STRUCTURE AND CHEMICAL BEHAVIOR OF AN ORGANOALUMINUM COMPOUND [R₂AlOCR′NPh]₂, A STEREOSPECIFIC CATALYST FOR POLYMERIZATION OF ACETALDEHYDE

HAJIME YASUDA, TAKEO ARAKI and HISAYA TANI

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan)

(Received June 21st, 1972)

SUMMARY

A series of organoaluminum compounds [R₂AlOCR′NPh]₂, which are the reaction products between trialkylaluminum compounds and secondary acid amides and are excellent catalysts for stereospecific polymerizations of aldehydes, were isolated in the crystalline state. Chemical behavior of such compounds toward Lewis acids and bases were interpreted in terms of the structures of [Me₂AlOCPh-NPh]₂ and its trimethylamine oxide complex Me₃NO·AlMe₂OCPhNPh which were determined by X-ray structure analyses. Reaction products of primary and tertiary acid amides with trialkylaluminum compounds were also studied.

INTRODUCTION

The use of a well defined catalyst which gives a stereo-regular polymer in an essentially quantitative yield is a prerequisite for the full understanding of a polymerization mechanism. The crystalline organoaluminum [R₂AlOCR′NPh]₂ which is obtained from a secondary acid amide and a trialkylaluminum is a representative catalyst in that it gives polyacetaldehyde essentially in a quantitative yield[1]. This type of compound (R=R′) is also obtained by the reaction between phenyl isocyanate and a trialkylaluminum, as reported by Reinheckel[3], Horder[4], and Jennings[5]. For these compounds, the structure [R₂AlOCR′NPh]₂ was proposed by us[1], [R₂Al-NPhCOR′]₂ by Mitrofanova[2], R₂AlNPhCOR′ by Reinheckel[3], and eight-membered ring structure bridged by O–C–N grouping by Horder and Jennings, but was determined unambiguously by X-ray structure analysis of single crystals of [Me₂-AlOCPhNPh]₂[6].

This paper describes the preparation, structure and chemical behavior toward Lewis acids and bases of this type of compounds. The preparation, structure and chemical behavior toward Lewis acids and bases of the aldehyde complexes of this type of compounds will be the subject of a later paper[7].

RESULTS AND DISCUSSION

A. The preparation and structure of [R₂AlOCR′NPh]₂

A toluene suspension of an equimolar mixture of AlR₃ (R=Me, Et, or i-Bu)

TABLE 1

CHARACTERIZATION OF REACTION PRODUCTS OBTAINED FROM R_3Al AND $R'CONR''R'''$

R	R'	R''	R'''	M.p. (°C)		Al[a] (%)	R/Al ratio[b]	R/R' CONR''R''' ratio[c]	Mol.wt.[d]
CH_3	C_6H_5	H	H	123–134 (dec.)	Calcd.	15.3	2.0	2.0	354
					Found	15.0	2.0	2.0	348
CH_3	CH_3	C_6H_5	H	130–131	Calcd.	14.0	2.0	2.0	382
					Found	13.8	2.0	1.9	403
CH_3	C_6H_5	C_6H_5	H	167	Calcd.	10.7	2.0	2.0	506
					Found	10.7	1.9	2.0	520
C_2H_5	CH_3	C_6H_5	H	58–59	Calcd.	12.3	2.0	2.0	438
					Found	12.3	2.1	2.2	461
C_2H_5	C_6H_5	C_6H_5	H	67–69	Calcd.	9.6	2.0	2.0	562
					Found	9.4	1.9	1.9	559
i-C_4H_9	CH_3	C_6H_5	H	67–68	Calcd.	9.8	2.0	2.0	550
					Found	10.2	1.8	2.0	531
CH_3	CH_3	C_6H_5	C_6H_5	114	Calcd.	9.5	3.0	3.0	283[e]
					Found	9.5	3.0	3.1	291
CH_3	C_6H_5	C_6H_5	C_6H_5	121–122	Calcd.	8.1	3.0	3.0	333[e]
					Found	7.9	3.1	3.0	330

[a] Determined by 8-hydroxyquinoline method. [b] Gasometry and gas chromatography after hydrolysis.
[c] Determined by the weight of acid amide isolated after hydrolysis and by peak areas in NMR spectra.
[d] Cryoscopically in benzene; calculated value is for the dimer. [e] Calculated for the monomer.

and a secondary acid amide $R'CONHPh$ ($R' = Me$ or Ph) prepared at $-78°$ became a colorless homogeneous solution (without any gas evolution) at about $-40°$. This fact suggests that a 1/1 complex is formed between these two components. Colorless crystals precipitated from the solution upon addition of n-hexane, but these were difficult to identify because of their thermal instability. When the temperature of this solution was raised up to $90°$, evolution of an equimolar amount of alkane (RH) was observed. The crystalline reaction products proved to be $[R_2AlOCR'NPh]_2$ by chemical analyses and molecular weights determined cryoscopically in benzene (Table 1).

$$AlR_3 + R'CONHPh \rightarrow R_3Al \cdot R'CONHPh \rightarrow \tfrac{1}{2}[R_2AlOCR'NPh]_2 \qquad (1)$$

$[Me_2AlOCMeNPh]_2$ obtained from $AlMe_3$ and acetanilide proved to be identical with that obtained from $AlMe_3$ and PhNCO by comparison of their m.p., IR and NMR spectra (eqn. 2). The former preparative method is superior, because the latter method cannot be applied to organoaluminums in which the alkyl groups attached to aluminum atoms and those to carbon atoms of the acid amide moieties are different.

$$AlMe_3 + MeCONHPh \xrightarrow{-RH} \tfrac{1}{2}[Me_2AlOCMeNPh]_2 \leftarrow AlMe_3 + OCNPh \quad (2)$$

Four- and eight-membered cyclic structures are conceivable for this type of organo-aluminum. The former resembles that of R_2AlOR'[8] and $R_2AlNR'_2$[9], and the latter was proposed by Horder[4] and Jennings[5], based on the study of IR spectra. The structure was determined to be the latter one (I) by X-ray structure analysis of single

(I)
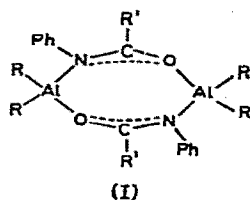
crystals of [Me₂AlOCPhNPh]₂[6]. The three-dimensional structure of this molecule (Fig. 1) reveals several characteristic features of this molecule. First, the molecular framework is composed of a centro-symmetrical eight-membered ring. Second, the configuration of aluminum atoms is a distorted tetrahedral one, and the Al–N distance (1.95 Å) is nearly equal to the sum of covalent radii of aluminum and nitrogen atoms (1.96 Å) and the Al–O distance (1.81 Å) is also a normal value. Third, the C–O distance in the acid amide moiety (1.28 Å) is slightly longer than the normal C=O bond distance (1.23 Å) in ketones and aldehydes, and the C–N distance (1.31 Å) is nearly equal to that in acetanilide. Since both C–O and C–N distances are intermediate values between corresponding single and double bonds and the carbonyl carbon atom of acetanilide moiety have nearly trigonal configuration, the electrons are delocalized over the O–C–N grouping. Fourth, two adjacent benzene rings occupy the *cis* position. IR and NMR spectra can be interpreted in terms of this structure.
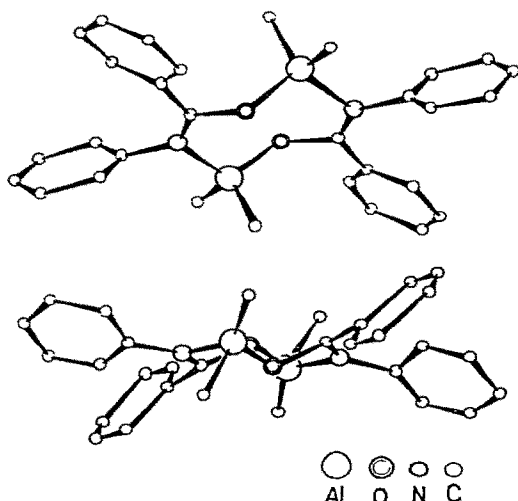

Fig. 1. The molecular structure of [Me₂AlOCPhNPh]₂.

Spectral studies revealed that those organoaluminums assumed two different conformations, *cis* and *trans*, depending on the nature of the substituents, concentration and temperature. The NMR spectrum of [R₂AlOCMeNPh]₂ (R = Me, Et, or i-Bu) recorded in benzene solution afforded information on the structure in solution. Two kinds of absorptions assignable to methyl groups attached to carbon atoms were observed. The peak area ratio of the higher to the lower field absorption depended on the bulkiness of alkyl groups attached to an aluminum atom: the ratio (at 38°) was
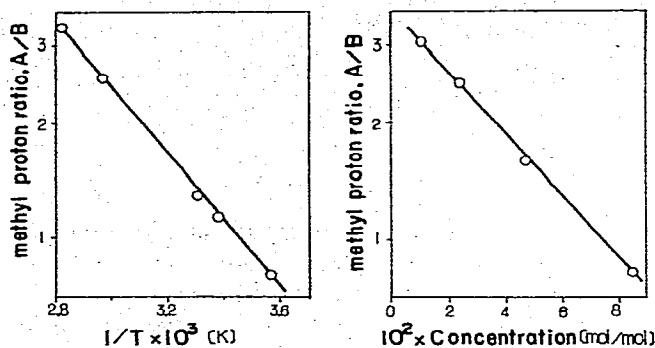
Fig. 2. Temperature and concentration dependences of the intensity ratio of methyl proton signal at higher (A) to that at lower field (B) in acetanilide moiety of $[Me_2AlOCMeNPh]_2$. Concentration was expressed by the molar ratio of the organoaluminum to benzene.

1/1 for methyl, 4/1 for ethyl, and 1/0 for isobutyl compound. The intensity of the peak at higher field decreased and that at lower field increased with the decrease in temperature or with the increase in concentration of solution, as shown in Fig. 2 for the methyl compound*. This phenomenon can be interpreted by referring to the following observations. First, $[Me_2AlOCMeNPh]_2$ has a dimeric structure independent of the concentration in benzene solution, as indicated by its molecular weight determined cryoscopically. Therefore, the possibility of dissociation phenomena can be excluded. Second, the chemical shift between two C-methyl signals (8–14 Hz) is nearly equal to that between *cis*- and *trans*-N-substituted acid amide (6 Hz)[10]. Third, the wave number of the IR absorption band assigned to O–C–N grouping (1567 cm^{-1}) is practically independent of the concentration of benzene solution (shifts are less than 2 cm^{-1}), while the relative intensity of C-methyl proton peaks in the NMR spectrum changes remarkably. This IR shift is too small to be ascribable to the structural change

(3)
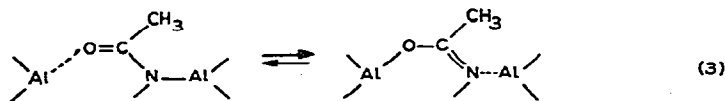
(eqn. 3) brought about by the electron shift[11]. Fourth, the wave number (1570 cm^{-1}) of an O–C–N grouping of the reaction products between $AlMe_3$ and 2-pyrrolidone or 2-piperidone, for which only the *cis* structure is possible, is nearly equal to that (1567 cm^{-1}) observed for $[Me_2AlOCMeNPh]_2$.

It is reasonable to conclude from these observations that the two signals observed for $[Me_2AlOCMeNPh]_2$ are assigned to the stabilized *cis* and *trans* forms, respectively. Molecular model examination shows that the steric hindrance between Al-alkyl and N-phenyl groups in the course of this type of conformational change (Fig. 3) is negligible for the methyl compound, and is sufficiently large for the isobutyl compound to be stabilized in the *trans* conformation. Thus, the conformational

----

* The spectrum of the sample of $[Me_2AlOCMeNPh]_2$ prepared from $AlMe_3$ and MeCONHPh was identical with that prepared from $AlMe_3$ and PhNCO, although Jennings[5] reported for the latter the presence of only one peak.
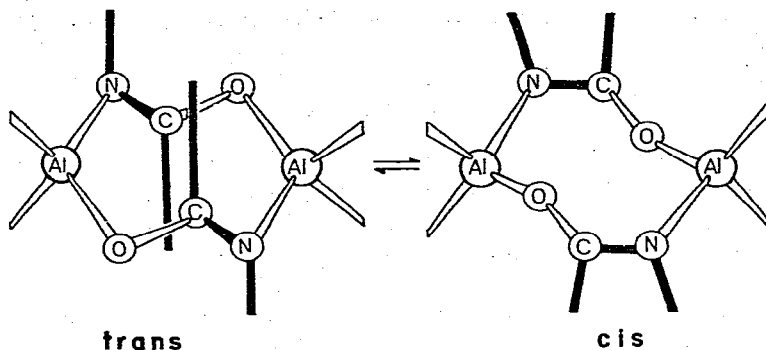
Fig. 3. The conformational change of [Me$_2$AlOCMeNPh]$_2$.

stability may be determined primarily by the steric factor, and the peak at a lower field may be assigned to *cis* methyl protons by the NMR spectrum of [i-Bu$_2$AlOCMe-NPh]$_2$ for which only one peak is observed, and by assuming that [Me$_2$AlOCMe-NPh]$_2$ takes *cis* conformation at lower temperatures or at higher concentrations, similarly to that observed for [Me$_2$AlOCPhNPh]$_2$.

B. Reactions of a trialkylaluminum with other acid amides

(a). *The reaction with a tertiary acid amide.* On mixing AlMe$_3$ with Me-CONPh$_2$ or PhCONPh$_2$ in benzene solution at room temperature, the crystalline 1/1 complex was obtained quantitatively without the occurrence of a Grignard-type addi-

TABLE 2

NMR AND IR[a] DATA OF THE REACTION COMPOUND FROM R$_3$Al AND R'CONR''R'''

R	R'	R''	R'''	NMR, δ (ppm)		IR (cm^{-1})	
				R[b]	R'(=CH$_3$)	O–C–N	Δv
CH$_3$	C$_6$H$_5$	H	H	−0.12 (s)		1567 1608	118
CH$_3$	CH$_3$	C$_6$H$_5$	H	−0.29 (s)	1.76 1.98	1568	132
CH$_3$	C$_6$H$_5$	C$_6$H$_5$	H	−0.13 (s)		1549	129
C$_2$H$_5$	CH$_3$	C$_6$H$_5$	H	1.42 (t) J 8 CH$_3$ 0.29 (q) J 8 CH$_2$	1.77 1.93	1570	130
C$_2$H$_5$	C$_6$H$_5$	C$_6$H$_5$	H	1.34 (t) J 8 CH$_3$ 0.33 (q) J 8 CH$_2$		1549	129
i-C$_4$H$_9$	CH$_3$	C$_6$H$_5$	H	2.06 (m) CH 1.24 (d) J 7 CH$_3$ 0.23 (d) J 7 CH$_2$	1.77	1572	128
CH$_3$	CH$_3$	C$_6$H$_5$	C$_6$H$_5$	−0.26 (s)	1.64	1580 1612	95
CH$_3$	C$_6$H$_5$	C$_6$H$_5$	C$_6$H$_5$	−0.38 (s)		1568 1612	100

[a] NMR and IR spectra were measured in 10% benzene solution. In NMR spectrum, the proton signals of benzene (7.27 ppm) was used as an internal standard. [b] s=singlet; d=doublet; t=triplet; q=quadruplet; m=multiplet.
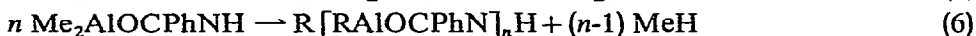
tion reaction (Table 1). These complexes gave the component tertiary acid amide quantitatively on hydrolysis.

$$AlR_3 + R'CONR''_2 \rightarrow R_3Al \cdot O{=}CR'NR''_2 \xrightarrow{H^+} R'CONR''_2 \tag{4}$$
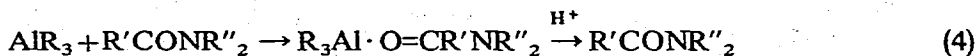
The structure $R_3Al \cdot O{=}CR'NR''_2$ (R = Me, R'' = Ph, R' = Me or Ph) was deduced from the IR spectrum (1600 and 1570 cm^{-1}) and the molecular weight determined cryoscopically in benzene. The observed shift of C=O band (from 1668 cm^{-1} to 1600 cm^{-1}) to a lower frequency is interpreted to be due to the delocalization of electrons over O–C–N grouping which is induced by the coordination of an oxygen atom to an aluminum atom. Thus, the structure (II) is proposed for this compound. The same type of structure was proposed for RCONHR' · BCl$_3$ (R = Me, H; R' = Me, Ph) by Gerrard[12] and for RCONHR' · SnCl$_4$ by Aggarwal[13].

(II)
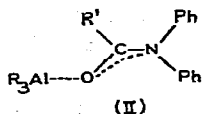
(b). *The reaction with a primary acid amide.* In an equimolar reaction of AlMe$_3$ with PhCONH$_2$ in toluene solution, only one of the two hydrogen atoms attached to the nitrogen atom reacts at 90° to give a crystalline compound Me$_2$Al-OCPhNH (eqn. 5). That this compound has the same type of structure as that of [Me$_2$AlOCPhNPh]$_2$ is deduced from the IR spectrum (NH, 3380 cm^{-1}; O–C–N, 1566 cm^{-1}) and the molecular weight determined cryoscopically in benzene. The second hydrogen atom reacts at temperatures higher than 150° to give a toluene insoluble product (eqn. 6).
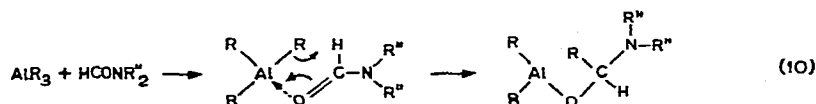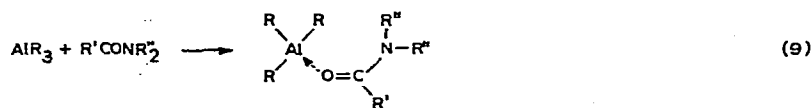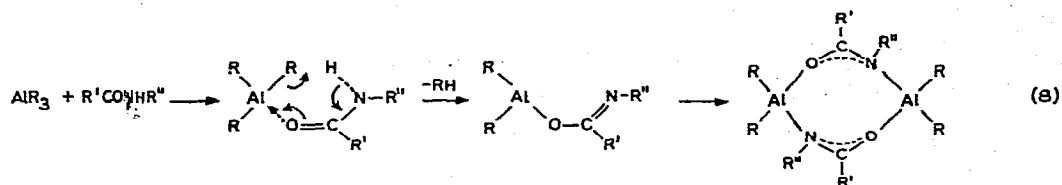
$$2\,Me_3Al + 2\,PhCONH_2 \rightarrow [Me_2AlOCPhNH]_2 + 2MeH \tag{5}$$

$$n\,Me_2AlOCPhNH \rightarrow R\,[RAlOCPhN]_nH + (n{-}1)\,MeH \tag{6}$$

(c). *The reaction with a disubstituted formamide.* HCONPh$_2$ reacts with AlMe$_3$ to give a Grignard-type addition product (eqn. 7) as reported by Jahnke et al.[14], similarly to the case of the reaction with an aldehyde. The NMR spectrum of this product has a quartet at 5.19 ppm (J 6 Hz) assigned to methyl protons and a doublet at 1.45 ppm (J 6 Hz) to a methine proton. Hydrolysis of this product gave acetaldehyde which was detected by GLC of the hydrolysate. A similar hydrolysis reaction accompanied by an addition reaction was recently reported in the case of ZnEt$_2$[15].

$$Me_3Al + OHCNPh_2 \rightarrow Me_2AlOCHMeNPh_2 \xrightarrow{H_2O} MeCHO + HNPh_2 \tag{7}$$

C. The course of reaction between a trialkylaluminum and an acid amide

The first type is the reaction of a primary and a secondary acid amide (eqn. 8). The oxygen atom of the carbonyl group coordinates to an aluminum atom to form a complex. This complex reacts, evolving alkane (RH) and forming presumably monomeric R$_2$AlOCR'NR''. This coordinatively unsaturated compound is stabilized forming a dimer.

The second type is the reaction of a tertiary acid amide. The complex formed is stable, because there is no active hydrogen atom and the coordination number of an aluminum atom is four (eqn. 9).
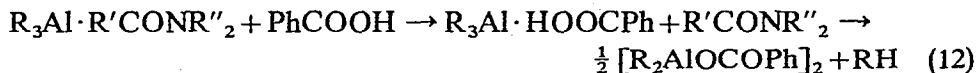
$$AlR_3 + R'CONHR'' \longrightarrow \cdots \xrightarrow{-RH} \cdots \longrightarrow \cdots \quad (8)$$

$$AlR_3 + R'CONR''_2 \longrightarrow \cdots \quad (9)$$

$$AlR_3 + HCONR''_2 \longrightarrow \cdots \longrightarrow \cdots \quad (10)$$

The third type is the reaction of N,N-disubstituted formamide. Since the formyl group reacts with a trialkylaluminum in the manner of an aldehyde group, the addition of the alkyl group to the carbonyl group is observed (eqn. 10). It is interesting to note that a primary, a secondary and a tertiary acid amide do not react in this manner. The difference in the mode of reaction may be ascribed to that in the electronic state: electrons are localized on C=O group in the formamide derivatives, while delocalized over O–C–N grouping in other acid amides.

D. The reaction with protic and aprotic acids

A protic acid reacts with $[R_2AlOCR'NPh]_2$ (R=Me, Et; R'=Me, Ph) to liberate the acid amide by cleaving the bond between the aluminum atom and the acid amide moiety. For example, the reaction with an equimolar amount of acetic acid or benzoic acid in toluene at $-50°$ gave the acid amide quantitatively as a precipitate without any gas evolution. When the reaction temperature was higher than $-20°$, complicated reactions occurred with the gas evolution of alkane. Thus, the reaction with a protic acid at lower temperatures is represented by eqn. (11).

$$[R_2AlOCR'NPh]_2 + 2\,R''COOH \longrightarrow [R_2AlOCOR'']_2 + 2\,R'CONHPh \quad (11)$$
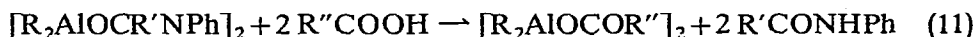
It is interesting to note that the rate of cleavage of aluminum–oxygen bonds is greater than that of aluminum–carbon bonds. The complex $R_3Al \cdot R'CONR''_2$ (R=Me, Et; R'=Me, Ph; R''=Ph) behaved similarly as shown in eqn. (12).

$$R_3Al \cdot R'CONR''_2 + PhCOOH \longrightarrow R_3Al \cdot HOOCPh + R'CONR''_2 \longrightarrow$$
$$\tfrac{1}{2}[R_2AlOCOPh]_2 + RH \quad (12)$$

The reaction with AlR_3, an aprotic or Lewis acid, resulted in the alkyl exchange reaction in which alkyl groups attached to an aluminum atom were exchanged intermolecularly. In this respect, $[R_2AlOCR'NPh]_2$ contrasts with $Et_2AlOCH_2CH_2$-NR'_2[17] and $Et_2AlOCH(CH_3)CH_2CH_2CN$[18] from which stable complexes with $AlEt_3$ were isolated. The alkyl exchange reaction is easily observed between two organoaluminums whose alkyl groups attached to an aluminum atom are different, for example between $AlEt_3$ and $[Me_2AlOCR'NPh]_2$. Analytical data (Table 3) of crystalline products isolated in quantitative yields, from the toluene solution by the
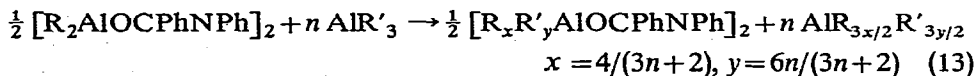
TABLE 3

CHARACTERIZATION OF THE ISOLATED REACTION PRODUCTS OBTAINED BY REACT-
ING 1 MOLE OF $R_2AlOCPhNPh$ WITH n MOLES OF AlR'_3

| R	R'	n		Al[a] (%)	R'/R[b]	(R+R')/Al[c]	PhNHCOPh/Al[d]	Mol.wt.[e]
C_2H_5	CH_3	1	Found	9.4	1.5	2.1	1.05	530
			Calcd.[f]	10.2	1.5	2.0	1.00	528
			Calcd.[g]	15.7	1.5	2.5	0.50	353
C_3H_5	CH_3	2	Found	9.7	3.0	2.1	1.01	535
			Calcd.[f]	10.4	3.0	2.0	1.00	520
			Calcd.[g]	19.0	3.0	2.7	0.33	425
CH_3	C_2H_5	1	Found	9.3	1.4	1.9	0.97	547
			Calcd.[f]	10.0	1.5	2.0	1.00	540
			Calcd.[g]	14.7	1.5	2.5	0.50	367
CH_3	C_2H_5	2	Found	9.7	2.9	1.9	0.99	550
			Calcd.[f]	9.8	3.0	2.0	1.00	548
			Calcd.[g]	16.8	3.0	2.7	0.33	481

[a] Determined by 8-hydroxyquinoline method. [b] Determined by GLC of the hydrolyzate (mole/mole).
[c] Determined by gasometry. [d] Determined by weight of the acid amide isolated after hydrolysis. [e] Molecular
weight was determined cryoscopically in benzene. [f] For $[R_{4/(3n+2)}R'_{6n/(3n+2)}AlOCPhNPh]_2$. [g] For
$R_2AlOCPhNPh \cdot nAlR'_3$.

addition of n-hexane, indicate that the alkyl exchange reactions can be expressed by
eqn. (13). A similar exchange reaction had been observed by Mole[19] for the AlR_3/R'_2-
$AlOR''$ system.

$$\tfrac{1}{2}[R_2AlOCPhNPh]_2 + n\,AlR'_3 \rightarrow \tfrac{1}{2}[R_xR'_yAlOCPhNPh]_2 + n\,AlR_{3x/2}R'_{3y/2}$$
$$x = 4/(3n+2),\; y = 6n/(3n+2) \quad (13)$$

Since an equilibrium reaction is involved, fully alkyl-exchanged products were ob-
tained in quantitative yields in two cases, R = Me, R' = Et and R = Et, R' = Me only in
the presence of a large excess of AlR_3.

The alkyl exchange reaction observed for a tertiary acid amide complex (eqn.
14) may proceed by the dissociation mechanism proposed by Brown[20] and Matte-
son[21].

$$Me_3Al \cdot PhCONPh_2 + \text{excess } AlEt_3 \rightarrow Et_3Al \cdot PhCONPh_2 \quad (14)$$
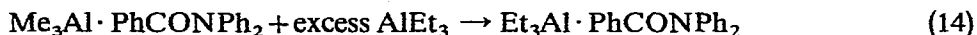
$[R_2AlOCR'NH]_2$, which is a reaction product of AlR_3 with a primary acid
amide $R'CONH_2$, has the potentiality to react further with AlR_3, but such a reaction
(eqn. 15) was observed only at temperatures around 130°.

$$[Me_2AlOCMeNH]_2 + 2\,AlMe_3 \rightarrow 2\,Me_2AlOCMeNAlMe_2 + 2\,MeH \quad (15)$$

E. Reactions with Lewis bases

Electron donors (Do) such as pyridine, triethylamine and tetrahydrofuran
are known to react with AlR_3 to give stable monomeric complexes $AlR_3 \cdot Do$[22],
while they cannot form such stable complexes with R_2AlOR'. $[R_2AlOCR'NPh]_2$
behaved similarly to R_2AlOR' toward weak electron donors, but formed stable com-
plexes with strong electron donors such as trimethylamine oxide (TMAO) and
hexamethylphosphoramide (HMPA). Colorless crystalline TMAO and HMPA
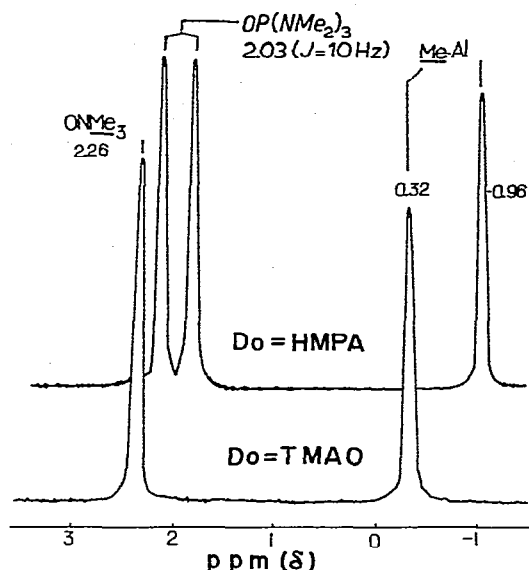
Fig. 4. NMR spectra (60 MHz) of the Me₂AlOCPhNPh · Do complex.

TABLE 4

ANALYTICAL DATA OF 1/1 DONOR COMPLEXES OF ORGANOALUMINUM COMPOUNDS, R₂AlOR'

Donor	Al compound	M.p. (°C)		R/Al[a]	R/OR'[b]	MeN/RAl[c]	Mol.wt.[d]
HMPA	Me₂AlOCPhNPh	63–64	Found	2.0	2.2	3.1	460
			Calcd.	2.0	2.0	3.0	432
TMAO	Me₂AlOCPhNPh	124	Found	2.0	2.0	1.5	328
			Calcd.	2.0	2.0	1.5	328
HMPA	Et₂AlO-sec-Bu		Found	1.9	2.0	3.1	340
			Calcd.	2.0	2.0	3.0	337
TMAO	Et₂AlO-sec-Bu	−37 to −40	Found	2.0	2.0	1.5	238
			Calcd.	2.0	2.0	1.5	233
HMPA	Me₃Al	74–75	Found	2.9		2.1	260
			Calcd.	3.0		2.0	251
TMAO	Me₃Al	110–111	Found	3.0		1.0	151
			Calcd.	3.0		1.0	147

[a] Gasometry and 8-hydroxyquinoline method. [b] Determined by the weight of isolated acid amide after hydrolysis and gas chromatography. [c] The ratio of methyl proton peak areas determined by NMR. [d] Cryoscopically in benzene.

complexes of [R₂AlOCR'NPh]₂ have compositions corresponding to the 1/1 complex R₂AlOCR'NPh · Do as indicated by chemical analyses and peak area ratios in NMR spectra (Fig. 4), and have monomeric structures (Table 4), similarly to the complexes of AlMe₃ and Et₂AlO-sec-Bu with TMAO and HMPA.

Two different structures (III) and (IV) are conceivable for the TMAO complex. The X-Ray structure analysis of single crystals of Me₂AlOCPhNPh · ONMe₃ substantiates unambiguously the structure (IV)[16].
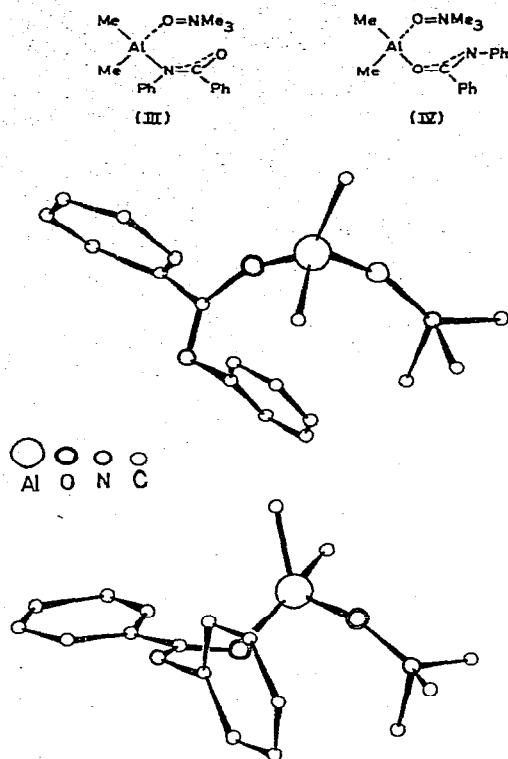
(III)   (IV)

○ ○ ○ ○
Al O N C

Fig. 5. The molecular structure of Me₂AlOCPhNPh·Me₃NO.

The three-dimensional structure (Fig. 5) reveals several characteristic structural features. First, the oxygen atom of TMAO moiety is linked to an aluminum atom and the oxygen atom of acid amide moiety is linked to the aluminum atom. Thus, the Al–N bond of [Me₂AlOCPhNPh]₂ is broken by the attack of TMAO. Second, two adjacent benzene rings occupy the more stable *trans* position, in contrast with the *cis* position in the organoaluminum [Me₂AlOCPhNPh]₂. Third, the nitrogen atom of the TMAO moiety assumes a nearly tetrahedral configuration and has no interaction with the aluminum atom. Fourth, the C–O distance (1.313 Å) is typical of that of an elongated double bond, whereas the C–N distance (1.277 Å) is that of a localized double bond. These interatomic distances agree with the IR spectral data (Table 5): the absorptions at 1608 and 1575 cm⁻¹ assigned to the O–C–N grouping lie at lower frequencies than that at 1660 cm⁻¹ assigned to O–C=N grouping in PhN=CPh–OMe[27]. It is important to note that the bond broken by the attack of the electron donor, TMAO, is Al–N, not Al–O bond. Since the same type of bond-breaking is observed for the attack of acetaldehyde[23], this type of bond-breaking is presumably of a general type for the attack by any electron donor.

(16)

(V)   (VI)   (VII)   (VIII)
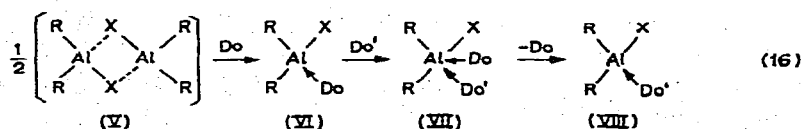
The reaction of a Lewis base with alkylaluminums of type R_2AlX in which X is an alkyl group, an alkoxyl group, an amino group, or an acid amide moiety can be expressed generally by eqn. (16).

TABLE 5

IR SPECTROSCOPIC DATA IN SOLID STATE (NUJOL MULL) AND IN SOLUTION (10% IN BENZENE)

Me₂AlOCPhNPh		*Me₂AlOCPhNPh·ONMe₃*	
Nujol	*Benzene*	*Nujol*	*Benzene*
1600	1601 w	1605	1607 m
1587	1588 m	1592	1589 m
1533	1547 s	1575	1570 m
		1538	1535 w
1493	1497 m	1486	1485 w
1450	1455 w	1445	1438 m
1405	1424 s	1375	1378 m
		1329	1329 s
1259	1296 w	1296	1296 w
1246	1249 w	1245	1245 w
1236	1235 m	1230	1230 w
1180	1190 s	1192	1195 w
1132	1138 m	1172	1176 m
		1112	1112 w
1072	1072 m	1067	1066 m
1026	1026 m	1020	1018 m
1000	1000 w	975	982 s
942	946 s	942	942 w
930	932 m	927	930 w
907	907 w	914	914 w
803	802 m	874	874 m
		820	824 w
786	782 m	752	755 s
745	752 m	705	705 w
718	718 w	683	680 m
675	693 s	666	660 m

In the first step, dimeric R_2AlX (V) reacts with an electron donor (Do) to form the monomeric donor complex (VI). The donor exchange reaction occurs when the donor complex (VI) reacts with another electron donor (Do') whose electron donating power is stronger. The presumed intermediate (VII) in which an aluminum atom assumes the pentacoordinate state is generally so unstable that a weaker electron donor is liberated to give a new tetra-coordinate complex (VIII).

The formation of a stable complex depends both on the Lewis acidity of an organoaluminum and on the Lewis basicity of an electron donor. In the case of $AlMe_3$, rather weak Lewis bases such as diethyl ether, tetrahydrofuran and amines give stable complexes[24]. In the case of $R_2AlNR'_2$, such as Me_2AlNPh_2, ethers cannot form stable complexes, but triethylamine and pyridine do so. In the case of R_2AlOR' or $[R_2AlOCR'NPh]_2$, triethylamine and pyridine cannot form stable complexes while HMPA and TMAO do so. Thus, it is concluded that the Lewis acidity of the

organoaluminum follows the order: $R_3Al > R_2AlNR'_2 > R_2AlOR' \approx [R_2AlOCR'-NPh]_2$.

The donor exchange reaction may afford the relative Lewis basicity of electron donors. The ligand $MeCONPh_2$ in the complex $Me_3Al \cdot MeCONPh_2$ was expelled completely by pyridine or triethylamine to give $Me_3Al \cdot C_5H_5N$ or $Me_3Al \cdot NEt_3$ and not by tetrahydrofuran (THF). In contrast with this, in the case of $Me_3Al \cdot PhCON-Ph_2$, an equimolar amount of THF is sufficient to liberate $PhCONPh_2$ completely to give $Me_3Al \cdot THF$ but diethyl ether could not displace $PhCONPh_2$. The ligand NEt_3 in $AlMe_3 \cdot NEt_3$ was easily expelled completely by HMPA and also TMAO. THF in $AlMe_3 \cdot THF$ was exchanged by NEt_3 in agreement with the results of Bonitz[22]. Therefore, these results indicate that the Lewis basicity follows the order; TMAO > HMPA > NEt_3 > Ph_2NCOMe > THF > Ph_2NCOPh > Ether, and the order parallels with its dipole moment[25,26] and its dissociation constant[28].

EXPERIMENTAL

General comments

All of the experimental operations were carried out under a dry argon atmosphere. The NMR spectra were recorded with Varian A-60 or T-60 spectrometers for the 10–20% benzene solution. Since tetramethylsilane (TMS) reacts with the organoaluminums, benzene was used as an internal standard (7.27 ppm). IR spectra were recorded with JASCO GC-402G spectrometer using liquid cell (cell width: 0.025 mm and 0.1 mm) which was flushed with argon gas, and compensated with the pure solvent.

The amount of the gaseous product evolved in the reaction was measured by gasometry and the nature of gaseous product was identified with GLC using a Yanagimoto GC-202 type gas chromatograph (silica gel column, 2m in length).

Materials

Acid amides were recrystallized from methanol solution. Trialkylaluminums (Ethyl Co.) were purified by distillation: $AlMe_3$; $102°/350$ mmHg, $AlEt_3$; $120°/35$ mmHg, Al-i-Bu_3; $87°/8$ mmHg. TMAO was purified by sublimation $(140°/10^{-4}$ mmHg) in the manner of Meisenheimer[29]. HMPA was dried over metallic sodium and then distilled $(68°/1$ mmHg). Toluene, benzene and tetrahydrofuran were distilled after drying over Na/K alloy.

Preparation

Equimolar reaction of AlR_3 and acid amide. Trimethylaluminum (0.05 mol) was added into the mixture of 20 ml of toluene and 0.04 mol of a primary or a secondary acid amide with stirring under dry argon at $-78°$. The suspension changed to a homogeneous solution on raising the temperature up to $-40°$ and gas evolution was observed at temperatures above $-20°$. The reaction was forced to completion by heating the mixture at $80°$ for 1 h. After the gas evolution was completed, 100 ml of n-hexane was added to the solution. Colorless needles, obtained quantitatively by allowing the solution to stand at room temperature, were recrystallized three times from toluene/n-hexane.

In cases of triethyl- or triisobutylaluminum, isooctane was used as a reaction

solvent, and the product was crystallized by allowing the reaction mixture to stand at
$-78°$. In the case of the tertiary acid amide, the procedure used for reaction and
crystallization was the same, except that no gas evolution was observed. Character-
istic constants of the products are summarised in Table 1.

Electron donor complexes of $[R_2AlOCR'NPh]_2$. TMAO or HMPA (0.1 mol)
was added to a solution of 0.1 mol of $[R_2AlOCR'NPh]_2$ in 100 ml of toluene with
stirring under argon atmosphere at room temperature. The reaction was forced to
completion by heating the mixture at $50°$ for 1 h.

The crystalline TMAO complex was obtained in nearly quantitative yield by
adding 40 ml of toluene to the mixture at $50°$ and cooling to room temperature. The
crystalline HMPA complex was obtained nearly quantitatively by adding 40 ml of
n-hexane at $50°$ and then cooling to $-20°$. Characteric constants of the complexes
are summarized in Table 4.

REFERENCES

1 H. Tani, T. Araki and H. Yasuda, *J. Polymer Sci., Part B*, 4 (1966) 727.
2 E. V. Mitrofanova and L. P. Stepovic, *Zh. Obshch. Khim.*, 36 (1966) 1488.
3 H. Reinheckel, D. Jahnke and G. Kretzschmar, *Chem. Ber.*, 99 (1966) 11.
4 J. R. Horder and M. E. Lappert, *J. Chem. Soc. A*, (1968) 2400.
5 J. R. Jennings, K. Wade and B. K. Wyatt, *J. Chem. Soc. A*, (1968) 2535.
6 Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda and H. Tani, *Chem. Commun.*, (1968) 1332;
   Y. Kai, N. Yasuoka, N. Kasai and M. Kakudo, *J. Organometal. Chem.*, 32 (1971) 165.
7 H. Yasuda, T. Araki and H. Tani, *J. Organometal. Chem.*, 49 (1973) 333.
8 K. Ziegler and W. R. Kroll, *Justus Liebigs Ann. Chem.*, 629 (1960) 167; T. Mole, *Aust. J. Chem.*, 19
   (1966) 381.
9 W. P. Neumann, *Justus Liebigs Ann. Chem.*, 667 (1963) 1.
10 R. M. Moriarty, *J. Org. Chem.*, 28 (1963) 1286.
11 T. Hirabayashi, T. Sakakibara and Y. Ishii, *J. Organometal. Chem.*, 32 (1971) C5.
12 W. Gerrard, M. E. Lappert and J. W. Wallis, *J. Chem. Soc.*, (1960) 2141.
13 R. C. Aggarwal and P. P. Singh, *J. Inorg. Nucl. Chem.*, 26 (1964) 2185.
14 H. Reinheckel and D. Jahnke, *Chem. Ber.*, 99 (1966) 23.
15 J. G. Noltes and J. Boersma, *J. Organometal. Chem.*, 16 (1969) 345.
16 Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda and H. Tani, *J. Chem. Soc. D*, (1971) 940.
17 T. Hurley, M. A. Robinson, J. A. Scruggs and S. I. Trotz, *Inorg. Chem.*, 6 (1967) 1310; H. Sato, R. Tarao
   and H. Higashi, *Bull. Chem. Soc. Jap.*, 42 (1969) 1588.
18 H. Sumitomo and K. Kobayashi, *17th Symp. Soc. Polymer Sci. Jap.*, (1968).
19 T. Mole, *Aust. J. Chem.*, 19 (1966) 381.
20 T. L. Brown and L. L. Murrell, *J. Amer. Chem. Soc.*, 94 (1972) 378.
21 D. S. Matteson, *Inorg. Chem.*, 10 (1971) 1555.
22 E. Bonitz, *Chem. Ber.*, 88 (1955) 742; *J. Amer. Chem. Soc.*, 67 (1945) 146.
23 Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda and H. Tani. *J. Chem. Soc. D*, (1969) 575.
24 C. H. Hendrickson and D. P. Eyman, *Inorg. Chem.*, 6 (1967) 1461; H. C. Brown and N. R. Davidson,
   J. Amer. Chem. Soc., 64 (1942) 316.
25 G. M. Philips, J. S. Hunster and L. E. Sutton, *J. Chem. Soc.*, (1945) 146.

26 D. Gurka and R. W. Taft, *J. Amer. Chem. Soc.*, 91 (1961) 4794.
27 J. Fabian and M. Legrand, *Bull. Soc. Chim. Fr.*, (1956) 287, 1461.
28 J. E. Bissey, *J. Chem. Educ.*, 44 (1967) 95.
29 J. Meisenheimer, *Justus Liebigs Ann. Chem.*, 397 (1913) 286.