\text{Li}[\text{Al}(\text{C}_6\text{F}_2\text{H}_2\text{Cl})\text{H}_2\text{F}]$ . These complexes, and those previously described, were not isolated but characterized by their hydrolysis and by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of the solutions.

## 12. Transition Metal-Organoaluminum Derivatives

A. Spectroscopic Studies. The area of aluminum chemistry in which aluminum alkyls are reacted with transition metal species continues to be active. Structures of several species are reported in section 2 and additional details concerning their spectra and reactions are given in this section.

Kristoff and Shriver<sup>103</sup> have reported that the changes in the asymmetric CO stretching frequency,  $\Delta_{\nu\text{CO}} \text{ asym.}$ , which occurs upon coordination of an acid to  $\pi\text{-CpFe}(\text{CO})_2\text{CN}$  provides a convenient probe for the electron pair acceptor strength of the acid and stated that in contrast with previous attempts to employ frequency shifts as probes of Lewis acids, this method is not affected by spurious kinematic coupling between the probe oscillator and other oscillators in the adduct. This technique was used to deduce the following relative electron pair acceptor strengths:  $\text{BH}_3 < \text{BF}_3 < \text{BCl}_3 \cong \text{BBr}_3, \text{BCl}_3 > \text{GaCl}_3 > \text{AlCl}_3$  and  $\text{Me}_3\text{Al} > \text{Me}_3\text{B} \cong \text{Me}_3\text{Ga}$ . It was stated that comparison of the trends in electron pair acceptor strength with acidity trends may yield insight into the details of Lewis-acid-base interactions and examples were cited.

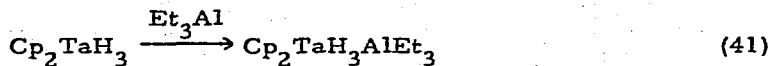
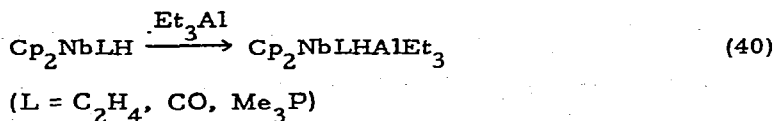
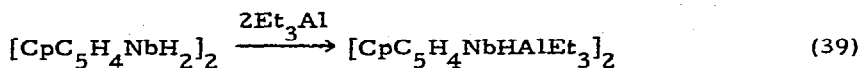
Kristoff, et al.,<sup>104</sup> also examined the infrared spectra of the complex  $\text{Co}_2(\text{CO})_8 \cdot \text{AlBr}_3$  and concluded it has the structure shown in XXIX and not a metal



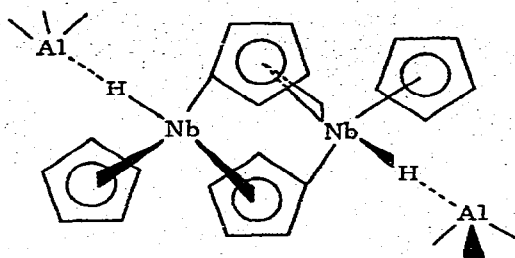
XXIX

cluster as originally proposed. This finding was suggested on the shift of the  $\text{C}\equiv\text{O}$  bridging carbonyl frequencies to lower energy and on other infrared assignments.

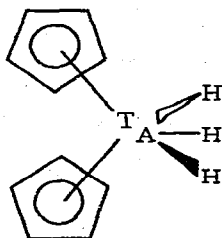
B. Preparation and Characterization of Compounds. A number of studies appeared on the preparation and reactions of new aluminum containing species. Tebbe<sup>105</sup> has characterized the reactions of dicyclopentadienyl niobium and tantalum hydrides with the alkyls of aluminum, gallium, zinc, cadmium and hafnium. Typical reactions are given in equations 39, 40 and 41. The exact



nature of these complexes has yet to be established but on the basis of the observed NMR spectra the following structures were proposed. A similar structure was suggested for the  $\text{Cp}_2\text{TaH}_3 \cdot \text{GaEt}_3$ . It also was shown that  $\text{Cp}_2$ -

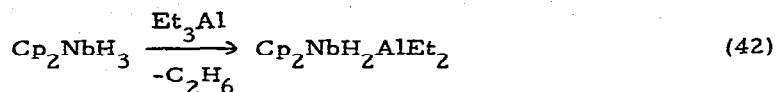


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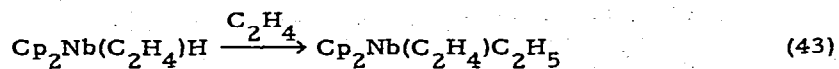


XXXI

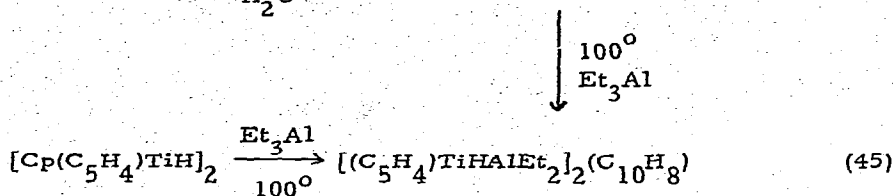
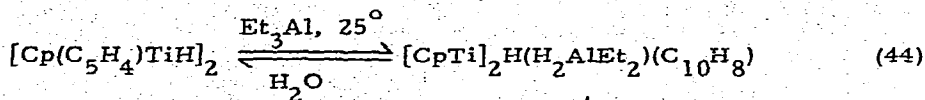
$\text{AlH}_3$  gave analogous complexes at  $-20$  to  $-50^\circ$  but that at room temperature the reaction indicated in 42 occurred with elimination of ethane. Further, it was



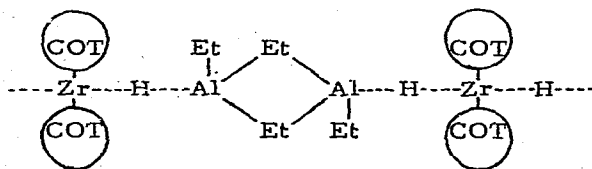
noted that  $\text{Et}_3\text{Al}$  deactivated the hydride ligand toward the insertion of ethylene as indicated in equation 43.



Guggenberger and Tebbe<sup>17</sup> also have reported the preparation of the compounds  $[\text{CpTi}]_2\text{H}(\text{H}_2\text{AlEt}_2)(\text{C}_{10}\text{H}_8)$  and  $[(\text{C}_5\text{H}_4)\text{TiHAlEt}_2]_2(\text{C}_{10}\text{H}_8)$  via the reactions shown in equations 44 and 45. The structures for these are given in section 2.



In other studies<sup>106</sup> it was shown that the insoluble complex  $(\text{COT})_2\text{Zr}$  ( $\text{COT} = \text{cyclooctatetraene}$ ) could be prepared by the reduction of  $\text{Zr}(\text{OR})_4$  with  $\text{Et}_3\text{Al}$  in the presence of  $\text{COT}$  or by the treatment of  $\text{R}_4\text{Zr}$  with  $\text{COT}$ . The complex dissolves in  $\text{Et}_2\text{AlH}$  readily to give 1/1 and 1/2 adducts of the form  $(\text{COT})_2\text{Zr}[\text{HAlEt}_2]_1$  or 2. These and other complexes have been studied by  $^1\text{H}$  NMR and on this basis the structure shown in XXXII was proposed for the hydride complex.

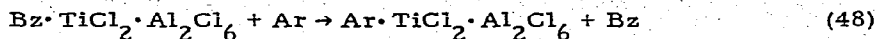
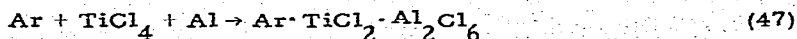


XXXII

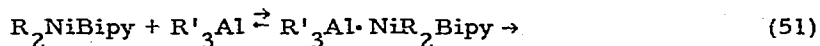
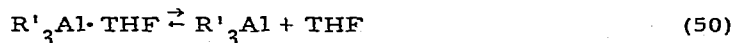
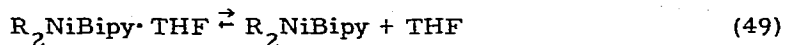
Bresler, et al.,<sup>107</sup> have reported that  $\text{Me}_3\text{Al}$  interacts with tetra-tert-butoxy titanium to give the dimer  $\text{Me}_4\text{Al}_2(\text{O}-t\text{-Bu})_2$  and  $\text{MeTi}(\text{O}-t\text{-Bu})_3$ . The NMR spectra of these products are unchanged after heating to  $75^\circ$  in toluene, thus indicating that the  $\text{MeTi}(\text{O}-t\text{-Bu})_3$  is stable under these conditions and does not undergo loss of methyl in the absence of excess  $\text{Me}_3\text{Al}$ .

On another study on titanium derivatives, Pasynkiewicz, et al.,<sup>108</sup> reported a new method for the preparation of  $\text{Ar}\cdot\text{TiCl}_2\cdot\text{Al}_2\text{Cl}_6$  complexes ( $\text{Ar} = \text{Me}_4\text{H}_2\text{C}_6$ ,  $\text{Me}_5\text{HC}_6$  or  $\text{Me}_6\text{C}_6$ ). These syntheses were accomplished by the reactions shown in 47 and 48.

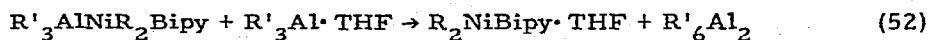




In a rather interesting sequence of reactions,  $\text{R}'_3\text{Al}$  and  $\text{R}'_2\text{AlOEt}$  ( $\text{R}' = \text{Me, Et, n-Pr}$ ) were reacted with a series of transition metal compounds including  $\text{MeTiCl}_3$ ,  $\text{R}_2\text{NiBipy}$ ,  $\text{EtGrCl}_2\text{Py}_3$ ,  $\text{R}_2\text{FeBipy}$  and  $\text{MeCu}(\text{PPh}_3)_3\text{C}_6\text{H}_5\text{Me}$ .<sup>109</sup> The kinetics of the cleavage of the TiMe bond in  $\text{MeTiCl}_3$  and the RNi bonds in  $\text{R}_2\text{NiBipy}$  by  $\text{R}'_3\text{Al}$  were studied in solution. In both cases the reactions were first order with respect to the alkyl-transition metal compounds. The pseudo first order rate constants for the decomposition of  $\text{R}_2\text{NiBipy}$  in THF solution on addition of  $\text{R}'_3\text{Al}$  were proportional to the concentration of  $\text{R}'_3\text{Al}$  for low concentrations of  $\text{R}'_3\text{Al}$  and to  $1/\text{R}'_3\text{Al}$  for high concentrations. Based on the observed kinetics the mechanism indicated in equations 49, 50 and 51 was proposed for the reaction. This involves the coordination of  $\text{R}'_3\text{Al}$  with  $\text{R}_2\text{NiBipy}$  followed by



splitting of the R-Ni bond in the adduct. The decrease in the rate constant at higher concentrations of  $\text{R}'_3\text{Al}$  was attributed to displacement of the complexed organoaluminum component by reaction with  $\text{R}'_3\text{Al} \cdot \text{THF}$  as indicated in 52. The

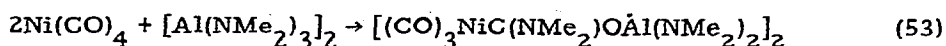


EPR spectra of catalytic systems  $\text{AlEt}_3$ -bis(acac)Co and  $\text{AlEt}_3$ -bis(acac)CoPPh<sub>3</sub> in PhMe,  $\text{C}_6\text{H}_6$ , cyclohexene, decane, Ar or  $\text{H}_2$  were measured at room temperature and liquid nitrogen temperature. The initial concentration of bis(acac)-

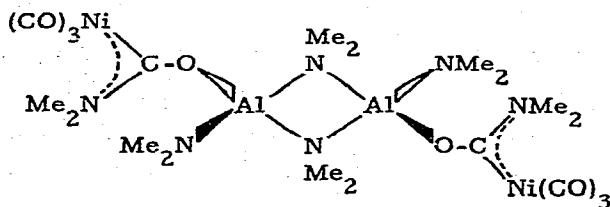
Co,  $\text{AlEt}_3$  and  $\text{PPh}_3$  in PhMe and  $\text{C}_6\text{H}_6$  were  $5 \times 10^{-2}$ , 0.5 and 0.2M respectively. A symbatic dependence of the EPR intensity and hydrogenation rate of cyclohexene on the Al/Co ratio was observed in the presence of the above catalytic system. The EPR signal with  $g = 2.16$  and  $\Delta H = 550$  Oe was attributed to one catalytically active complex (with the number of unpaired electrons  $> 1$ ) in the hydrogenation of cyclohexene. The structure of the catalytically active complex was suggested.

In another study Yamamoto, et al.,<sup>111</sup> have shown that the manganese hydride complex,  $\text{MnH}(\text{THF})_{1.5}$  can be prepared from  $\text{MnI}_2$  and  $\text{Et}_3\text{Al}$  in THF. Binary complexes of composition  $\text{MnAl}_2\text{Me}_4\text{I}_4(\text{THF})_4$  and  $\text{MnAl}_2\text{Et}_4\text{I}_4(\text{THF})_4$  were obtained by reaction of  $\text{Mn}_2\text{I}_{10}$  in THF with  $\text{Et}_3\text{Al}$  or  $\text{Me}_3\text{Al}$  and were found to be composed of  $\text{MnI}_2$  and  $\text{R}_2\text{AlI}$  units. These binary complexes reacted further with  $\text{R}_3\text{Al}$  to give the hydrido-manganese complex,  $\text{MnAlH}_4\text{I}_6(\text{THF})_8$ . The complexes were characterized by elementary analysis, infrared studies, magnetic susceptibility measurements, and chemical reactions.

Petz<sup>112</sup> reported the formation of a nickel carbene complex via the reaction indicated in 53 and proposed the structure shown in XXXIII on the basis of



NMR and infrared studies.



XXXIII

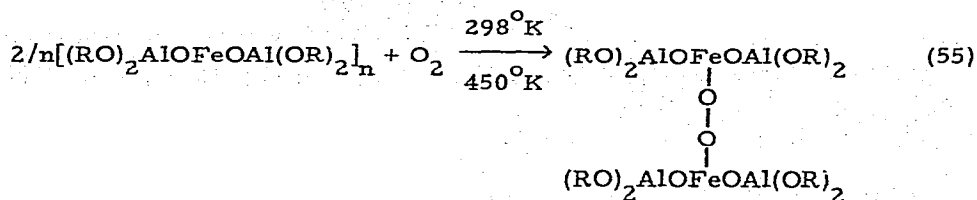
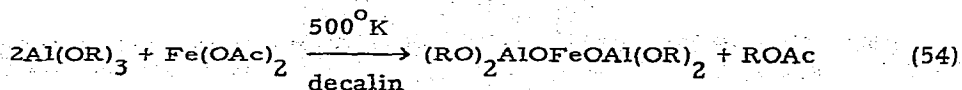
C.  $\text{N}_2$  and  $\text{O}_2$ -Aluminum-Transition Metal Complexes. Several studies

have appeared in which  $N_2$  or  $O_2$  metal complexes have been shown to react with aluminum alkyls or involve aluminum alkyls in their formation. Chatt, et al.,<sup>113</sup> have investigated the formation of adducts of the type  $M\text{-XY}\cdot\text{AlR}_3$  by reaction of the Lewis acid  $\text{R}_3\text{Al}$  ( $\text{R} = \text{Me}, \text{Ph}$  or  $\text{Cl}$ ) with  $\text{Mo}(0)$  and  $\text{W}(0)$ ,  $\text{Rh}(\text{I})$  and  $\text{Os}(\text{II})$  complexes containing  $\text{X-Y}$  ( $\text{X-Y} = \text{N}_2$  or  $\text{CO}$ ) in benzene solution. They have examined the complexes by infrared and NMR spectroscopy and in some cases by isolation of the crystalline 1/1 adducts. The order of relative basic strengths toward  $\text{Me}_3\text{Al}$  in benzene solution has been deduced as follows by study of the  $^1\text{H}$  NMR spectra of equilibrium mixtures of  $\text{Me}_3\text{Al}$ , the compounds, and ether in benzene solution.

$\text{THF} > \text{trans}[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4] > \text{trans}[\text{Mo}(\text{N}_2)_2(\text{Dpe})_2] > \text{trans}[\text{W}(\text{N}_2)_2(\text{Dpe})_2] > \text{trans}[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_2(\text{P}(\text{OMe})_3)_2] > \text{trans}[\text{ReCl}(\text{CO})(\text{PMe}_2\text{Ph})_4] > \text{Et}_2\text{O} > \text{mer-}[\text{OsCl}_2(\text{N}_2)(\text{PEt}_2\text{Ph})_3]$  ( $\text{Dpe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ). Comparison of the dipole moments of the pair of compounds  $\text{trans-}[\text{ReCl}(\text{XY})(\text{PMe}_2\text{Ph})_4]$  shows that the dinitrogen ligand is only slightly more negatively charged than the carbonyl group.

Aresta<sup>114</sup> has reported the preparation and properties of the 2/1 adducts of  $\text{Et}_3\text{Al}$  with  $\text{cis-Mo}(\text{N}_2)_2\text{L}_4$ ,  $\text{cis-Mo}(\text{CO})_2\text{L}_4$  ( $\text{L} = \text{PhMe}_2\text{P}$ ),  $\text{trans-Mo}(\text{N}_2)_2\text{L}'_4$  ( $\text{L}' = \text{PhEt}_2\text{P}$ ),  $\text{trans-Mo}(\text{N}_2)(\text{Dpe})_2$ ,  $\text{cis-}$  and  $\text{trans-Mo}(\text{CO})_2(\text{Dpe})_2$ . He reports that chemical and spectroscopic evidence shows that  $\text{Et}_3\text{Al}$  is bound to the oxygen atom in the CO complexes and to the terminal nitrogen in the  $\text{N}_2$  complexes. He also states that  $\text{trans-Mo}(\text{CO})_2(\text{Dpe})_2$  isomerizes to the  $\text{cis}$  derivative in the presence of catalytic amounts of  $\text{Et}_3\text{Al}$ .

Ouhadi, et al.,<sup>115</sup> have reported the reaction shown in 54. An aluminum-iron complex is formed which can reversibly take up oxygen as indicated in equation 55. Their conclusions regarding this complex were drawn from analysis and from studies on the u. v. visible and EPR spectra and molecular weight

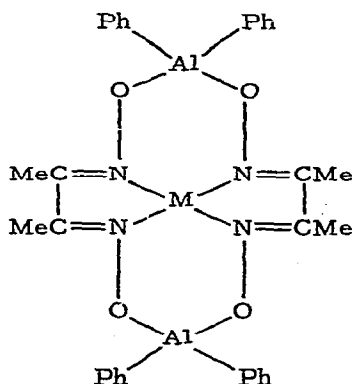


### 13. Aluminum Coordination Compounds

Several conventional studies have been reported on the formation of aluminum complexes. Sen and White,<sup>116</sup> for example, have prepared monomeric complexes of the type  $\text{R}_2\text{MQ}$  ( $\text{R} = \text{Me}, \text{Et}, i\text{-Bu}$ ;  $\text{M} = \text{Al}, \text{Ga}, \text{In}$ ;  $\text{Q} = \text{quinoline-8-olate anion}$ ) and have characterized these by analysis and by infrared, electronic, NMR and mass spectroscopy. The molecular weight of  $\text{Et}_2\text{GaQ}$  was determined by osmometry. The reactivity of the C-M bond seemed much less than that in the free alkyl. The chemical shifts of the NMR spectra were rationalized on the assumption of delocalization of the C-M bonding electrons by participation in the s and d orbitals of the metal atom, which was in turn said to reduce the C-M bond reactivity. Electronic spectra suggested ligand  $\pi \rightarrow$  metal d (or s) transitions. Metal-nonmetal vibrations  $\nu_1$  and  $\nu_2$  could be identified for  $(i\text{-Bu})_2\text{MQ}$  in the region  $535 - 380 \text{ cm}^{-1}$ . These authors<sup>117</sup> also prepared complexes of the form  $\text{R}_3\text{MLH}$  and  $(\text{R}_2\text{-ML})_2$  ( $\text{M} = \text{Al}, \text{Ga}, \text{In}$ ;  $\text{R} = \text{Me}, \text{Et}, \text{Me}_2\text{CHCH}_2$ ;  $\text{LH} = \text{piperidene}$ ) and characterized them. It was suggested, on the basis of infrared and NMR spectral studies, that the C-M bond polarity in  $\text{R}_3\text{MLH}$  was enhanced inductively by coordination, but that replacement of one covalent C-M bond by N-M compensated for this effect. The inductive effect was more influenced by the size of M and possible participation of the d orbitals in bonding than by the electronegativity of M.

Abbott and Martell<sup>118</sup> have reported the NMR spectra of a series of pyridoxal-amino acid Schiff base complexes of Al(III) in D<sub>2</sub>O solution in the Pd range 3 - 5.5. Under these conditions the complexes formed contain a 1/1 molar ratio of Schiff base to metal ion. The spectra reported were similar to those reported earlier for the 1/1 pyridoxylidenealanatoaluminum system, with the exception that in this work no evidence was found for a complex containing an uncoordinated carboxylate group. The rapid changes in the NMR spectra were interpreted in terms of formation intermediates which were discussed in terms of the role which they may play in a general model for the metal-catalyzed reactions of vitamin B<sub>6</sub>.

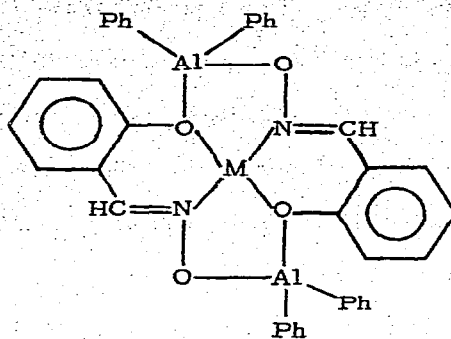
Voiculescu, et al.,<sup>119</sup> have investigated the reaction of Ph<sub>3</sub>Al with ML<sub>2</sub> (M = Ni, Pd, Cu; HL = dimethylglyoxime). The reaction products were charac-



XXXIV

terized by chemical analysis, magnetic measurements and infrared spectra. The X-ray diffraction data indicate that all of the compounds are amorphous.

This same research group<sup>120</sup> also studied the salicylaldehyde metal complexes with Ph<sub>3</sub>Al and proposed the structure shown in XXXV on the basis of

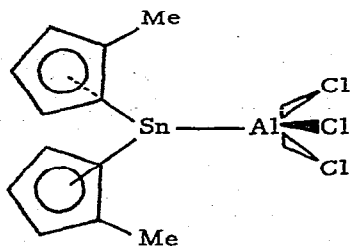


XXXV

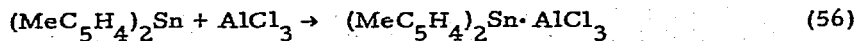
their studies. The reaction of this complex with pyridine gave adducts with the amine bound to the aluminum atom and not the metal M.

#### 14. Aluminum-Tin Bonded Compounds

The rather novel aluminum-tin bonded species shown in XXXVI is formed by the addition of the two components as shown in equation 56.<sup>121</sup> The infrared

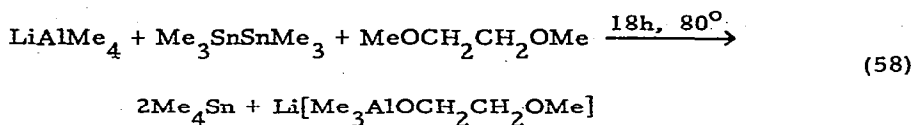
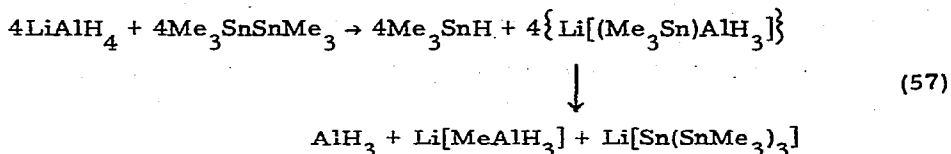


XXXVI



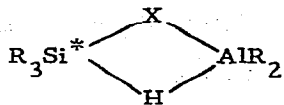
spectrum of this complex has been observed and the normal modes assigned by comparison with bis(methylcyclopentadienyl)tin. These studies led to the proposed angular "sandwich" complex.

Weibel and Oliver<sup>122</sup> have investigated the reaction of  $\text{LiMR}_4$  ( $M = \text{Tl}, \text{Al}, \text{Ga}, \text{B}; R = \text{Me}, \text{H}$ ) with  $\text{Me}_6\text{Sn}_2$ . For thallium, aluminum and gallium derivatives, Sn-Sn bond cleavage was observed with formation of intermediates containing Sn-M bonds as shown in equation 57. With  $\text{LiAlMe}_4$  reaction 58 also was shown to occur. The reaction products were characterized by NMR spectroscopy and in some instances by chemical analysis.



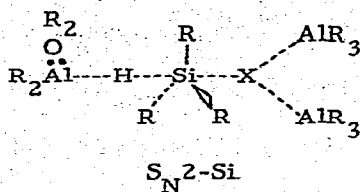
### 15. Miscellaneous Reactions

Sommer, et al.,<sup>123</sup> have studied the reduction of  $\text{R}_3\text{Si}^*\text{OCHMe}_2$  in ether and  $\text{R}_3\text{Si}^*\text{F}$  in hexane and of  $\text{R}_3\text{Si}^*\text{F}$  and  $\text{R}_3\text{SiCl}$  in ether with  $i\text{-Bu}_2\text{AlH}$ . They found that they could correlate the molecularity of the transition state with the stereochemical course of the reaction. Thus, for the first two examples which proceed with retention the  $\text{S}_{\text{N}}\text{i-S}_{\text{i}}$  mechanism with transition state XXXVII was suggested and for the latter two reactions which proceed with inversion and presumably by an  $\text{S}_{\text{N}}2\text{-S}_{\text{i}}$  mechanism, the transition state in XXXVIII was suggested.



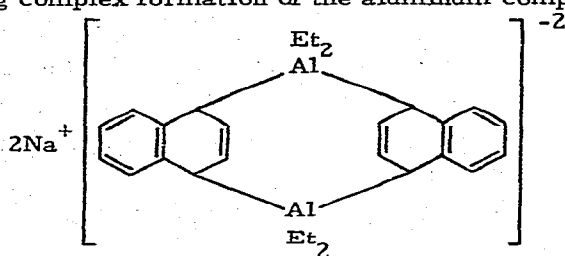
$\text{S}_{\text{N}}\text{i-S}_{\text{i}}$

XXXVII



XXXVIII

While in another study the competitive action of 1/1 H<sub>2</sub>O/D<sub>2</sub>O mixtures on the complexes shown in XXXIX showed that protolysis of this is preceded by rate determining complex formation of the aluminum compound.



XXXIX

In a final study the relative and absolute intensities of chemiluminescence of Me<sub>3</sub>Al on reaction with atomic oxygen has been studied.<sup>125</sup>

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