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MONOMER-CATALYST COMPLEXES IN THE STEREOSPECIFIC POLYMERIZATION OF ALIPHATIC ALDEHYDE. THE STRUCTURE AND CHEMICAL BEHAVIOR OF THE ALDEHYDE COMPLEX OF $[R_2AlOCR'NPh]_2$

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SUMMARY

The reaction between some aliphatic aldehydes (acetaldehyde, propionaldehyde and butyraldehyde) and the typical stereospecific polymerization catalyst $R_2AlOCR'NPh$ has been studied in an attempt to elucidate the initiation mechanism of the polymerization reaction. The monomer-catalyst (1/1) complexes obtained from these aldehydes and $R_2AlOCR'NPh$ possess excellent catalytic activity towards the stereospecific polymerization. The structure of the complex in solution has been determined by NMR and IR spectra and compared with the structure determined by X-ray structure analysis. The presence of pentacoordinate aluminum in the complex has been demonstrated, for the first time, by X-ray studies.

The structure of the aromatic monoaldehyde complex has also been studied and shown to be identical with that of the aliphatic aldehyde complex mentioned above. The chemical behavior of these aldehyde complexes towards Lewis bases and Lewis acids has also been studied. The aldehyde moiety of the $R_2AlOCR'NPh \cdot MeCHO$ complex is liberated by the action of a strong Lewis base such as trimethylamine oxide and hexamethylphosphoramide, and is easily exchanged for another kind of aldehyde. The trimethylaluminum complex, $Me_2AlOCPhNPh \cdot MeCHO \cdot AlMe_3$, which only leads to the formation of amorphous polyacetaldehyde in contrast to $Me_2AlOCPhNPh \cdot MeCHO$, has been isolated and its structure determined by IR, NMR and X-ray studies in order to establish the relationship between its structure and its chemical behavior.

INTRODUCTION

The isolation and determination of the structure of monomer-catalyst complexes or compounds which exhibit a catalytic activity towards polymerization reactions has been little studied despite the importance of the coordination of the monomer to the catalyst during the initiation and propagation steps in the stereospecific polymerization of some polar monomers such as aliphatic aldehydes[1–4] and alkylene oxides[5,6]. The homogeneous catalyst $[R_2AlOCR'NPh]_2$, whose structure and chemical behavior have been described previously[7,8] exhibits the charac-

teristic property that only below the ceiling temperature (−40°) does the stereospecific polymerization reaction occur, while above that temperature only the complexation reaction occurs. This all-or-none type of behavior contrasts sharply with the usual behavior of organoaluminum compounds. In addition, no side reaction such as ester or ketone formation occurs between this type of catalyst and aldehydes. This paper describes the preparation, structure and chemical behavior toward Lewis bases and acids of complexes of $[R_2AlOCR'NPh]_2$ with some aldehydes, mainly acetaldehyde.

RESULTS AND DISCUSSION

I. The structure of the aldehyde complex

1. *Reaction with aliphatic and aromatic monoaldehydes*

A series of 1/1 complexes of $R_2AlOCR'NPh$ with aliphatic and aromatic monoaldehydes have been isolated quantitatively in a crystalline form by mixing both components in toluene in equimolar ratios (Table 4). No other reaction product was detected in these reaction mixtures, in contrast to the behavior of common organoaluminum compounds *i.e.* those represented by R_2AlX (X=R, OR', NR_2, OCOR', etc.), from which the corresponding ester and/or ketone may be generated by Tishchenko reaction and Oppenauer oxidation[9,10]. The 1/1 complexes isolated in this study decompose on contact with air or water liberating the aldehyde component quantitatively (eqn. 1).

$$1/2[R_2AlOCR'NPh]_2 + R''CHO \rightarrow R_2AlOCR'NPh \cdot R''CHO \xrightarrow{H_2O} R''CHO \quad (1)$$

Determination of the molecular weight cryoscopically in benzene indicated that the aldehyde complex is, in general, an equilibrium mixture of the monomer and

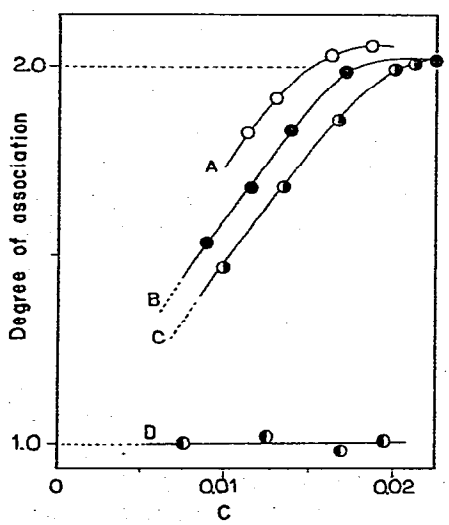


Fig. 1. Dependence of the degree of association of the aldehyde complexes $R_2AlOCR'NPh \cdot MeCHO$ on the concentration: A: R=Me, R'=Ph; B: R=R'=Me; C: R=Et, R'=Me; D: R=i-Bu, R'=Me. The concentration C is expressed in terms of the molar ratio of the organoaluminum compound to benzene.

the dimer with the equilibrium composition shifting towards the monomer when the concentration of the solution is decreased and/or when the alkyl group(s) linked to the aluminum atom and to the carbon atom are bulkier (Fig. 1). For example, $i\text{-}Bu_2AlOCMeNPh \cdot MeCHO$ is monomeric irrespective of the concentration, while the other two complexes studied, *viz.* $Et_2AlOCMeNPh \cdot MeCHO$ and $Me_2AlOCMeNPh \cdot MeCHO$, are monomeric only when the solution is sufficiently dilute.

2. The molecular structure of the aldehyde complex

The NMR spectrum of $R_2AlOCMeNPh \cdot MeCHO$ (R = Me, Et or i-Bu) measured in benzene solution exhibits a doublet (δ 1.7–1.8 ppm, J 6 Hz) which is assigned to the methyl protons and a quartet (δ 5.2–5.3 ppm, J 6 Hz) which is assigned to a methine proton as shown in Table 1, whereas the spectrum of free acetaldehyde exhibits a doublet (δ 1.6 ppm, J 3 Hz) and a quartet (δ 9.6 ppm, J 3 Hz). The coupling constant of the complexed acetaldehyde suggests that the carbonyl carbon of the acetaldehyde moiety of the complex possesses an sp^3 configuration. The signal assigned to an aldehyde methine proton is observed at *ca.* δ 5.2–5.5 ppm in all of the aliphatic aldehyde complexes examined. Thus, the carbonyl carbon of the aldehyde

TABLE 1

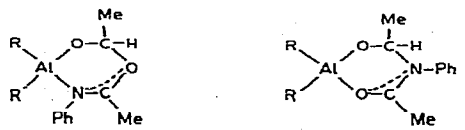
NMR AND IR DATA FOR THE ALDEHYDE COMPLEX $R_2AlOCR'NPh \cdot R''CHO$[a]

R	*R'*	*R''*	*NMR ppm* (δ)				*IR* (cm^{-1})	
			R		*R'* (=CH_3)	*R''*		*O–C–N*
CH_3	CH_3	CH_3	−0.23		1.54	1.75 5.23	CH_3 CHO	1612 1587
C_2H_5	CH_3	CH_3	1.68 0.45	CH_3, J 8 Hz CH_2, J 8 Hz	1.60	1.76 5.24	CH_3 CHO	1613 1590
i-C_4H_9	CH_3	CH_3	2.24 1.40 0.38	CH CH_3, J 7 Hz CH_2, J 7 Hz	1.56	1.67 5.26	CH_3 CHO	1612 1591
CH_3	CH_3	C_2H_5	−0.18		1.60	1.02 2.25 5.12	CH_2 CH_3 CHO	1612 1588
CH_3	CH_3	n-C_3H_7	−0.13		1.57	0.93 2.20 5.25	CH_2 CH_3 CHO	1612 1588
CH_3	C_6H_5	CH_3	−0.19		—	2.01 5.60	CH_3 CHO	1602 1565
C_2H_5	C_6H_5	CH_3	1.64 0.42	CH_3, J 8 Hz CH_2, J 8 Hz	—	1.96 5.65	CH_3 CHO	1602 1565
CH_3	CH_3	C_6H_5	−0.25		1.48	—		1572
CH_3	CH_3	*p*-$CH_3C_6H_4$	−0.29		1.55	2.13	CH_3	1572
CH_3	CH_3	*o*-$CH_3C_6H_4$	−0.26		1.55	2.28	CH_3	—

[a] NMR and IR spectra were recorded for 10% benzene solution at 25°. Benzene was used as an internal standard (7.27 ppm) in the NMR measurement.

moiety in this type of complex is presumed to possess an sp^3 configuration irrespective of the nature of the aldehyde component and of the bulkiness of the alkyl groups attached to an aluminum atom.

The methyl protons of the acetanilide moiety of $Me_2AlOCMeNPh \cdot MeCHO$ exhibit only one singlet in the NMR spectrum, in contrast to the two singlets (*cis* and *trans*[8]) observed in that of $[Me_2AlOCMeNPh]_2$. The two absorption bands observed at 1608 and 1580 cm^{-1} in the IR spectrum of the aldehyde complex may be assigned to the stretching vibration of the O–C–N group. These NMR and IR data may be interpreted by assuming either structure A or B for the acetaldehyde complex, in which the acetaldehyde is inserted into either an Al–O or an Al–N bond, respectively.



(A) (B)

Although the results of studies of the hydrolysis of the acetaldehyde complex, in which both acetaldehyde and acetanilide are obtained in quantitative yield, are compatible with both structures A and B, the structure of the trimethylamine oxide complex, $Me_3NO \cdot R_2AlOCPhNPh$[11], favors structure B.

In this study, the correct structure was determined unambiguously by X-ray structure analysis of single crystals of $Me_2AlOCPhNPh \cdot MeCHO$. The structure illustrated in Fig. 2 reveals several characteristic features of this type of molecule[12]. First, the carbonyl carbon atom of the acetaldehyde moiety possesses an sp^3 configuration through its bonding with the nitrogen atom of the acid amide moiety, and as a result can exist in either an *R* or *S* configuration. The C–O distance in the aldehyde moiety (1.43 Å) is longer than that in the free acetaldehyde[13,14] and is equal to the ordinary single bond distance. Second, the molecule is dimeric and possesses a two-

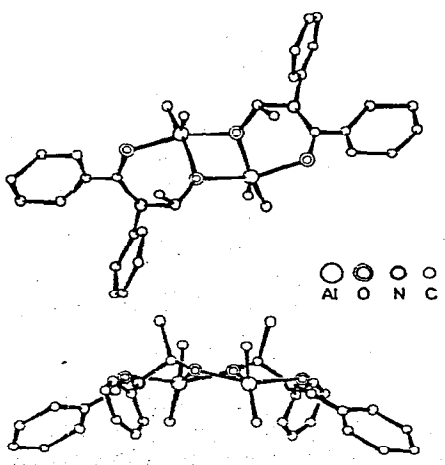
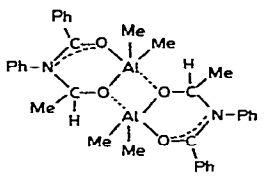


Fig. 2. The molecular structure of $[Me_2AlOCPhNPh \cdot MeCHO]_2$.

fold axis. Thus, since the dimeric molecule contains two asymmetric carbon atoms, two enantiomers, *R–R* and *S–S*, should exist. Examination of a molecular model shows that the isomer *R–S* is less stable than *R–R* and *S–S* due to steric hindrance. Third, the carbonyl carbon atom of the acetaldehyde moiety is linked to the nitrogen atom of the acid amide moiety and the carbonyl oxygen atom of the acetaldehyde moiety is linked to the aluminum atom. Fourth, the oxygen atom in the acetaldehyde moiety is linked to two aluminum atoms and assumes an sp^2 configuration. Fifth, both the C–O (1.226 Å) and the C–N (1.373 Å) distances in the acid amide moiety do not exhibit any substantial deviation from those in $[Me_2AlOCPhNPh]_2$ and correspond to values intermediate between those for ordinary single and double bonds. The two benzene rings in the molecule are *cis* relative to each other. Sixth, of the two types of bond between the aluminum and the oxygen atoms of the acetaldehyde moiety, one (1.944 Å) is significantly longer than the other (1.856 Å). This fact agrees well with the suggestion that the longer bond is preferentially broken to give two monomer molecules having a six-membered cyclic structure on dilution of the solution of the complex. Seventh, the aluminum atoms in the dimer are pentacoordinate and exist in a distorted trigonal bipyramidal structure[12]. This is the first example of a pentacoordinate aluminum atom firmly established by X-ray structure analysis, although such coordination has been suggested in $AlH_3 \cdot 2NMe_3$[15].

Finally, the dimeric aldehyde complex is in equilibrium with its monomer in benzene solution (eqn. 2). The mode of association of the monomeric molecule indicates that the oxygen atom of the aldehyde moiety has a higher electron density than that of the acid amide moiety. IR spectra of this complex in solution and in the solid state suggest that the structure determined by X-ray analysis also exists in solution (Table 3).

(B) $\rightleftharpoons$  (2)

Aromatic monoaldehyde complexes (Table 4) have similar structures to those of aliphatic complexes and yield the component aldehydes and acid amides quantitatively by hydrolysis in an argon stream.

The molecular weights of these complexes as determined cryoscopically in benzene decreased as the concentration of the solutions decreased in a similar manner to the aliphatic monoaldehyde complexes. Thus, aromatic monoaldehyde complexes also exist as equilibrium mixtures of monomers and dimers.

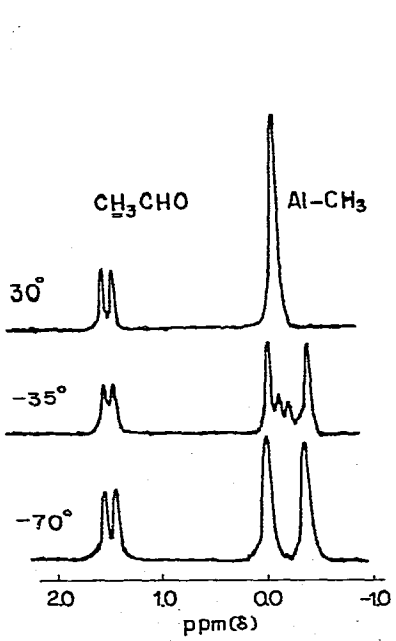
The frequencies of the C–O stretching vibrations (1700 cm^{-1}) in the IR spectra of typical aromatic monoaldehydes such as benzaldehyde and *p*-tolualdehyde were lower than those observed for the aliphatic monoaldehydes (1728 cm^{-1}). This indicates that the carbonyl groups in aromatic monoaldehydes have smaller polarities than those in aliphatic monoaldehydes presumably due to resonance between the aryl and carbonyl groups. However, the IR spectra of the aromatic monoaldehyde complexes of $Me_2AlOCR'NPh$ (R′ = Me or Ph) are nearly identical to those of the corresponding aliphatic monoaldehyde complexes over the spectral range 1500 to

1800 cm^{-1} and exhibit two absorption bands at 1608 and 1572 cm^{-1}. It is not unreasonable to assume, therefore, that the structure of the aromatic monoaldehyde complex is essentially identical with that of the acetaldehyde complex.

3. *Temperature dependence of the NMR spectra of $Me_2AlOCR'NPh \cdot R''CHO$*

The NMR spectrum of $Me_2AlOCPhNPh \cdot MeCHO$ has been studied over the temperature range 30° to −80° in 10% toluene-d_8 or tetrahydrofuran-d_8 solution. The proton signals of the two methyl groups linked to a given aluminum atom are influenced by the temperature. When the temperature is decreased, a sharp singlet observed at 30° is split into four complicated peaks at about −35° which simplify to two symmetrical peaks (chemical shift difference, 24 Hz) at −70° as shown in Fig. 3.

Similar temperature dependences are also observed for the aromatic aldehyde complexes. Thus the NMR spectrum of $Me_2AlOCMeNPh \cdot PhCHO$ has been recorded over the temperature range 70° to −80° in toluene-d_8 solution. A singlet assigned to the methyl groups linked to the aluminum atom observed at temperatures above 50° is split into two unsymmetrical singlets at about 30° (Fig. 4). The ratio between the two singlets also varies with the concentration of the solution, the peak at lower field increasing as the concentration of the solution is decreased. At temperatures below −50° the peak at lower field disappears, and that at higher field is split into two symmetrical peaks (chemical shift difference, 15 Hz). This characteristic



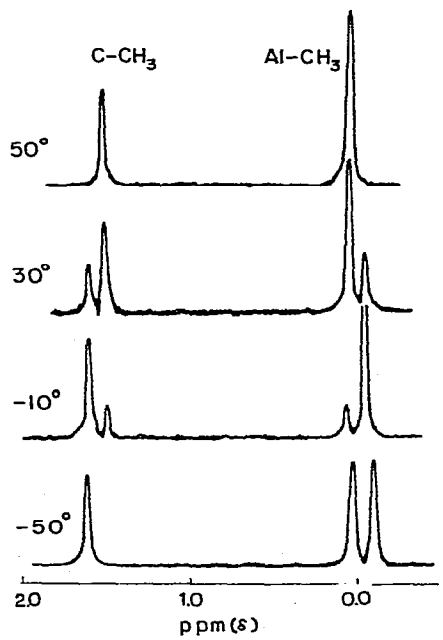


Fig. 3. Temperature dependence of the NMR spectrum (60 MHz) of $Me_2AlOCPhNPh \cdot MeCHO$ in toluene-d_8 solution.

Fig. 4. Temperature dependence of the NMR spectrum (60 MHz) of $Me_2AlOCMeNPh \cdot PhCHO$ in toluene-d_8 solution.

feature suggests that the aromatic monoaldehyde complex has the same type of structure as the aliphatic monoaldehyde complex. Similar results have been obtained for the *o*- and *p*-tolualdehyde complexes of $Me_2AlOCMeNPh$, the chemical shift difference also being 15 Hz in both cases.

The two singlets in the spectra of aromatic aldehyde complexes observed at relatively high temperatures between 30° and −30° may be interpreted in terms of the aluminum methyl protons of the monomeric and the dimeric complexes, the singlet at lower field being assigned to the monomer and that at higher field to the dimer. This interpretation is supported by the following observations. The molecular weights of these aromatic monoaldehyde complexes as determined cryoscopically in benzene decrease as the concentration of the solution is decreased, in a similar manner to that observed with aliphatic monoaldehyde complexes (Fig. 5). This observed value of the molecular weight agrees well with the average degree of association calculated from the NMR data using the above assignment, although the former is a little smaller than the latter because of the difference in the experimental temperature (in the former 35°; in the latter *ca.* 5°). The above separation could not be observed with aliphatic aldehyde complexes probably due to overlapping of the two singlets.

Two different interpretations may be advanced to explain the splitting into two peaks observed at temperatures below −50°. First, one of the two methyl groups linked to an aluminum atom may assume an axial position while the other assumes an equatorial one. Second, the two methyl groups linked to an aluminum atom may function differently from each other due to differences in their surroundings in the pentacoordinate aluminum compound brought about by the stabilization of a definite conformation. The difference in chemical shifts of the axial and the equatorial methyl protons of the *gem*-dimethyl group in cyclohexane derivatives is usually less than 6 Hz[16,17] while that of the *gem*-dimethyl group in $Me_2AlOCPhNPh \cdot MeCHO \cdot AlMe_3$, as reported later in this paper, is only 2–3 Hz. Thus, stabilization

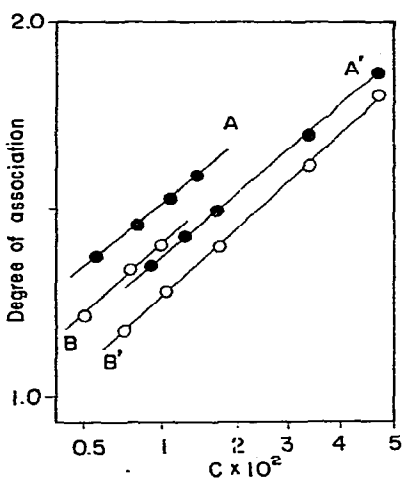


Fig. 5. Dependence of the degree of association of the aromatic aldehyde complex $Me_2AlOCMeNPh \cdot ArCHO$ on the concentration: (A) and (A'): $Ar = C_6H_5$; (B) and (B'): $Ar = p\text{-}CH_3\text{-}C_6H_4$. (A) and (B) were determined from the NMR spectrum (60 MHz), and (A') and (B') cryoscopically in benzene. The concentration C is expressed in terms of the molar ratio of the organoaluminum compound to benzene.

of a definite conformation seems to be the more plausible explanation for the large chemical shift difference. A similar separation for the aluminum methyl protons observed in $[AlMe_3]_2$ at lower temperatures has been ascribed to the presence of stabilized bridge and terminal methyl protons[18,19]. Thus, the seemingly similar behavior observed in these two cases is apparently due to quite different phenomena.

A difference in the temperature at which the singlet assigned to the aluminum methyl protons splits into two singlets has also been observed: $[Me_2AlOCMeNPh \cdot MeCHO]_2$ shows no splitting even at temperatures as low as $-60°$, while $[Me_2AlOCPhNPh \cdot MeCHO]_2$ and $[Me_2AlOCMeNPh \cdot PhCHO]_2$ exhibit a characteristic splitting at $-50°$. This difference is probably due to the difference in the conformational stability of the dimer, being mainly due to the nature of the bond between the aldehyde and the acid amide moieties in the complex. This suggestion is supported by the IR spectral data: the absorption frequency corresponding to the O–C–N group in the former compound (1590 cm^{-1}) is higher than that for the latter two compounds (1565 and 1572 cm^{-1} respectively). This result shows that the O–C–N group in the former compound is loosely bound to the aluminum atom and to the carbon atom of the aldehyde moiety.

II. The aldehyde exchange reaction

A very important and interesting aldehyde exchange reaction has been discovered during the course of studies of the chemical behavior of the aldehyde complex.

The addition of an equimolar amount of a higher aldehyde such as propionaldehyde and butyraldehyde to a benzene solution of $[Me_2AlOCMeNPh \cdot MeCHO]_2$ at 10° results in the formation of another aldehyde complex in which the acetaldehyde is partially replaced by the higher aldehyde. In contrast, the addition of an equimolar

TABLE 2

EQUILIBRIUM COMPOSITIONS IN THE ALDEHYDE EXCHANGE REACTION INVOLVING 1 MOLE OF $Me_2AlOCMeNPh \cdot RCHO$ AND n MOLES OF R'CHO[a]

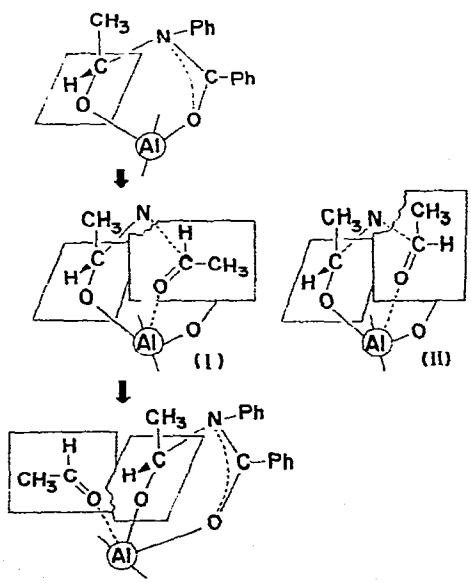
R	R'	*Content of R'CHO in the complex*		
		$n=1$	$n=3$	$n=5$
C_2H_5	CH_3	92	98	99
n-C_3H_7	CH_3	85	97	99
CD_3	CH_3	14	33	56
CH_3	C_2H_5	10	35	50
CH_3	n-C_3H_7	15	42	65
CH_3	i-C_3H_7	0	0	0
C_6H_5	*p*-$CH_3C_6H_4$	27	58	69
C_6H_5	*o*-$CH_3C_6H_4$	26	53	64
p-$CH_3C_6H_4$	C_6H_5	33	62	75
CH_3	C_6H_5	0	0	0
C_6H_5	CH_3	100	100	100

[a] The aldehyde R'CHO was allowed to react with a toluene solution containing the complex of a second aldehyde RCHO for 10 min at 10°.

amount of acetaldehyde to a higher aldehyde complex, $Me_2AlOCMeNPh \cdot RCHO$ (R = Et, Pr) results in the quantitative formation of the acetaldehyde complex (Table 2). These results show that in these aldehyde exchange reactions the stability of the aldehyde complex decreases as the bulkiness of the alkyl group of the aldehyde moiety in the complex increases: *i.e.* the stability decreases in the order $CH_3CHO > C_2H_5CHO > n\text{-}C_3H_7CHO > i\text{-}C_3H_7CHO$.

The corresponding exchange reaction has also been examined for the aromatic aldehyde complex. In this case, 60% of the benzaldehyde in the complex was replaced by *p*-tolualdehyde when a five molar excess of *p*-tolualdehyde was added to the benzaldehyde complex. Unexpectedly, however, *o*-tolualdehyde did behave in the same manner as *p*-tolualdehyde despite the fact that steric hindrance would have been expected to be much more important in *o*-tolualdehyde. These results indicate that there is apparently little difference between the stabilities of the benzaldehyde, *o*-tolualdehyde and *p*-tolualdehyde complexes.

The relative stabilities of the aliphatic and aromatic monoaldehyde complexes has also been examined. In the aromatic complexes benzaldehyde was completely replaced on addition of an equimolar amount of acetaldehyde to the solution of benzaldehyde complex, whereas in the aliphatic complexes acetaldehyde could not be replaced even when excess benzaldehyde was added. Hence the aliphatic monoaldehyde complex is considerably more stable than the aromatic complex. The instability of the aromatic monoaldehyde complex may be due to the decreased polarity of its aldehyde group relative to that of the aliphatic monoaldehyde. The aldehyde exchange reaction is considered, essentially, to consist of a type of donor exchange reaction[8] in which two possible modes of approach involving the incoming



SCHEME 1

acetaldehyde molecule, as illustrated by I and II, respectively, in Scheme 1, are conceivable. The repulsive forces acting between the methyl group of the incoming acetaldehyde and that of the coordinated acetaldehyde favor the type of approach depicted by I. This type of approach should lead to the formation of a complex with a configuration identical to that of the mother complex.

III. Reactions of the aldehyde complex

1. *Reaction with a Lewis acid*

On adding protic acids such as acetic acid and benzoic acid to a toluene solution of $Me_2AlOCR'NPh \cdot R''CHO$ at low temperature, the aldehyde R''CHO and the acid amide R'CONHPh are liberated in nearly quantitative yield, without the evolution of gaseous methane.

In contrast, reaction of the aliphatic aldehyde complex with AlR_3, a Lewis acid, is much more simple. The reaction product obtained from the reaction between equimolar quantities of $Me_2AlOCR'NPh \cdot MeCHO$ and $AlMe_3$ in n-hexane solution was isolated as colorless crystals on cooling the solution. It should be noted that the reaction proceeded quantitatively without the involvement of any side reaction, *e.g.* a Grignard-type addition reaction, even when a large excess of $AlMe_3$ was used.

The composition of the products obtained as determined from chemical analyses and their peak area ratios in the NMR spectra ($C_6H_5/CHO/CH_3-CHO/CH_3Al = 10/1/3/15$) correspond to those of 1/1 addition compounds of the two reactants.

$$Me_2AlOCR'NPh \cdot MeCHO + AlMe_3 \rightarrow Me_2AlOCR'NPh \cdot MeCHO \cdot AlMe_3 \quad (3)$$

These AlR_3 complexes are quite stable thermally and possess sharp melting points, whereas the aldehyde complexes from which they are derived decompose above 20°. Their molecular weights as determined cryoscopically in benzene correspond to those of the monomer (Table 5). The IR spectra of $Me_2AlOCR'NPh \cdot MeCHO \cdot AlMe_3$ exhibit only one peak (R'=Me, 1548 cm^{-1}; R'=Ph, 1578 cm^{-1}) in the spectral range 1500 to 1800 cm^{-1}, the C–O and C–N absorptions of the acid amide moiety in these compounds apparently overlapping. The formation of these addition compounds apparently involves the attack of an $AlMe_3$ molecule preferentially at the oxygen atom of the aldehyde moiety and not at the nitrogen or oxygen atoms of the acid amide moiety, *e.g.* $Me_2AlOCPhNPh \cdot MeCHO$, as suggested by the structure of the dimer of this complex (see eqn. 2). The correctness of this mode of formation is fully supported by the results of an X-ray structure analysis of single crystals of $Me_2AlOCPhNPh \cdot MeCHO \cdot AlMe_3$[20].

The three-dimensional structure of this molecule exhibits several characteristic features (Fig. 6). First, the molecule is monomeric. Second, the $AlMe_3$ moiety is linked through its aluminum atom to the oxygen atom of the aldehyde moiety. Four atoms, Al(1), Al(2), and the O and C atoms of the aldehyde carbonyl moiety, lie in a plane, and hence the oxygen atom assumes the planar sp^2 type of configuration. Third, the oxygen atom of the aldehyde moiety remains in a 3-coordinate state, while the aluminum atom of the aldehyde complex changes from being pentacoordinate in $[Me_2AlOCPhNPh \cdot MeCHO]_2$ to tetracoordinate in the addition compound. Fourth, the C O and C–N distances in the acid amide moiety and the

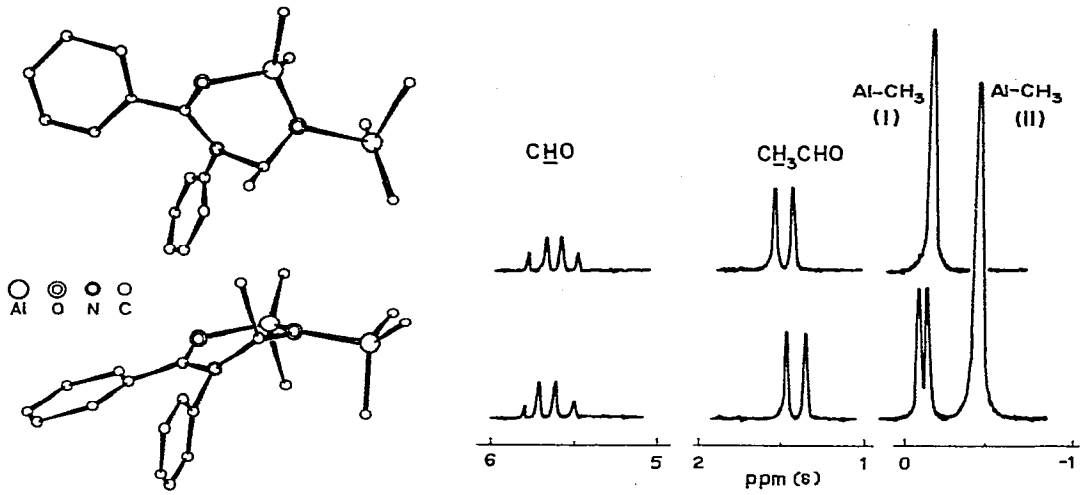


Fig. 6. The molecular structure of $Me_2AlOCPhNPh \cdot MeCHO \cdot AlMe_3$.

Fig. 7. NMR spectra (60 MHz) of $Me_2AlOCPhNPh \cdot MeCHO$ (I) and $Me_2AlOCPhNPh \cdot MeCHO \cdot AlMe_3$ (II).

bond angles between them are similar to the corresponding values in $[Me_2AlOCPhNPh]_2$ and $[Me_2AlOCPhNPh \cdot MeCHO]_2$, thus indicating that electron delocalization over the O–C–N group also occurs in this case.

The structure determined by X-ray diffraction analysis is also apparently similar to that in solution as no significant difference is observed between the IR spectrum in the solid state (Nujol mull) and that in solution (benzene) as shown in Table 3.

The NMR spectrum of $Me_2AlOCPhNPh \cdot MeCHO \cdot AlMe_3$ has also been measured in toluene-d_8 solution (Fig. 7). The signals corresponding to the methine and methyl protons of the acetaldehyde moiety in this complex appear at δ 5.67 (quartet, J 6 Hz) and δ 1.78 ppm (doublet, J 6 Hz). These values are closely similar to those (δ 5.60 (quartet, J 6 Hz) and δ 2.01 ppm (doublet, J 6 Hz)) in $Me_2AlOCPhNPh \cdot MeCHO$ as might be expected from the results of X-ray studies. The signal of the aluminum methyl proton at a lower field, Me(I), is assigned to that of the $Me_2AlOCPhNPh \cdot MeCHO$ moiety while the signal at a higher field, Me(II), is attributed to the $AlMe_3$ moiety as the peak area ratio of Me(II) to Me(I) is 3/2. The signal assigned to Me(I) is split into two peaks. The chemical shift differences between these two peaks in $Me_2AlOCPhNPh \cdot MeCHO \cdot AlMe_3$ and $Me_2AlOCMeNPh \cdot MeCHO \cdot AlMe_3$ (3 and 2 Hz) may possibly be interpreted in terms of an axial and an equatorial methyl group attached to an aluminum atom since the magnitude of the observed values are very nearly equal to those attributed to axial and equatorial methyl groups observed in cyclohexane derivatives, as mentioned above.

An alternative interpretation, based on the assumed structure C, in which the splitting is attributed to bridge and terminal methyl groups, is excluded since in the three-dimensional structure (Fig. 6) no bridge methyl group is found and the shortest

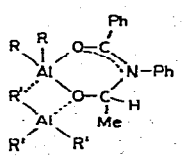
TABLE 3

IR SPECTROSCOPIC DATA RELATING TO THE SOLID STATE AND SOLUTION

$Me_2AlOCPhNPh \cdot CH_3CHO$		$Me_2AlOCPhNPh \cdot CH_3CHO \cdot AlMe_3$	
Nujol	*Benzene*	*Nujol*	*Benzene*
1603	1603 s	1600	1600 m
1590	1591 m	1586	1585 m
1565	1565 s	1550	1546 s
		1505	1505 w
1496	1495 m	1494	1493 w
		1466	1467 m
1434	1435 s	1446	1446 m
1365	1360 m	1380	1380 m
1331	1329 m	1336	1337 m
1305	1305 w	1290	1289 w
1272	1268 m	1263	1265 w
1186	1190 m	1192	1190 s
1166	1159 w	1180	
1130	1124 m		
1110	1110 m	1100	1100 s
1072	1072 m	1076	1076 w
1060	1062 m	1061	1056 m
1025	1022 w	1023	1023 w
1000	1002 w	1002	1001 w
975	980 m	976	973 w
928	920 m		
920	915 s	912	908 s
788	788 m	795	796 m
758	760 m	712	713 s
726	723 s		
685	695 s	695	696 m
665	660 s	632	631 m
		611	611 m

contact distance between the methyl carbon and the aluminum (3.397 Å) is too great to allow the formation of a bridging bond between them. Furthermore, no change occurs in the NMR spectrum over the temperature range 50° to −80° and no splitting of methyl groups ascribable to terminal and bridge methyls is observed at low temperatures.

These AlR_3 complexes react easily with Lewis bases (donor) such as THF, pyridine and triethylamine in n-hexane solution liberating $[Me_2AlOCR'NPh \cdot MeCHO]_2$ and electron-donor complexes of $AlMe_3$, as shown in eqn. (4). The

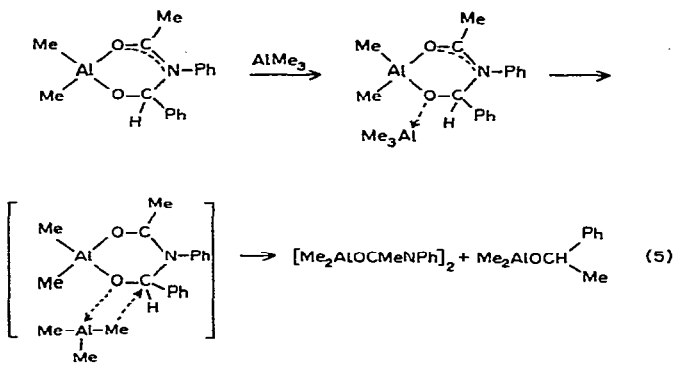


(c)

former was obtained in quantitative yield in a crystalline form while the presence of the latter was confirmed by hydrolysis of the distillate of the mother liquor. From these experimental results, it is concluded that the electron density on the oxygen atom of the aldehyde moiety is less than that on THF.

$$Me_2AlOCPhNPh \cdot MeCHO \cdot AlMe_3 + Donor \longrightarrow [Me_2AlOCR'NPh \cdot MeCHO]_2 + Donor \cdot AlMe_3 \quad (4)$$

The reaction of the aromatic monoaldehyde complex with AlR_3 is quite different from that of the aliphatic complex. Reaction of a 1/1 mixture of $Me_2AlOCMeNPh \cdot PhCHO$ and $AlMe_3$ gave 1-phenylethanol in quantitative yield after hydrolysis. This indicates that the linkage between the oxygen atom of the benzaldehyde entity and the nitrogen atom of the acid amide moiety is cleaved by $AlMe_3$ and that this is followed by an attack on the carbonyl carbon atom of the aldehyde molecule by the methyl group attached to the aluminum atom. Assuming that the structure of $Me_2AlOCPhNPh \cdot MeCHO \cdot AlMe_3$ is as described above, the reaction between the aromatic monoaldehyde complex and AlR_3 may be expressed as in eqn. (5):



(5)

The occurrence of the addition reaction with the benzaldehyde complex but not with the acetaldehyde complex may be attributed to the lower polarity of the carbonyl group in benzaldehyde relative to that in acetaldehyde. In practice, the C–O bond distance of the acetaldehyde moiety is decreased by complexation with $AlMe_3$, and attack of $AlMe_3$ on the oxygen atom of the benzaldehyde moiety in the complex results in the elimination of the benzaldehyde molecule.

2. Reaction of the aldehyde complex with a strong Lewis base

Hexamethylphosphoramide (HMPA), a strong Lewis base, reacts with the acetanilide derivative $Me_2AlOCMeNPh \cdot MeCHO$ at 30° to form the 1/1 complex which may be obtained as a crystalline compound on addition of excess n-hexane at −40° (Table 6). A similar addition compound may also be obtained from the reaction between equimolar quantities of $Me_2AlOCMeNPh \cdot HMPA$ and acetaldehyde.

$$\left.\begin{array}{l} Me_2AlOCMeNPh \cdot MeCHO + OP(NMe_2)_3 \\ Me_2AlOCMeNPh \cdot OP(NMe_2)_3 + MeCHO \end{array}\right\rbrace \longrightarrow Me_2AlOCMeNPh \cdot MeCHO \cdot OP(NMe_2)_3 \quad (6)$$

The NMR spectrum of this addition compound in toluene-d_8 solution exhibits signals attributable to the methyl and methine protons of the acetaldehyde moiety at δ 1.33 ppm (doublet, J 6 Hz) and δ 5.04 ppm (quartet, J 6 Hz), respectively. These values are nearly equal to those observed in the spectrum of the initial acetaldehyde complex. The NMR spectrum of $Me_2AlOCMeNPh \cdot MeCHO \cdot HMPA$ recorded at $-80°$ exhibits no splitting of the signal assigned to the aluminum methyl proton (singlet, δ -0.59 ppm at 30°) in contrast to the case of $Me_2AlOCPhNPh \cdot MeCHO$. The molecular weight of this HMPA complex indicated that the material is monomeric. For these reasons, the structure of the complex is reasonably represented by formula (D) in eqn. 7.

The NMR spectrum of the corresponding benzanilide derivative, $Me_2AlOCPhNPh \cdot MeCHO \cdot HMPA$, exhibited somewhat different features. At $-70°$ the spectrum is similar to that of $Me_2AlOCMeNPh \cdot MeCHO \cdot HMPA$ exhibiting only one peak corresponding to the aluminum methyl proton and proton signals attributable to the complexed acetaldehyde. However, on increasing the temperature to 30°, two kinds of acetaldehyde proton signals were observed; one was attributed to free acetaldehyde (CH_3-, δ 1.63 ppm, doublet, J 3 Hz; $-CHO$, δ 9.47 ppm, quartet, J 3 Hz) while the other was due to complexed acetaldehyde (CH_3-, δ 1.37 ppm, doublet, J 6 Hz; $-CHO$, δ 5.05 ppm, quartet, J 6 Hz). This increase in temperature also led to the se-

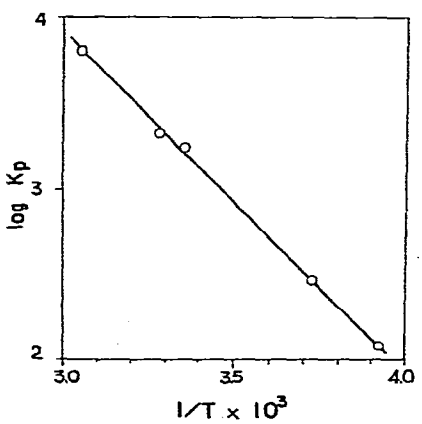


Fig. 8. Temperature dependence of the equilibrium constant K_p of reaction (7).

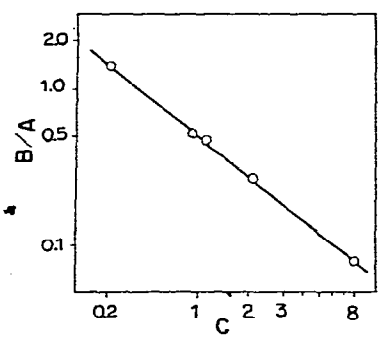
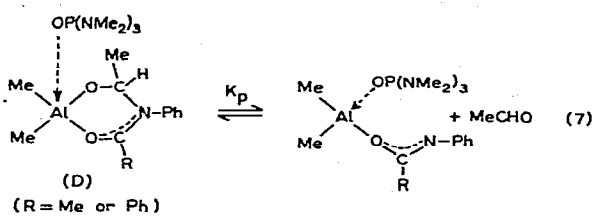


Fig. 9. The effect of the concentration of acetaldehyde on the equilibrium between $Me_2AlOCPhNPh \cdot HMPA$ and MeCHO. The equilibrium composition was measured by NMR spectroscopy using the ratio of the intensities of the aluminum methyl protons of $Me_2AlOCPhNPh \cdot HMPA \cdot MeCHO$ (A) to those of $Me_2AlOCPhNPh \cdot HMPA$ (B). The concentration C is expressed in terms of the molar ratio of MeCHO to $Me_2AlOCPhNPh \cdot MeCHO$.

paration of the aluminium methyl proton signal into two peaks (chemical shift difference, 11 Hz). The lower field peak was assigned to $Me_2AlOCPhNPh \cdot HMPA$ as the corresponding peak of this compound when synthesized separately and added to the solution completely overlapped the lower field peak. The higher field peak may possibly be assigned to the aluminum methyl proton of $Me_2AlOCPhNPh \cdot MeCHO \cdot HMPA$. The intensities of the peaks assigned to the methyl protons of free acetaldehyde and

the aluminum methyl group in $Me_2AlOCPhNPh \cdot HMPA$ decrease as the temperature is decreased. These observations may be explained on the basis of the equilibrium reaction depicted in eqn. 7, and in fact, in agreement with this equation, elimination of acetaldehyde occurs quantitatively from the solid complex at 40° in vacuo (1 mmHg) to yield $Me_2AlOCPhNPh \cdot HMPA$.



A linear relationship is observed between the reciprocal of e absolute temperature and the equilibrium constant K_p of reaction (7) as calculated from the NMR spectra (see Fig. 8). The activation energy calculated from this plot (10 kcal · mol^{-1}) is very close to that observed in the polymerization of acetaldehyde (8.5 kcal · mol^{-1})[22]. This indicates that the Lewis basicity of HMPA is nearly equal to, but a little stronger than that of acetaldehyde. The NMR data obtained in the presence of various amounts of acetaldehyde indicate that the above equilibrium is shifted towards the left in proportion to the amount of acetaldehyde added as shown in Fig. 9.

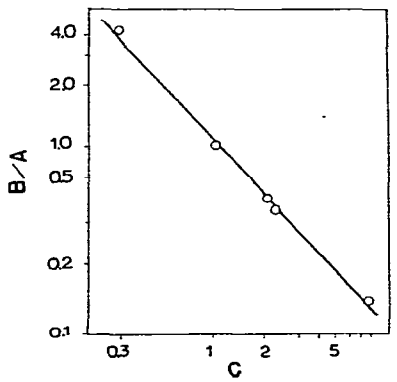


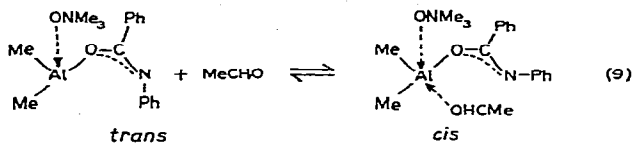
Fig. 10. Dependence of the ratio of the intensities of the aluminum-methyl protons of $Me_2AlOCPhNPh \cdot ONMe_3$ at higher field (B) to those at lower field (A). The concentration C is expressed in terms of the molar ratio of MeCHO to $Me_2AlOCPhNPh \cdot ONMe_3$.

In contrast to the HMPA complex, the crystalline TMAO complex $Me_2AlOCPhNPh \cdot ONMe_3$ is precipitated in quantitative yield and acetaldehyde may be recovered quantitatively by adding an equimolar amount of trimethylamine oxide (TMAO) to the benzene solution of $Me_2AlOCPhNPh \cdot MeCHO$. Furthermore, no stable complex was isolated from the reaction between $Me_2AlOCPhNPh \cdot ONMe_3$ and excess acetaldehyde (eqn. 8).

$$Me_2AlOCPhNPh \cdot MeCHO + ONMe_3 \rightarrow Me_2AlOCPhNPh \cdot ONMe_3 + MeCHO \quad (8)$$

Despite these observations, however, interaction between acetaldehyde and the TMAO complex is apparent in the NMR spectrum obtained from a benzene solution containing an equimolar mixture of both components. Two peaks attributable to the aluminum methyl protons (chemical shift difference, 10 Hz) were observed together with only one kind of aldehyde proton signal. The signals corresponding to the methyl protons at δ 1.65 ppm (doublet, J 3 Hz) and methine proton at δ 9.51 ppm (quartet, J 3 Hz) are similar to those observed for the free acetaldehyde.

A straight-line plot was observed between the ratio of the intensities of the peaks attributable to the lower and higher field aluminum methyl protons and the concentration of free acetaldehyde (Fig. 10). The difference in the chemical shift of the two aluminum methyls may therefore be ascribed to the conformational change of the acid amide moiety from *trans* to *cis* brought about by weak coordination or solvation of acetaldehyde as shown in eqn. (9).



(9)

The fact that the two adjacent benzene rings in $Me_2AlOCPhNPh \cdot ONMe_3$ are *trans* to each other while those in $[Me_2AlOCPhNPh \cdot MeCHO]_2$ are *cis* makes this suggestion plausible.

CONCLUSION

In sharp contrast to the tendency of common organoaluminum compounds such as AlR_3 and AlR_2X (X = OR, NR_2, OCOR, $ON{=}CR_2$, etc.) to form esters or ketones on reaction with an aldehyde at 10°, $[R_2AlOCR'NPh]_2$ forms a complex under the same conditions. Such a complex, which is well known as a Meerwein complex[23,24], is postulated as an intermediate in the addition reaction of an organoaluminum compound with a carbonyl compound to give an aluminum alkoxide. The aldehyde in $R_2AlOCR'NPh \cdot R''CHO$ may be easily liberated on treatment of the complex with either a different kind of aldehyde or with a strong Lewis base despite the fact that the aldehyde moiety in the complex is sufficiently stabilized through the formation of chemical bonds with the nitrogen atom of the acid amide moiety and with the aluminum atom to enable isolation of the complex in a crystalline form. This complex may therefore be described as a "stabilized Meerwein complex" or "modified Meerwein complex".

This complexation reaction is similar to the initiation process which occurs in the stereospecific polymerization of acetaldehyde. The aldehyde exchange reaction, whose course is stereospecifically controlled, affords valuable information regarding the stereoregulating mechanism in the isotactic polymerization of acetaldehyde. The importance of these reactions in the stereospecific polymerization of acetaldehyde will be discussed in a following paper[26].

EXPERIMENTAL

All experimental operations were carried out under a dry argon atmosphere.

NMR spectra were recorded using a Varian A-60 or T-60 spectrometer while IR spectra were recorded using a JASCO GC-202G spectrometer.

Materials

Acetaldehyde was prepared by the decomposition of paraldehyde using toluene-*p*-sulfonic acid (1 mol-%) at 30° and purified by distillation after drying over calcium hydride for one week. Propionaldehyde, butyraldehyde, benzaldehyde and tolualdehyde were purified by distillation in an argon atmosphere after drying the commercial sample over calcium hydride. HMPA (hexamethylphosphoramide) was dried over metallic sodium and purified by distillation (68°/1 mmHg).

The aldehyde complex of $R_2AlOCR'NPh$

0.03 mol of $[R_2AlOCR'NPh]_2$ was dissolved in 20 ml of toluene in a Schlenk-type vessel (inner volume, 200 ml) which had been previously flushed with dry argon. To this solution, 0.05 mol of an aldehyde was added with vigorous stirring at 0°C followed by 100 ml of n-hexane. The complex was obtained as colorless flat plates in quantitative yield by allowing the solution to stand at 0°. The crystalline product, which was separated from the supernatant liquid by removing the latter with a syringe, was recrystallized from a toluene/n-hexane mixture (20 ml/100 ml).

The recrystallization conditions were governed by the solubility of the product.

TABLE 4

ANALYTICAL DATA FOR THE ALDEHYDE COMPLEX $R_2AlOCR'NPh \cdot R''CHO$

R	*R'*	*R''*	*Analysis Found (calcd.) (%)*			
			Al (%)[a]	*R/R''*[b]	*R'CONHPh/Al*[c]	*R''CHO/Al*[d]
CH_3	CH_3	CH_3	11.3 (11.5)	2.0 (2.0)	0.9 (1.0)	0.9 (1.0)
C_2H_5	CH_3	CH_3	10.0 (10.3)	1.9 (2.0)	0.9 (1.0)	1.1 (1.0)
i-C_4H_9	CH_3	CH_3	8.1 (8.4)	2.0 (2.0)	0.9 (1.0)	1.0 (1.0)
CH_3	CH_3	C_2H_5	11.0 (10.8)	1.9 (2.0)	1.0 (1.0)	1.0 (1.0)
CH_3	CH_3	n-C_3H_7	9.7 (10.3)	1.8 (2.0)	1.0 (1.0)	1.2 (1.0)
CH_3	C_6H_5	CH_3	8.9 (9.1)	1.9 (2.0)	1.0 (1.0)	1.0 (1.0)
C_2H_5	C_6H_5	CH_3	8.3 (8.3)	2.1 (2.0)	0.9 (1.0)	0.9 (1.0)
CH_3	CH_3	C_6H_5	9.0 (9.1)	2.0 (2.0)	1.0 (1.0)	1.1 (1.0)
CH_3	CH_3	*p*-CH_3-C_6H_4	8.5 (8.8)	2.0 (2.0)	0.9 (1.0)	1.1 (1.0)
CH_3	CH_3	*p*-CH_3-C_6H_4	8.6 (8.8)	2.0 (2.0)	0.9 (1.0)	1.1 (1.0)

[a] Determined by the 8-hydroquinoline method. [b] Determined by the peak area ratio in the NMR spectrum. [c] Determined by the weight of acid amide isolated and by the peak area ratio in the NMR spectrum. [d] Determined by a GLPC method.

For example, the more insoluble higher aldehyde complex of $Me_2AlOCRNPh$ could be recrystallized from 40 ml of toluene, while the more soluble acetaldehyde complex of $i\text{-}Bu_2AlOCMeNPh$ and the tolualdehyde complex of $Me_2AlOCMeNPh$ were recrystallized from a toluene/n-hexane mixture (10 ml/100 ml) at −20°.

All these complexes, which crystallized as square flat plates, gradually decomposed on standing at room temperature. Since all these complexes decomposed rapidly on heating, no discrete melting points could be observed. The characteristic constants of these complexes are summarised in Table 4.

The $AlMe_3$ complex of $R_2AlOCR'NPh \cdot MeCHO$

The reaction solution, prepared by adding 0.03 mol of $AlMe_3$ to a solution of 0.03 mol of $Me_2AlOCRNPh \cdot MeCHO$ in 15 ml of n-hexane, was allowed to stand at 20° for 20 min, to allow the reaction to go to completion. After addition of 100 ml of n-hexane, the product was produced from the solution at −20° as colorless long plates. The product, which was identified as $Me_2AlOCRNPh \cdot MeCHO \cdot AlMe_3$ (see Table 5), was sufficiently thermally stable to exhibit a definite melting point, in contrast to the initial aldehyde complex $Me_2AlOCRNPh \cdot MeCHO$.

The 1/1 addition compound of hexamethylphosphoramide (HMPA) with the aldehyde complex

To a solution of 0.03 mol of $Me_2AlOCRNPh \cdot MeCHO$ in 20 ml of toluene,

TABLE 5

CHARACTERIZATION OF $Me_2AlOCRNPh \cdot MeCHO \cdot AlMe_3$ (FOUND (CALCD.))

R	*m.p.* (°C)	*Al* (%)	*Me(II)/Me(I)*[a]	*Me(I)/MeCHO*[a]	*Mol. Wt.*[b]
Me	87–88	17.9	1.50	1.98	360
		(17.6)	(1.50)	(2.00)	(307)
Ph	105–106	14.2	1.49	1.98	373
		(14.6)	(1.50)	(2.00)	(369)

[a] Determined by the peak area ratio in the NMR spectrum. Me(II) is assigned to the methyl protons of the $AlMe_3$ moiety and Me(I) to those of the $Me_2AlOCRNPh \cdot MeCHO$ moiety. [b] Determined cryoscopically in benzene.

TABLE 6

CHARACTERIZATION OF $Me_2AlOCRNPh \cdot MeCHO \cdot HMPA$ (FOUND (CALCD.))

R	*RCONHPh/Al*[a]	*MeCHO/HMPA*[b]	*Me–N/Me–Al*[c]	*Mol. Wt.*[d]
Me	1.0	1.0	3.0	420
	(1.0)	(1.0)	(3.0)	(414)
Ph	1.0	0.9	3.1	492
	(1.0)	(1.0)	(3.0)	(476)

[a] Calculated from the amount of acid amide isolated and the aluminum content as determined by the 8-hydroxyquinoline method after hydrolysis. [b] Determined by GLPC analysis of the hydrolyzate. [c] Calculated from the intensities of the methyl proton peaks in the NMR spectra. [d] Cryoscopically in benzene.

0.03 mol of HMPA was added at room temperature. After addition of 100 ml of n-heptane, the solution was allowed to stand at $-40°$ to yield a crystalline product. This crystalline material was separated from the mother liquor and dried carefully at $-30°$ under reduced pressure (1 mmHg) because of its thermal instability. The substance was identified as $Me_2AlOCRNPh \cdot MeCHO \cdot HMPA$ by the peak area ratio exhibited in the NMR spectrum and by hydrolysis which give acetaldehyde and the acid amide RCONHPh in quantitative yield as shown in Table 6.

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