understood in terms of (a) the probable linear O–Cu–O arrangement that tends to buttress the altered GeO_4 structure and (b) the possibility that extensive GeO_6 octahedra formation may not occur with the first few per cent of Cu_2O added. The infrared results for both binary and ternary glasses suggest that further additions of Cu_2O can create extensive network depolymerization *via* GeO_6 octahedra formation.

Copper(II) appears to play an important network-bridging role in all ternary glasses studied that contain more than 78 mol % GeO_2. Although it may continue to do so in the smaller GeO_2 content Cu(II):Cu(I) = 0.150 glasses, its influence is diminished because the relatively large amounts of Cu_2O (glass M has 21.8 mol % Cu_2O) have greatly depolymerized the GeO_4 network *via* extensive GeO_6 octahedra formation. In essence, as the GeO_2 content decreases for the Cu(II):Cu(I) = 0.150 glasses, (a) both copper(I) and copper(II) appear to buttress the open network at higher GeO_2 levels and (b) the structure-breaking effect of copper(I) outweighs the structure-making effect of copper(II) at lower GeO_2 levels.

It is possible to confirm GeO_4 network polymerization changes that have been suggested from other physical property measurements for such oxide glasses by monitoring the frequency of the main infrared-active Ge–O vibration as a function of composition. The trends between infrared isofrequency contours for ν_{Ge-O} appear to be reasonably sensitive indicators of the contrasting roles played by copper(I) and copper(II) in altering or maintaining such oxide networks. This latest application of the aforementioned spectral technique thus serves to strengthen its validity as a structural survey tool for ternary oxide glass systems that involve network depolymerization.

Acknowledgment. Mr. J. Sprinkle assisted with the preparation and analysis of the glasses and also with the measurement of some of the densities and refractive indices.

Registry No. $[(CH_3)_3C]_2PF_3$, 29120-68-1; $[(CH_3)_3C]_2PCl$, 13716-10-4.

Contribution from the Department of Polymer Science, Faculty
of Science, Osaka University, Toyonaka, Osaka, 560, Japan

Bis(dialkylaluminum) Oxide from Lithium Dialkylaluminates and Dialkylaluminum Chlorides[1,2]

NORIKAZU UEYAMA, TAKEO ARAKI,* and HISAYA TANI

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A synthetic method for the preparation of bis(dialkylaluminum) oxides using the condensation of lithium dialkylaluminates and dialkylaluminum chlorides was investigated. The reaction products were found to show identical properties with the bis(dialkylaluminum) oxides obtained by Storr, Jones, and Laubengayer in the hydrolysis of trialkylaluminum with water in a 2:1 ratio under high dilution. Synthetic studies indicate that the new method is promising for preparing some derivatives of the bis(aluminum) oxides. On the basis of ir and conductivity experiments, the nature of the Al–O–Al bond in the $Et_2AlOAlEt_2$ compound is suggested to be considerably polarizable. 5,6-Benzoquinolinate complexes were isolated in crystalline forms and investigations of the complexes together with their related compounds showed that the monocoordinated complexes are more stable than the dicoordinated ones. The unusual electron-accepting nature of the $R_2AlOAlR_2$ compounds can be due to the bidentate property of two aluminum atoms in a molecule.

Introduction

Bis(dialkylaluminum) oxides have been synthesized by the hydrolysis of the corresponding trialkylaluminums.[3,4] Recently, Storr, Jones, and Laubengayer[4] presented a report on the characterizations of the bis(dialkylaluminum) oxides obtained by this method under highly diluted conditions. Since there is little information on the mechanism of the hydrolysis of trialkylaluminum compounds,[5] however, one might have considered the product to be a mixture of the hydrolysates involving different numbers of the Al–O bonding unit. In one study[6] the Lewis acidity of the system containing the hydrolysates was suggested to increase with extensive hydrolysis of the triethylaluminum, $AlEt_3$. In such a case, attack of a water molecule on the bis(dialkylaluminum) oxide formed would be more probable than attack on trialkylaluminum, resulting in the higher members of condensation product. In order to clarify the problems involved in the bis(dialkylaluminum) oxide compound, it would be desirable to find a new synthetic procedure of preparing such compounds by a different route. Although several reactions giving this compound have been reported,[7-12] few are useful because of the formation of organoaluminum by-products.

(1) This study constitutes a part of the Ph.D. thesis of Dr. N. Ueyama, Osaka University, 1970.

(2) Preliminary publications: (a) H. Tani, T. Araki, N. Oguni, and N. Ueyama, *J. Amer. Chem. Soc.*, 89 173 (1967); (b) T. Araki, T. Aoyagi, N. Ueyama, T. Aoyama, and H. Tani, *J. Polym. Sci., Part A-1*, 11, 699 (1973).

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Recently, we disclosed[13,14] a method for preparing alkali metal dialuminates (R_2AlOM) by equimolar reactions of trialkylaluminum and alkali metal hydroxide. Upon treating the Et_2AlOLi compound with diethylaluminum chloride a product having the constitution $Et_2AlOAlEt_2$ was obtained.[2] The catalytic behavior of this product in polymerizing acetaldehyde and some epoxides was essentially identical with that of the hydrolysate of triethylaluminum (by 0.5 molar equiv of water[2b]). In the present study we achieved the preparation of some derivatives of the bis(dialkylaluminum) oxide by the new condensation reaction, showing that the method is promising for other syntheses. In addition, some fundamental properties of the compounds which were investigated agreed with the descriptions of Storr, *et al.*[4]

Our present work will contribute not only to the field of binuclear organoaluminum chemistry but also to the field of polymerization chemistry because the AlR_3-H_2O systems have been recognized as important stereoregulating catalysts for a wide variety of polar monomers.

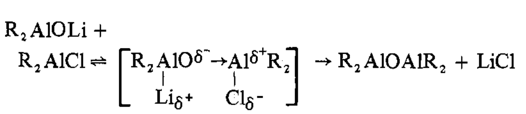
Results and Discussion

Reaction of R_2AlOLi and R_2AlCl. According to the method reported previously,[14] R_2AlOLi compounds were prepared (eq 1) in ligroin (bp 100-140°) for R = Et and *i*-Bu and in anisole for R = Me. The less soluble by-product, $[R_2AlOLi]\cdot[AlR_3]$ complex, was carefully separated.

$$AlR_3 + LiOH \rightarrow R_2AlOLi + RH \quad (R = Me, Et, i\text{-}Bu) \tag{1}$$

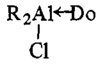
On agitating an equimolar mixture of the *n*-hexane solutions of R_2AlOLi and R_2AlCl compounds, lithium chloride was precipitated. After complete separation of the LiCl followed by evaporation of the solvent, a colorless liquid having a constitution corresponding to $R_2AlOAlR_2$ was obtained. The behavior of the methyl derivatives was somewhat different: as the reaction of Me_2AlCl with Me_2AlOLi (insoluble in *n*-hexane) proceeded, the heterogeneity of the system was decreased by the formation of a soluble intermediate complex between the two compounds followed by the precipitation of LiCl. In this case, prolonged stirring was required for completion of the reaction.

In the presence of basic compounds, such as ethers or amines, the rate of deposition of LiCl decreased with increasing basicity. The steric crowding of the alkyl groups in the R_2AlOLi and R_2AlCl compounds also exerts a retarding effect on the rate. Thus, the reaction can be represented as shown in the eq 2.



$$\begin{array}{l} R_2AlOLi + \\ R_2AlCl \rightleftharpoons \left[\begin{array}{cc} R_2\underset{\displaystyle Li_{\delta^+}}{\underset{|}{AlO^{\delta-}}} \rightarrow & \underset{\displaystyle Cl_{\delta^-}}{\underset{|}{Al^{\delta+}}}R_2 \end{array}\right] \rightarrow R_2AlOAlR_2 + LiCl \end{array} \tag{2}$$

Since the observed values of the specific conductivity of the R_2AlOLi compound are considerably higher than those of R_2AlCl (*e.g.*, $\kappa_{Et_2AlOLi} = 5.6 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ and $\kappa_{Et_2AlCl} = 5.5 \times 10^{-10}\ \Omega^{-1}\ cm^{-1}$, respectively, at 25°, 1.47 *M* in toluene), the coordination of the R_2AlOLi molecule to the R_2AlCl presumably results in a $[R_2AlOAlR_2Cl]^-Li^+$ complex which dissociates rapidly into the $R_2AlOAlR_2$ compound and LiCl. When the R_2AlCl carries a donor molecule the R_2AlOLi molecule has to exchange with the donor molecule. If the R_2AlOLi compound is donor free, the donor molecule on the R_2AlCl molecule can readily migrate onto the aluminum atom of the R_2AlOLi molecule by 1,3 rearrangement through a four-membered cyclic transition state. On the contrary, when the R_2AlOLi compound carries a donor molecule, certain difficulties in obtaining a reasonable product are frequently experienced. Probably this is due to a mixed coordination of the donor molecule with the Al and Li atoms.



$$R_2\underset{\displaystyle Cl}{\underset{|}{Al}}\leftarrow Do$$

Syntheses of the several derivatives were carried out using $R_2AlCl\cdot Do$ (eq 3), $R_2AlOLi\cdot Do$ (eq 4), RClAlZ (eq 5), or R'_2AlCl (eq 6) compounds. For compounds of type **1**,

$$R_2AlOLi + R_2AlCl\cdot Do \rightarrow \underset{\mathbf{1}}{[R_2AlOAlR_2]\cdot Do} + LiCl \tag{3}$$

$$R_2AlOLi\cdot Do + R_2AlCl \rightarrow \underset{\mathbf{1}}{[R_2AlOAlR_2]\cdot Do} + LiCl \tag{4}$$

$$R_2AlOLi + RClAlZ \rightarrow \underset{\mathbf{2}}{R_2AlOAlRZ} + LiCl \tag{5}$$

$$R_2AlOLi + R'_2AlCl \rightarrow \underset{\mathbf{3}}{R_2AlOAlR'_2 \text{ or } RR'AlOAlRR'} + LiCl \tag{6}$$

$[Me_2AlOAlMe_2]\cdot THF$ (eq 3), $[Me_2AlOAlMe_2]\cdot PhOMe$ (mp −50°, by eq 4), and $[Et_2AlOAlEt_2]\cdot THF$ (eq 3) were obtained and characterized by nmr spectroscopy. In the preparation of various tertiary aminates of type **1**, such as triethylaminate, quinolinates, and benzoquinolinates (pyridine gave a resinous colored product), the apparent retardation of the reaction by eq 3 depended upon the steric crowding around the nitrogen atoms, and the crystallizabilities of the products were roughly paralleled by the melting points of the amines used. Among them, 5,6-benzoquinolinate could be obtained as pale yellow needles (mp 75° dec) and thus allowed a reasonable identification.

The formation of the $Et_2AlOAlEt_2$-styrene oxide complex exemplifies a direct complexation process (eq 7) leading to the type **1** compound. In most of the cases tested, however, this route is not widely applicable, presumably due to the formation of a mixture of $[R_2AlOAlR_2]\cdot Do$ and $[R_2AlOAlR_2]\cdot 2Do$ complexes and their aggregates. Thus, the nature of the donor compound seems important for the route (7). We can conclude that the route of eq 3 is the most promising for the syntheses of the type **1** complexes.

$$R_2AlOAlR_2 + Do \rightarrow [R_2AlOAlR_2]\cdot Do \tag{7}$$

For the compounds of type **2**, bornylate was obtained as colorless needles but acetylacetonate as a yellow oily product which gradually disproportionated into $Al(acac)_3$. For the compounds of type **3**, a bis(aluminum) oxide derivative containing mixed-alkyl groups ($Et_2AlOAlMe_2$ or EtMeAlOAlEtMe) was obtained from the reaction of Et_2AlOLi and Me_2AlCl.

Our condensation procedure offers at least three significant advantages: the process is not highly exothermic and requires no supply of external heat; the end point of the reaction is detectable by analysis of chloride or lithium ions in an aliquot of the organic layer; furthermore, the LiCl formed can readily be separated from the system. The major disadvantage of the process, on the other hand, is the limited supply of R_2AlOLi compound[14] which must be extensively freed from AlR_3 or $[R_2AlOLi]\cdot[AlR_3]$. Although R_2AlOLi can be replaced by R_2AlONa, when available, further work will be needed for the preparation of this type of compound.

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Characterization, Structures, and Properties of Bis(dialkylaluminum) Oxides and Their Derivatives. $R_2AlOAlR_2$. The $R_2AlOAlR_2$ compounds obtained are colorless liquids at room temperature. They are completely soluble in nonpolar solvents such as *n*-hexane and *n*-pentane, showing the inclusion of no significant amount of the *n*-hexane-insoluble polymeric $-(RAlO)_n-$ compound.[2b]

Measurement of the molecular weight indicated $Et_2AlOAlEt_2$ to be a tetrameric aggregate, on the average, at a given concentration.[2b] Although this value is not consistent with the reported trimeric value,[4] the discrepancy might be due to the concentration dependence in the association of this compound.[15,16] Considering that the compound contains "two" electron-deficient Al atoms and "one" electron-donating oxygen atom per molecule and that the rotational barrier around the Al-O-Al bond is relatively low, it seems rather difficult for the compound to assume any definite structure in the associated state. Owing to the steric requirement of the *i*-Bu group, the degree of association of $(i\text{-}Bu)_2AlOAl(i\text{-}Bu)_2$ compound varies within a range from 1.1 (extrapolation to zero concentration) to 1.5 (which is probably a convergence limit of the degree of association (see Figure 5)).

A compound of the type $R_2AlOAlR_2$ disproportionates into AlR_3 and polymeric $-(RAlO)_n-$ substances readily by heating under reduced pressure (for safe handling, >3 mm at room temperature is recommended for removal of solvents) and slowly on storage at room temperature. Similar behavior has been observed for $Et_2AlOAlEt_2$ obtained from the water system under specified high dilution[4] and in the conventional reaction.[2b]

$Et_2AlOAlEt_2$ shows considerable conductance at 25° in toluene. Concentration dependence of the specific conductivity is as follows: $\kappa = 2.1 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 1.47 *M*, $4.9 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 0.735 *M*, and $3.2 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ at 0.368 *M*, respectively. The value at 1.47 *M* is slightly lower than that of Et_2AlOLi but higher than that of Et_2AlCl by a factor of 10^5. The Al-O-Al bond in the $Et_2AlOAlEt_2$ compound can be represented as a partially polarized bond

$$Et_2Al^{\delta+}\cdots O^{\delta-}\overline{\cdots\cdots} AlEt_2 \leftrightarrow Et_2Al\overline{\cdots} O^{\delta-}\cdots Al^{\delta+}Et_2$$

Since the Et-Al group of this compoud does not give any Grignard addition product in the reaction with acetaldehyde,[2b] the polarization of the Et-Al group is not responsible for the conductivity.

The infrared spectrum of $Et_2AlOAlEt_2$ in cyclohexane highly resembles that reported by Storr, *et al.*[4] (Table I). The patterns of $R_2AlOAlR_2$ appeared to be composed of the absorptions of AlR_3 plus some broad absorptions around 700-800 cm^{-1}. Recording the spectrum of the $Et_2AlOAlEt_2$ compound in cyclohexane by a careful compensation technique with a solution of $AlEt_3$ in cyclohexane gave a clear-cut resultant spectrum reasonably ascribable to the ν_{AlOAl} frequencies (Figure 1). By use of this result, the ν_{AlOAl} frequencies of $(i\text{-}Bu)_2AlOAl(i\text{-}Bu)_2$ and $Me_2AlOAlMe_2$ can be explicitly identified (Table II). The Al-O-Al frequencies compare reasonably with the reported $\nu_{1(AlOAl)}$ frequency of aluminum suboxide (Al_2O).[17]

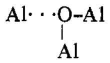
Table I. Infrared Spectra of $Et_2AlOAlEt_2$ (cm^{-1})

Prepared from Et_2AlOLi and Et_2AlCl (in cyclohexane)	Prepared from $AlEt_3$ and water[4] (in benzene)	Assignments
1225 m	1225 m	} $\gamma(CH_2\text{-}Al)$
1197 m	1195 m	
. . .	1165 m	Al-O-H ? ⋮ Al
989 s	985 s	} $\nu(CC)$
956 m	955 m	
924 m	924 m	
795 vs, br	790–815 vs, br	} $\nu(Al\text{-}O\text{-}Al)$
	755–770 vs, br	
700 vs, br	735 vs, br	
660 vs	654 vs	ν_{as}
547 m	545 m	ν_s

Table II. $\nu(Al\text{-}O\text{-}Al)$ Frequencies in $R_2AlOAlR_2$ Compounds (cm^{-1})

Compd	ν_a	ν_b	$\nu_a - \nu_b$
$Me_2AlOAlMe_2$	815	705	110
$Et_2AlOAlEt_2$	795	700	95
$(i\text{-}Bu)_2AlOAl(i\text{-}Bu)_2$	780	710	70

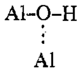
The two absorptions in the ν_{AlOAl} region may arise from the isolated Al-O-Al (ν_a—at higher wave number) and the associated



$$\begin{array}{c} Al\cdots O\text{-}Al \\ | \\ Al \end{array}$$

(ν_b—at lower wave number) groupings. The bond energy of the latter appears almost independent of the nature of the alkyl group, while that of the former varies significantly in the decreasing order of $(i\text{-}Bu)_2AlOAl(i\text{-}Bu)_2 > Et_2AlOAlEt_2 > Me_2AlOAlMe_2$. This order can be regarded as a reflection of the polarized property of the Al-O-Al bonds.

Although Storr, *et al.*,[4] reported a medium absorption at 1165 cm^{-1} for the $Et_2AlOAlEt_2$ compound, this band can probably be due to the



$$\begin{array}{c} Al\text{-}O\text{-}H \\ \vdots \\ Al \end{array}$$

bending vibration since this band was not detected in our $Et_2AlOAlEt_2$ compound. Kolesnova[18] has reported the vibration frequency in $Al(OH)_3$ compound at 1060 and 1020 cm^{-1}, and Wilhoit, *et al.*,[19] observed the band in the partial hydrolysate of the $Al(OR)_3$ compound at 1350 cm^{-1}. In fact, examination of $(i\text{-}Bu)_3Al\text{-}H_2O$ (2:1) product prepared by a conventional procedure showed a considerably intense absorption around 1160 cm^{-1}, compatible with the appearance of a weak but broad resonance due to the OH protons at ~4 ppm in its nmr spectrum.

The nmr spectrum of the $Et_2AlOAlEt_2$ compound is finely resolved into one methyl triplet and one methylene quartet[20] showing all of the ethyl groups are equivalently attached to the aluminum atoms. The chemical shifts of the resonances and the internal chemical shift values $\Delta\delta = \delta_{CH_2} - \delta_{CH_3}$ are tabulated in Table III together with those of some related organoaluminum compounds. The value of the $\Delta\delta$ and consequently the electronegativity of the Al atoms in the $Et_2AlOAlEt_2$ compound seems to be intermediate between those of $AlEt_3$ and Et_2AlCl compounds.

The compound $Me_2AlOAlMe_2$ showed a single resonance indicating the methyl groups are also equivalent. The spec-

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(15) Monomeric[3] or dimeric[16] values have also been reported. However, the material used in the ref 3 was a distillate of $Et_2AlOAlEt_2$, and the value in the ref 16 was obtained in a system of $AlEt_3$ and water *in situ*.

(16) H. Fujii, S. Yasui, T. Saegusa, and J. Furukawa, *Kogyo Kagaku Zasshi*, 68, 976 (1965).

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(20) The fine structures are observed in the resonances, but these are consistent with those observed commonly in Et_2AlCl, Et_3Al, Et_2Zn, or their complexes.

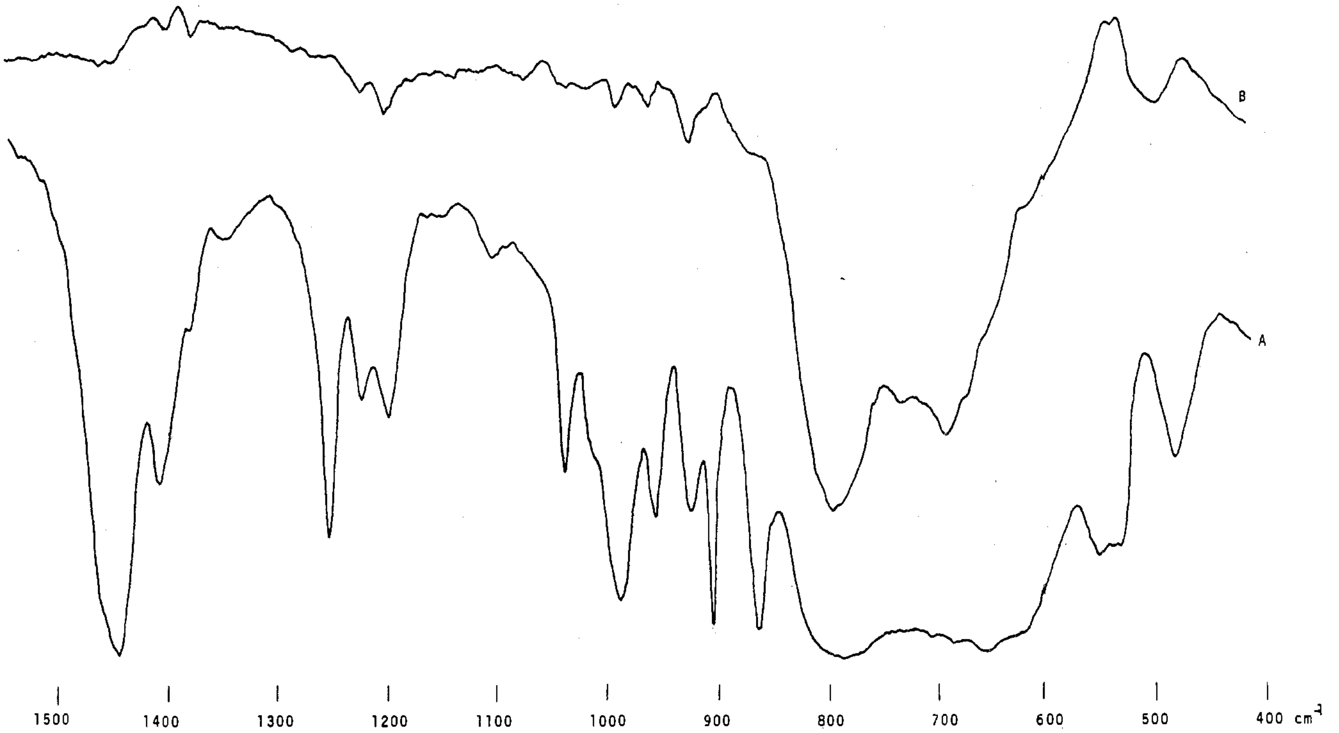

Figure 1. Infrared spectra of $Et_2AlOAlEt_2$: A, spectrum in cyclohexane solution; B, resultant spectrum of compensation with a cyclohexane solution of $AlEt_3$.

Table III. Nmr Data of Organoaluminum Compounds: Uncomplexed Compounds

Compd	Nmr resonances (group, δ in ppm,[a] splitting[b])			$\Delta\delta = \lvert\delta_{CH_3} - \delta_{CH_2}\rvert$
$AlEt_3$	CH_3, 0.45, t	CH_2Al, −0.30, q		0.75
Et_2AlCl	CH_3, 0.51, t	CH_2Al, −0.33, q		0.84
Et_2AlOLi	CH_3, 0.74, br s	CH_2Al, −0.60, br s		1.34
$Et_2AlOAlEt_2$	CH_3, 0.47, t	CH_2Al, −0.34, q		0.81
$Et_2AlOAlMe_2$	CH_3C, 0.43, t	CH_2Al, −0.56, q	CH_3Al, −0.84, s	1.04
$AlEt_3 + AlMe_3$ (1:1)	CH_3C, 0.41, t	CH_2Al, −0.53, q	CH_3Al, −0.77, s	0.88
Me_2AlCl	CH_3Al, −0.50, s			. . .
$Me_2AlOAlMe_2$	CH_3Al, −0.95, s			. . .
$(i\text{-Bu})_2AlCl$	CH_3, 0.76, d	CH, 1.76, m	CH_2Al, 0.18, d	0.58
$(i\text{-Bu})_2AlOLi$	CH_3, 0.70, br s	CH, 1.57, br s	CH_2Al, −0.52, br s	1.22
$(i\text{-Bu})_2AlOAl(i\text{-Bu})_2$	$CH_3 \begin{cases} 0.54, d \\ 0.65, br \end{cases}$	CH, 1.57, m	$CH_2Al \begin{cases} -0.11, d \\ +0.05, br \end{cases}$	0.65
$(i\text{-Bu})_2AlOAl(i\text{-Bu})_2 + Al(i\text{-Bu})_3$	CH_3, 0.52, d	CH, 1.51, m	CH_2Al, −0.19, d	0.71

[a] Externally standardized from TMS as δ 0.00 ppm or internally standardized from benzene protons (solvent) as δ 6.57 ppm, which is the average chemical shift of benzene protons (externally standardized from TMS) in the presence of the organoaluminum compounds. [b] Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

trum of $(i\text{-Bu})_2AlOAl(i\text{-Bu})_2$ consists of finely resolved *i*-Bu resonances superimposed on the somewhat broad ones. This indicates that in the associated part of the compound the *i*-Bu groups have different mobilities due to their steric factors. In comparison, the $\Delta\delta$ values of $(i\text{-Bu})_2AlCl$, $(i\text{-Bu})_2AlOLi$, and $Al(i\text{-Bu})_3$ compounds are listed in the Table III. The fact that addition of a small amount of $Al(i\text{-Bu})_3$ to the $(i\text{-Bu})_2AlOAl(i\text{-Bu})_2$ increased the $\Delta\delta$ value by 6 Hz and significantly decreased the intensities of the broad resonances suggests the above interpretation of the spectrum is reasonable.

Complexes of $R_2AlOAlR_2$. The complex $[Et_2AlOAlEt_2]\cdot$BQ (BQ = 5,6-benzoquinolinate) prepared according to the eq 3 was monomeric at a wide range of concentrations in benzene (<32%) and was confirmed to be a 1:1 complex by nmr spectroscopy. In benzene-d_6 a finely split methyl triplet, methylene quartet, and BQ ring multiplet (Figure 2 and Table IV) were observed with relative intensities of 12:8:9. The spectra of BQ protons[21-24] exhibited a pattern typical of its coordinated state, where all of the resonances espe-

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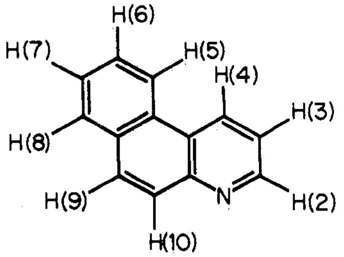
(21) For assignment of the protons of the BQ ring, the coupling constants are assumed as follows: J_{23} = 5–5.5 (obsd), J_{24} = ~1.5 (obsd), J_{34} = ~8.5 (obsd), J_{45} = ~4, $J_{4,10}$ = ~1 (obsd), J_{56} = ~8, J_{57} = ~2.5, J_{59} = ~1 (obsd), J_{67} = 6.5, J_{68} = ~2.5, J_{78} = ~8, $J_{9,10}$ = 9–9.5 (obsd), $J_{89} < 1$ Hz. These values except for J_{45} and J_{89} appear to be reasonable when compared with the reported coupling constants of the substituted quinolines.[22-24] In order to explain the observed broadening of the H(9) doublet, relative to the H(10) doublet, J_{89} was assumed not to be zero. The multiplicity in the H(4) resonance can be understood by assuming the J_{45} as ~4 Hz. Further confirmation of the validity of J_{89} and J_{45} requires more detailed studies, since there is a limitation caused by the closeness of the resonances of H(5)–H(8) protons in this type of compound.



(22) T. Schaefer, *Can. J. Chem.*, 39, 1864 (1961).

(23) F. A. N. Anet, *J. Chem. Phys.*, 32, 1274 (1960).

(24) W. Seiffert, *Angew. Chem., Int. Ed. Engl.*, 1, 215 (1962).

Table IV. Nmr Data of Organoaluminum Compounds: Complexed Compounds[a]

Compd	Nmr resonances (group, δ in ppm[b], splitting[c])		$\Delta\delta = \lvert\delta_{CH_3} - \delta_{CH_2}\rvert$
$[Et_3Al]\cdot BQ$	CH_3, 0.71, t; CH_2-Al, −0.22, q; ring H		0.93
$[Et_2AlCl]\cdot BQ$	CH_3, 0.72, t; CH_2-Al, +0.10, q; ring H		0.62
$[Et_2AlOLi]\cdot BQ$[d]	CH_3, 2.94, br s; CH_2-Al, +3.74, br s; ring H	Dioxane: CH_2O, 0.00	1.39
$[Et_2AlOAlEt_2]\cdot BQ$	CH_3, 0.70, t; CH_2-Al, −0.27, q; ring H		0.97
$[Et_2AlOAlEt_2]\cdot 2BQ$	CH_3, 0.85, t; CH_2-Al, −0.05, q; ring H		0.90
$[Me_3Al]\cdot BQ$	CH_3-Al, −0.58, s; ring H		. . .
$[Me_2AlCl]\cdot BQ$	CH_3-Al, −0.48, s + −0.37, vw, s; ring H		. . .
$[Me_2AlOAlMe_2]\cdot BQ$	CH_3-Al, −0.51, s + −0.59, vw, s; ring H		. . .
$[Et_2AlOAlMe_2]\cdot BQ$	CH_3-C, 0.90, t; CH_2-Al, −0.01, q; CH_3-Al, −0.63, s (−0.50 vw); ring H		0.91
$[Et_2AlOAlEt_2]\cdot THF$	CH_3, 0.84, t; CH_2-Al, −0.39, q	THF: CH_2, 1.02, m; CH_2O, 3,21, m	1.23
$[Me_2AlOAlMe_2]\cdot THF$	CH_3-Al, −0.94, s + −1.05, s	THF: CH_2, 0.66, m; CH_2O, 2.99, m	. . .
$[Me_3Al]\cdot PhOMe$	CH_3-Al, −1.25, s	Anisole: CH_3O, 2.94, s	4.19[e]
$[Me_2AlOLi]\cdot PhOMe$	CH_3-Al, −1.09, s	Anisole: CH_3O, 2.74, s	3.83[e]
$[Me_2AlOAlMe_2]\cdot PhOMe$	CH_3-Al, −1.16, s	Anisole: CH_3O, 2.93, s	4.09[e]

[a] In C_6D_6 or in C_6H_6, at room temperature. [b] See the footnote *a* in Table III. [c] See the footnote *b* in Table III. [d] In dioxane. [e] $\lvert\delta_{CH_3O} - \delta_{CH_3Al}\rvert$.

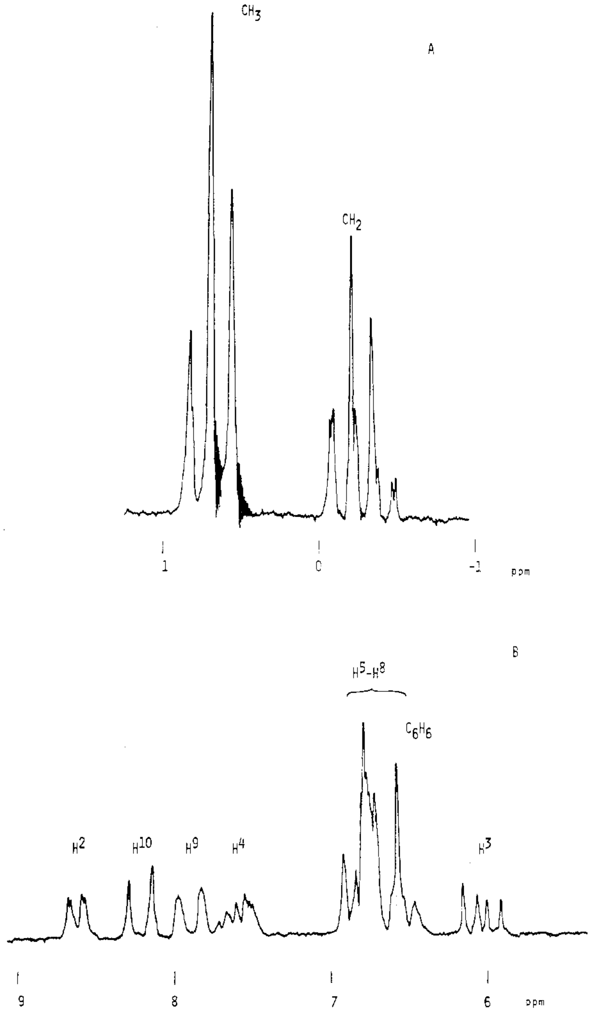
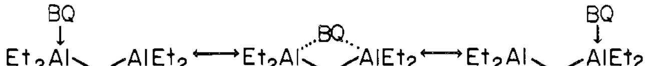


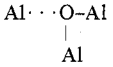
Figure 2. Nmr spectra of $[Et_2AlOAlEt_2]\cdot BQ$ complex in C_6D_6 at room temperature: A, resonances of Et-Al protons; B, resonances of 5,6-benzoquinoline ring protons.

cially of H_2, H_{10}, H_9, and H_4 are shifted independently to the lower field (Table V). The spectrum of the BQ ring protons strongly resembled in shape those of $[AlEt_3]\cdot BQ$ or $[Et_2AlCl]\cdot BQ$ complexes but differed in the chemical shift and the $\Delta\delta_{CH_3-CH_2}$ values.

Since only one kind of Et-Al group was observed and the compound was essentially monomeric at the concentration of the nmr study (see Figure 5), the BQ molecules can be inferred as rapidly fluctuating between the two Al atoms in the $Et_2AlOAlEt_2$ molecule resulting in a high stability of the complex. Similar descriptions can be applied to the $[Me_2AlOAlMe_2]\cdot BQ$ and ether complexes mentioned above.

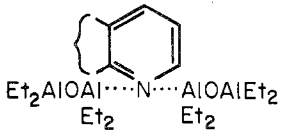


The ν_{AlOAl} frequency of the $[Et_2AlOAlEt_2]\cdot BQ$ complex appeared as a single band (Figure 3), suggesting a very low possibility for the existence of aggregated



$$\begin{array}{l} Al\cdots O\text{-}Al \\ \quad\;\;\, | \\ \quad\;\, Al \end{array}$$

bonds. Hence, the association of this compound at high concentrations (>45%) may be viewed as the intermolecular bridging of the BQ nitrogen atom



The bond order of the Al-O-Al linkage of this complex seems somewhat decreased (ν_a ~780 cm^{-1}) compared with that of the corresponding uncomplexed molecule (ν_a 795 cm^{-1}). The donation of the BQ molecule can thus exert an effect of increasing polarizability of the Al-O-Al bond to some extent. Such an effect of the donor molecule could clearly be exemplified by the formation of an electroconductive complex at 1:1 molar ratio of $Et_2AlOAlEt_2$ and tetrahydrofuran compounds (Figure 4). A stable complex monotetrahydrofuranate was shown by nmr to carry an unopened THF molecule in the complex.

From the reaction of $[Et_2AlCl]\cdot BQ$ and $[Et_2AlOLi]\cdot BQ$ complexes a crystalline complex $[Et_2AlOAlEt_2]\cdot 2BQ$ was obtained. However, it changed into a colored oily substance at room temperature in a few days. The fact that the change in the nmr spectrum indicated by the multiplication in the ring H(3) protons (finely split quartet in the original state) indicates the following dissociation is plausible: $[Et_2AlOAlEt_2]\cdot 2BQ \rightarrow [Et_2AlOAlEt_2]\cdot BQ + BQ$.

The readiness in obtaining the 1:1 rather than the 1:2 complexes agrees well with the case of trimethylaminate complex observed by Storr, *et al.*[4] This property can be considered as characteristic for this type of organoaluminum compound.

Table V. Nmr Resonances of the Ring Protons in Organoaluminum 5,6-Benzoquinolinates[a]

Compd	Chem shift, δ, ppm[b]					$\Delta\delta_{H(2)-H(3)} =$
	H(2)	H(3)	H(4)	H(9)	H(10)	$\lvert\delta_{H(2)} - \delta_{H(3)}\rvert$, ppm
BQ	7.31	5.37	~6.07	6.76		1.94
$[Et_3Al]\cdot BQ$	8.24	6.19	7.25	7.45	7.81	2.05
$[Et_2AlCl]\cdot BQ$	8.42	6.03	7.25	7.46	7.88	2.39
$[Et_2AlOAlEt_2]\cdot BQ$	8.61	6.03	7.57	7.88	8.19	2.58
$[Et_2AlOAlEt_2]\cdot 2BQ$	*c*	6.15	7.30	7.52	7.88	*c*
$[Me_3Al]\cdot BQ$	8.32	6.06	6.96	7.58	8.12	2.26
$[Me_2AlCl]\cdot BQ$	8.48	6.02	7.34	7.59	8.03	2.46
$[Me_2AlOAlMe_2]\cdot BQ$	8.48	6.06	7.35	7.54	8.10	2.42
$[Et_2AlOAlMe_2]\cdot BQ$	8.30	6.23	7.37	7.65	7.82	2.07

[a] In C_6D_6 at room temperature. [b] See the footnote *a* in Table III. [c] Not determined.

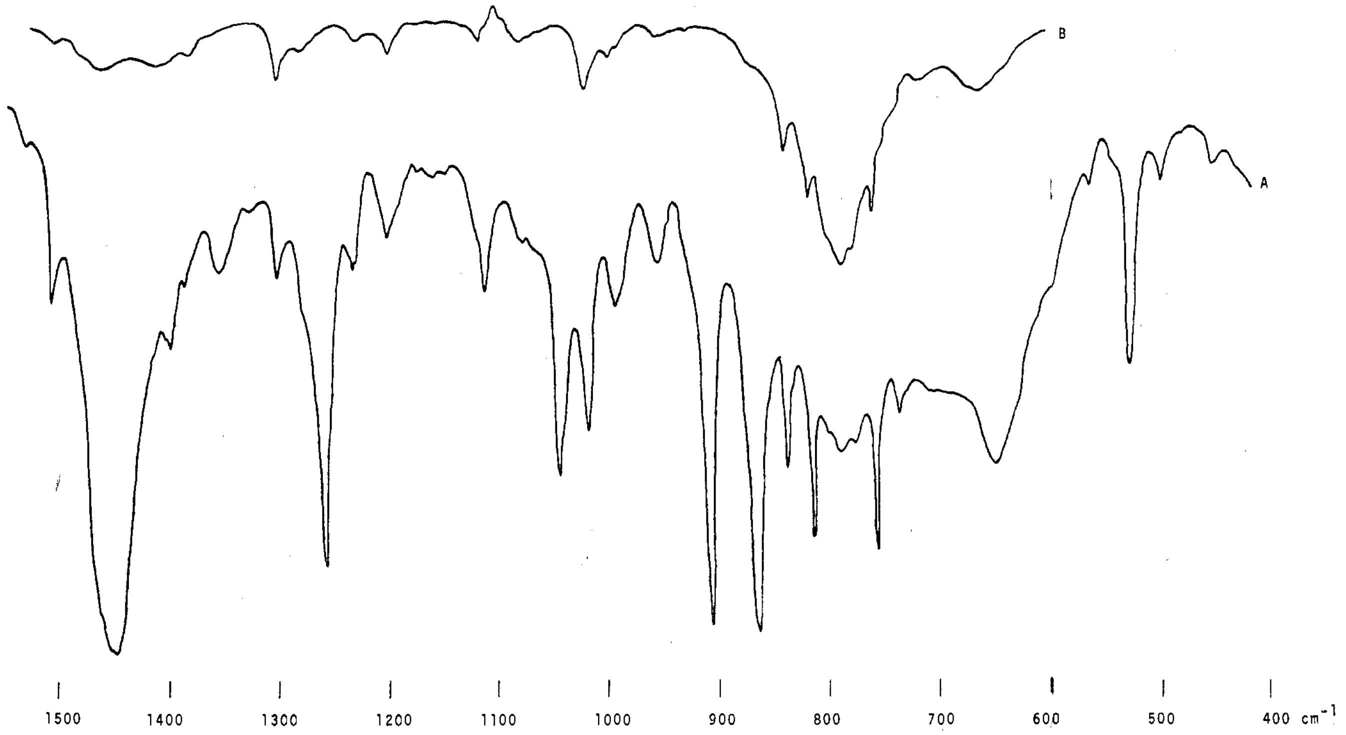


Figure 3. Infrared spectra of $[Et_2AlOAlEt_2]\cdot BQ$ complex: A, spectrum in cyclohexane solution; B, resultant spectrum of compensation with a cyclohexane solution of $[AlEt_3]\cdot BQ$.

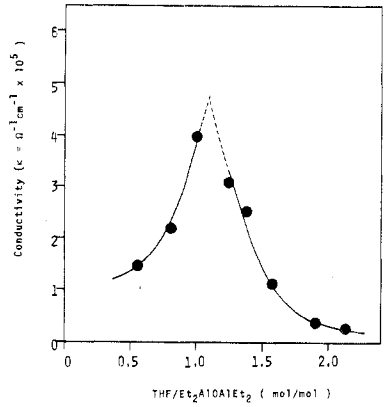
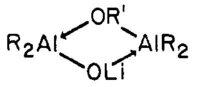


Figure 4. Change in specific conductivity of the mixtures of $Et_2AlOAlEt_2$ and tetrahydrofuran.

Relative to this, we have pointed out[25] the stability of a four-membered coordinating structure of the type



furthermore, a number of examples of a stable four-membered dimer of R_2AlOR' have been reported.[26] Present results show that within the bonded Al-O-Al linkage, in spite of its considerable flexibility, the cyclization into a rigid four-membered ring is also highly probable.

In the methyl-aluminum series of compounds, where the Al atoms can accept a donor molecule more strongly, the existence of $[R_2AlOAlR_2]\cdot Do$ complex containing the nonequivalent alkyl groups seems possible, in principle. One of the examples may be a $[Me_2AlOAlMe_2]\cdot THF$ complex (see Table IV).

The increase in the separation between H(2) (appeared at the lowest field) and the H(3) (appeared at the highest field) ring protons in the nmr spectra of the BQ complex (Table V) can be related to the increase in the strengths of coordination of the BQ molecule. The $\Delta\delta_{H(2)-H(3)}$ values observed for the $[R_2AlOAlR_2]\cdot BQ$ complexes are found to be comparable with or somewhat higher than those for the corresponding $[R_2AlCl]\cdot BQ$ complexes and considerably higher than those for $[AlR_3]\cdot BQ$ complexes.

In the study of the uncomplexed $Et_2AlOAlEt_2$ compound

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(25) T. Araki, K. Hayakawa, T. Aoyagi, Y. Nakano, and H. Tani, *J. Org. Chem.*, 38, 1130 (1973).

(26) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 1, 3rd ed., Methuen, London, 1967, p 295. *Cf.* ref 12, p 13.

(tetramer), we have mentioned that electronegativity of this type of compound lies between those of Et_2AlCl and $AlEt_3$ (dimers). The estimated strength of coordination in $[Et_2AlOAlEt_2]\cdot BQ$ complex, however, was higher than expected from the electronegativity of the Al atom in the uncomplexed compound associated. Although straightforward estimation of electronegativities for the uncomplexed compounds in monomeric states was not derived from the measurements on the associated compounds, this observation may be considered relating to the fact that the monocoordinated complex of $Et_2AlOAlEt_2$ is more stable than the corresponding dicoordinated complex. This can be due to the "bidentate electron acceptor" nature of the $Et_2AlOAlEt_2$ compound, just as a bidentate electron donor forms a stable chelate complex. It is interesting that the mononuclear $Et_2AlOCH(CH_3)$-C_2H_5 compound, which is geometrically similar to Et_2AlO-$AlEt_2$, rarely produces any stable complex with amines or ethers.

After we had succeeded in isolating the crystalline $[Et_2AlOAlEt_2]\cdot BQ$ complex, some complexes of the type $[EtZnN(t\text{-}Bu)ZnEt]\cdot$(ether) were isolated in this laboratory.[27] The latter can also be regarded as the same type of bidentate acceptor complex. In contrast with the well-known chelating donors, we prefer to give the bidentate electron acceptor a term of "chelaptor".

Experimental Section

All of the experimental procedures were carried out under a dried-argon atmosphere.

Materials. Hydrocarbon solvents were purified normally,[14] then refluxed over Na-K alloy, and distilled just before use. Organoaluminum compounds were purified by distillation under reduced pressure: $AlEt_3$ (bp 82° (4 mm)), $AlMe_3$ (bp 124–125° (760 mm)), $(i\text{-}Bu)_3Al$ (bp 68° (4 mm)), and Me_2AlCl (bp 127–128° (760 mm)). Et_2AlCl was purified by distillation in the presence of pure NaCl under reduced pressure (bp 54.5° (1.5 mm)) according to Ziegler's method.[28] $(i\text{-}Bu)_2AlCl$ was prepared by the reaction of $AlCl_3$ with $Al(i\text{-}Bu)_3$ (1:2) in *n*-pentane at 0° and then purified by distillation under reduced pressure (bp 100° (1 mm)).[29]

Preparation of Organoaluminum Compounds. R_2AlOLi. **Et_2AlOLi** was prepared according to the separately described method[14] except the reaction was performed in dry ligroin (bp 100–140°). *Anal.* Calcd for $C_4H_{10}AlOLi$: Al, 25.0; Et:Al ratio, 2.0. Found: Al, 24.2; Et:Al ratio, 1.9. **$(i\text{-}Bu)_2AlOLi$** was similarly synthesized in ligroin (bp 90°) at 50°. It is highly soluble in hydrocarbons such as *n*-hexane and toluene. *Anal.* Calcd for $C_8H_{18}OLiAl$: Al, 16.5; Li, 4.3. Found: Al, 16.1; Li, 3.9. The same synthetic procedures were applied to the preparation of $(i\text{-}Bu)_2AlONa$. **Me_2AlOLi** was prepared in anisole according to the method reported separately.[14] *Anal.* Calcd for C_2H_6OLiAl: Al, 33.8; Li, 8.8. Found: Al, 33.4; Li, 8.0.

Bis(dialkylaluminum) Oxides $R_2AlOAlR_2$. With some modifications of our method described previously,[2b] **$Et_2AlOAlEt_2$** was obtained from the reaction of Et_2AlCl (0.03 mol) with Et_2AlOLi (0.03 mol) in *n*-hexane (100 ml) under stirring at −20° for 24 hr, followed by evaporation of the hexane layer under reduced pressure. After redissolving the residue in *n*-hexane, the solution was allowed to stand at −20° for 24 hr. A small amount of newly formed LiCl was separated from the solution. These procedures were repeated several times until no further precipitation was observed. After the final evaporation, $Et_2AlOAlEt_2$ (*ca.* 92%) was obtained as an oily material. *Anal.* Calcd for $C_8H_{20}OAl_2$: Al, 29.0; Et:Al ratio, 2.0. Found: Al, 27.7; Et:Al ratio, 1.9. The precipitated LiCl was combined (95%) and washed with *n*-hexane. Content of Al in the LiCl was found to be negligible. $Et_2AlOAlEt_2$ is highly soluble in hydrocarbons and ethers.

$(i\text{-}Bu)_2AlOAl(i\text{-}Bu)_2$ was obtained similarly by the reaction of $(i\text{-}Bu)_2AlCl$ with $(i\text{-}Bu)_2AlOLi$ (or $(i\text{-}Bu)_2AlONa$) at 0° for 24 hr. The $(i\text{-}Bu)_2AlOAl(i\text{-}Bu)_2$ obtained was a colorless liquid whose chemical properties were quite similar to $Et_2AlOAlEt_2$. *Anal.* Calcd for $C_{16}H_{36}OAl_2$: Al, 18.1. Found: Al, 17.6. Molecular weight depends on the concentration of the benzene solution in cryoscopy (Figure 5); yield, *ca.* 85%; LiCl (or NaCl) yield, 93%.[30]

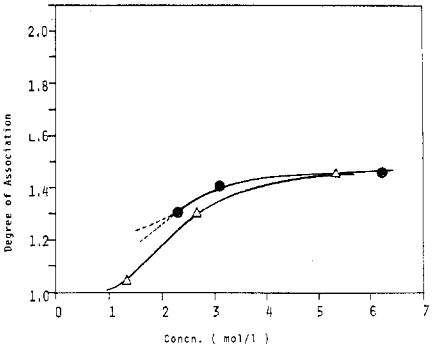

Figure 5. Concentration dependencies of degree of association in benzene: ●, $(i\text{-}Bu)_2AlOAl(i\text{-}Bu)_2$; △, $[Et_2AlOAlEt_2]\cdot BQ$.

$Me_2AlOAlMe_2$ was prepared as follows. To a suspension of *n*-pentane (50 ml) containing Me_2AlOLi (0.02 mol), which was freed from anisole, Me_2AlCl was added at 0° and stirring was continued for 2 days. After the absence of the chloride ion in an aliquot of the pentane layer was confirmed by $AgNO_3$ test, the procedures for $Et_2AlOAlEt_2$ were applied. The compound is colorless liquid; yield, *ca.* 92%; LiCl yield, 92%. *Anal.* Calcd for $C_4H_{12}OAl_2$: Al, 41.5; Me:Al ratio, 2.0. Found: Al, 40.6; Me:Al ratio, 1.9. It is highly soluble in hydrocarbons and ethers. **$Et_2AlOAlMe_2$** (or EtMeAlOAlEtMe) was obtained from the equimolar reaction mixture of Et_2AlOLi and Me_2AlCl in benzene–hexane. The colorless liquid obtained (94%) showed chemical properties similar to those of $Et_2AlOAlEt_2$. Nmr indicated the ratio of Me to Et groups to be consistently 1:1, and the $\Delta\delta_{CH_3-CH_2}$ value was different from that of the equimolar mixture of $AlEt_3$ and $AlMe_3$. In the ir spectrum intense bands due to the Al–O–Al grouping were observed around 700–800 cm^{-1}.

Donor Complexes of $R_2AlOAlR_2$. $[Et_2AlOAlEt_2]\cdot BQ$ Complex. $[Et_2AlCl]\cdot BQ$ and Et_2AlOLi were allowed to react in benzene–hexane at 0° for 2 hr. [The $[Et_2AlCl]\cdot BQ$ existed as colorless needles. *Anal.* Calcd for $C_{17}H_{19}NClAl$: Al, 9.0; Et:Al ratio, 2.0. Found: Al, 9.1; Et:Al ratio, 1.96.] From the concentrated organic layer a crystalline residue was obtained. It was washed with cold hexane, followed by recrystallization from warm hexane, yielding pale yellow needles, mp 75° dec; yield, *ca.* 60% after recrystallization. *Anal.* Calcd for $C_{21}H_{29}NOAl_2$: Al, 14.79; Et:Al ratio, 2.0; Et:BQ ratio, 4. Found: Al, 14.82; Et:Al ratio, 1.9; Et:BQ ratio, 3.98. For molecular weight, see Figure 5. The compound is slightly soluble in benzene or toluene. Similarly, an equimolar reaction of $[Me_2AlCl]\cdot BQ$ and Me_2AlOLi in benzene at room temperature gave needles of the **$[Me_2AlOAlMe_2]\cdot BQ$** complex. It was recrystallized from *n*-hexane; yield, 45% after recrystallization. Me:BQ ratio: calcd, 4.0; found, 3.9. For nmr data, see Tables IV and V. Upon allowing equimolar amounts of $[Me_2AlCl]\cdot BQ$ and Et_2AlOLi to react in benzene–ligroin at room temperature, **$[Et_2AlOAlMe_2]\cdot BQ$** was obtained as needles in *ca.* 70% yield. The Et:Me and Et:BQ ratios observed were 1.15 and 1.02, respectively. For nmr data, see Tables IV and V.

$[Et_2AlOAlEt_2]\cdot 2BQ$ Complex. An equimolar reaction of $[Et_2AlCl]\cdot BQ$ and $[Et_2AlOLi]\cdot BQ$ (powdery, soluble in toluene or ethers, slightly soluble in hexane, containing 9.6% Al (calcd, 9.4%)) in benzene at room temperature afforded needlelike crystals after evaporation; yield, *ca.* 35% after recrystallization from *n*-hexane. *Anal.* Calcd for $C_{34}H_{38}N_2OAl_2$: Al, 9.9; Et:Al ratio, 2.0; Et:BQ ratio, 2.0. Found: Al, 9.0; Et:Al ratio, 1.82; Et:BQ, 1.8 by nmr relative intensities. For nmr data, see Tables IV and V. The compound is soluble in benzene or toluene but slightly soluble in hexane. It decomposed into brownish yellow oil upon storage at room temperature.

$[Et_2AlOAlEt_2]\cdot THF$. From an equimolar reaction of Et_2AlOLi and $[Et_2AlCl]\cdot THF$ (liquid) the $[Et_2AlOAlEt_2]\cdot THF$ complex was obtained as a colorless oil in a yield of *ca.* 90%. For nmr data, see Table IV. Upon distilling under vacuum, the $AlEt_3\cdot THF$ complex was eluted and a polymeric compound corresponding to $-(EtAlO)_n-$ remained. Similarly, $[Me_2AlOAlMe_2]\cdot THF$ was obtained from $[Me_2AlCl]\cdot THF$ and Me_2AlCl. The compound is a colorless liquid; yield, *ca.* 90%. For nmr data, see Table IV.

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(27) H. Tani and N. Oguni, *J. Polym. Sci., Part B*, **7**, 769 (1969).

(28) K. Ziegler, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, p 200.

(29) M. Roha, L. C. Kreider, M. R. Frederic, and W. L. Beers, *J. Polym. Sci.*, **38**, 51 (1959).

(30) The $(i\text{-}Bu)_2AlCl$ contained a small amount of $(i\text{-}Bu)_3Al$. Upon reacting with $(i\text{-}Bu)_2AlOLi$, the latter precipitated together with LiCl by forming $[(i\text{-}Bu)_2AlOLi]\cdot[Al(i\text{-}Bu)_3]$.[14]

The $[Me_2AlOAlMe_2]\cdot PhOMe$ complex was obtained from equimolar reaction of $[Me_2AlOLi]\cdot PhOMe$[14] and Me_2AlCl in hexane; mp −16°; yield, *ca.* 50% after recrystallization from *n*-hexane at −50°. For nmr data, see Table IV. Upon distillation, the $[AlMe_3]\cdot PhOMe$ complex was eluted, leaving a polymeric material of $-(MeAlO)_n-$. The $[AlMe_3]\cdot PhOMe$ complex was colorless needles at −78° and was nmr spectroscopically identical with the complex prepared from $AlMe_3$ and anisole (see Table IV).

$[Et_2AlOAlEt_2]\cdot StO$. In the presence of $Et_2AlOAlEt_2$ an equimolar amount of styrene oxide (StO) was added dropwise at −20°. Colorless needles were formed instantaneously in a yield of *ca.* 60%; mp −10 to −20°. The complex was soluble in benzene. Similary, $[Me_2AlOAlMe_2]\cdot StO$ could be obtained as needlelike crystals melting at *ca.* −20° in *ca.* 70% yield. Hydrolysis of these compounds gave the corresponding alkanes and styrene oxide polymers.

Triethylbornyldialuminoxane, $Et_2AlOAlEt(OC_{10}H_{17})$. Equimolar reaction of Et_2AlCl and borneol at −20° in toluene afforded $EtClAl(OC_{10}H_{17})$ as needlelike crystals. *Anal.* Calcd for $C_{12}H_{22}OClAl$: Al, 11.0. Found: Al, 9.5. This bornylate was allowed to react with Et_2AlOLi in hexane to give crystalline products when concentrated under reduced pressure. It was recrystallized from *n*-hexane; yield, *ca.* 60% after recrystallization. Hydrolysis of the compound resulted in 95% of the theoretical amount of ethane and in 98% of that of borneol.

Triethylacetylacetonatodialuminoxane, $Et_2AlOAlEt(acac)$. Equimolar reaction of EtAlCl(acac) (colorless liquid, bp 58° (0.5 mm), containing 13.7% Al (calcd, 14.2)) with Et_2AlOLi gave an oily compound in a yield of *ca.* 85%. Prisms grown from the compound upon storage were confirmed as $Al(acac)_3$ by comparing with the authentic sample; yield, *ca.* 30%.

Analyses. The Al content was determined volumetrically by the 8-hydroxyquinoline method. Analysis of Li was performed according to the method described by Ziegler[31] for the analysis of $LiAlH_4$. The neutralization point in the titration was found to be at around pH 7 independent of the ratio of Li to Al. Gasometry was undertaken according to the method described previously.[14] Molecular weights of the organoaluminum compounds were measured cryoscopically in the benzene solutions.

Spectroscopy. A Nihon Bunko Type DS-402G infrared spectrometer was employed for the ir spectroscopy of the organoaluminum compounds in cyclohexane solution. A variable-spacing cell device was used for the compensation techniques. Nmr spectra of the benzene or benzene-d_6 solutions of the organoaluminum compounds were recorded with a Varian A-60 spectrometer (60 MHz) at room temperature. The chemical shifts were externally standardized with TMS (δ 0.00) or internally standardized with the benzene protons (δ 6.57, an average value of the benzene protons in the presence of the organoaluminum compounds when externally standardized with TMS).

Electric Conductivity. The specific conductivities of the organoaluminum compounds, sealed under argon, were determined in toluene (10^{-1}–10^{-3} *M*) at 25° using an alternating current potentiometer for the samples of higher conductivity and a direct current galvanometer for those of lower conductivity. The latter can detect 10^{-12} A. The cells (cell constant $K = 0.41470$ and 0.44638) contain 10 mm × 10 mm platinum black electrodes.

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Registry No. Et_2AlOLi, 20888-82-8; $(i\text{-}Bu)_2AlOLi$, 31471-19-9; $(i\text{-}Bu)_2AlONa$, 41156-38-1; Me_2AlOLi, 31390-21-3; $Et_2AlOAlEt_2$, 1069-83-6; Et_2AlCl, 96-10-6; $(i\text{-}Bu)_2AlOAl(i\text{-}Bu)_2$, 998-00-5; $(i\text{-}Bu)_2AlCl$, 1779-25-5; $Me_2AlOAlMe_2$, 29429-58-1; $Et_2AlOAlMe_2$, 41021-32-3; EtMeAlOAlEtMe, 29429-59-2; $[Et_2AlOAlEt_2]\cdot BQ$, 40961-82-8; $[Et_2AlCl]\cdot BQ$, 41021-42-5; $[Me_2AlCl]\cdot BQ$, 40961-83-9; $[Me_2AlOAlMe_2]\cdot BQ$, 40961-84-0; $[Et_2AlOAlMe_2]\cdot BQ$, 39322-86-6; $[Et_2AlOAlEt_2]\cdot BQ_2$, 40961-85-1; $[Et_2AlOLi]\cdot BQ$, 40902-30-5; $[Et_2AlOAlEt_2]\cdot THF$, 40961-87-3; $[Et_2AlCl]\cdot THF$, 40961-88-4; $[Me_2AlOAlMe_2]\cdot THF$, 40961-89-5; $[Me_2AlCl]\cdot THF$, 41007-93-6; $[Me_2AlOAlMe_2]\cdot PhOMe$, 40961-90-8; $[AlMe_3]\cdot PhOMe$, 20791-22-4; $[Et_2AlOAlEt_2]\cdot StO$, 40961-92-0; $[MeAlOAlMe_2]\cdot StO$, 40961-86-2; $Et_2AlOAlEt(OC_{10}H_{17})$, 40907-47-9; $EtClAl(OC_{10}H_{17})$, 41021-33-4; $Et_2AlOAlEt(acac)$, 24803-77-8; Me_2AlCl, 1184-58-3; $[Me_2AlOLi]\cdot PhOMe$, 40902-31-6; $C_{10}H_{17}OH$, 507-70-0; EtAlCl(acac), 40961-78-2; $[Et_3Al]\cdot BQ$, 40961-79-3; $[Me_3Al]\cdot BQ$, 40961-80-6.

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Contribution from the Department of Chemistry, University of
Massachusetts, Amherst, Massachusetts 01002

Pentacoordinated Molecules. XVIII.[1] Molecular Structure of Bis(*tert*-butyl)trifluorophosphorane from Infrared and Laser Raman Spectroscopy

ROBERT R. HOLMES,* G. TING-KUO FEY,[2a] and ROBERT H. LARKIN[2b]

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The liquid-state infrared spectrum of bis(*tert*-butyl)trifluorophosphorane was recorded in the range 3000–33 cm^{-1}. Corresponding Raman displacements are reported as well as polarization measurements. Detailed assignments of the fundamental frequencies are shown to be consistent with C_s symmetry with strong preference given to a trigonal bipyramid with equatorially oriented *tert*-butyl groups. The C_s symmetry suggests a staggered conformation for the neighboring *tert*-butyl groups and the presence of hindered rotation due to the mutual steric interference of these groups. Comparison of fundamental frequencies with those of related *tert*-butylphosphorus compounds and trifluorophosphoranes reveals a correlation between increasing axial PF stretching frequency and increasing group electronegativity in the series X_2PF_3 as X is changed.

Introduction

Vibrational analysis has established the structural symmetry of several members of the pentacoordinate series X_2PF_3 (where X = Cl,[3] Br,[4] H,[1,5,6] and CH_3[7]). In each instance, a trigonal-bipyramidal framework with the X lig-

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