BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3388—3396 (1972)

The Crystal Structure of the Polymerization Catalyst of Acetaldehyde and Its Derivatives. II.[1] The Crystal and Molecular Structure of the Trimethylamine Oxide Adduct of Dimethylaluminum *N*-Phenylbenzimidate, $[(CH_3)_2Al \cdot O \cdot C(C_6H_5):N(C_6H_5),\ ON(CH_3)_3]$

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(Received May 13, 1972)

The molecular structure of a stereospecific (*isotactic*) polymerization catalyst of the acetaldehyde-Lewis base adduct $[Me_2Al \cdot O \cdot CPh: NPh, ONMe_3]$ has been determined from three-dimensional X-ray data collected on a single crystal diffractometer. The crystal belongs to the triclinic system (space group $P\bar{1}$), with two formula units in a cell with dimensions of; $a=8.517\pm0.004$, $b=10.096\pm0.005$, $c=12.256\pm0.005$ Å, $\alpha=104.67\pm0.04$, $\beta=106.97\pm0.04$, and $\gamma=98.10\pm0.04°$. The structure was solved by the symbolic addition method and refined by the block-diagonal, least-squares procedure. The molecule is monomeric, and both amide and $ONMe_3$ groups are connected to the aluminum atom through oxygen atoms. The amide moiety has an imino-ether type structure and two adjacent benzene rings take *trans* configuration about the N–C bond. The co-ordinated $ONMe_3$ group has a structure similar to that of the free molecule.

This work is a part of a series of molecular-structural studies[1–5] of the stereospecific polymerization catalysis of acetaldehyde. In recent years, Tani and his coworkers have found that, among the catalytic systems of the stereospecific polymerization reaction of aldehydes, the reaction products of trialkylaluminums and acid amides show excellent catalytic activities for the *isotactic* polymerization of acetaldehyde and methylmethacrylate.[6–9]

This catalytic system has attractive features which facilitate stereochemical investigations. First, the catalytic system contains few side reactions and gives a very high yield of the stereospecific polymer. Therefore, a rather simple reaction mechanism can be expected. Second, the polymerization reaction is mild, and many interesting complexes can be isolated in a pure crystalline form.

The series of complexes selected for molecular-structural studies in this catalytic system are:

(I) $[Me_2Al \cdot O \cdot CPh:NPh]_2$,[10]
(II) $[Me_2Al \cdot O \cdot CPh:NPh,\ MeCHO]_2$,
(III) $[Me_2Al \cdot O \cdot CPh:NPh,\ MeCHO,\ AlMe_3]$, and
(IV) $[Me_2Al \cdot O \cdot CPh:NPh,\ ONMe_3]$.

The complex I is a highly stereospecific polymerization catalyst of acetaldehyde obtained from an equimolar reaction of trimethylaluminum and benzanilide; its molecular structure has been reported previously.[1,2] The polymerization catalyst-monomer complex II shows the same catalytic activities as I. The co-ordinated aldehyde can be replaced by a free aldehyde present in the solution, but it can not be replaced by other electron donors, such as pyridine or tetrahydrofuran. Using the complex III, a Lewis acid adduct of II, as a catalyst, an *atactic* polymer of acetaldehyde is obtained.

The complex IV is a strong Lewis base adduct of

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[1] Part I, Y. Kai, N. Yasuoka, N. Kasai, and M. Kakudo, *J. Organometal. Chem.*, **32**, 165 (1971).

[2] Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda, and H. Tani, *Chem. Commun.*, **1968**, 1332.

[3] Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda, and H. Tani, *ibid.*, **1969**, 575.

[4] Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda, and H. Tani, *ibid.*, **1970**, 1243.

[5] Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda, and H. Tani, *ibid.*, **1971**, 940.

[6] H. Tani, T. Araki, and H. Yasuda, *J. Polym. Sci., Part B*, **4**, 727 (1966).

[7] H. Tani, T. Araki, and H. Yasuda, *ibid.*, **6**, 389 (1968).

[8] H. Tani and H. Yasuda, *ibid.*, **7**, 17 (1969).

[9] H. Tani and H. Yasuda, Private communications.

[10] Throughout the paper, methyl, ethyl, and phenyl groups will be expressed as Me, Et, and Ph respectively.

the polymerization catalyst; it is obtained from an equimolar mixture of I and $ONMe_3$ in benzene at room temperature:

$$\underset{\text{I}}{[Me_2Al\cdot O\cdot CPh:NPh]_2} \xrightarrow[\text{in benzene at room temperature}]{+ONMe_3} \underset{\text{IV}}{[Me_2Al\cdot O\cdot CPh:NPh, ONMe_3]}$$

This complex is the most stable one in argon among the four complexes mentioned above. However, it does not show any catalytic activities, and significant differences can be expected between the molecular structures of the polymerization catalyst, [$Me_2Al\cdot O\cdot CPh:NPh$]$_2$ and this complex. The structure determination was undertaken by means of X-ray diffraction. The preliminary results were communicated earlier.[5)]

Experimental

The colorless, prismatic crystals were prepared and supplied by Tani and Yasuda of this University. As the crystals decompose immediately in the air, they were sealed in thin-walled glass capillary tubes in argon.

Nickel-filtered Cu$K\alpha$ radiation was used for the preliminary X-ray experiments. Oscillation and Weissenberg photographs showed that the crystal has no crystallographic symmetry, and the space group is $P\bar{1}$ or $P1$.

Both the determination of the unit-cell dimensions and the collection of the intensity data were carried out on a Rigaku on-line controlled, four-circle, single crystal diffractometer. Zirconium-filtered Mo$K\alpha$ radiation was used. The setting angles of each reflection were computed by the Busing-Levy method[11)] on an Aicom-C2 computer attached to the diffractometer. The method requires precise values of the centering angles, 2θ, ω, χ, and ϕ, of three linearly-independent reflections of known indices in order for us to determine the orientation of the crystal and the dimensions of the unit cell. The reflections chosen were 500, 030, 007, 0$\bar{3}$0, and 00$\bar{7}$. During the intensity measurement of each quadrant of the reciprocal lattice, three of the five chosen reflections included in the quadrant were used. The crystal data are listed in Table 1. The accuracies of the cell parameters were estimated from the reproducibilities of the cell parameters as calculated from different sets of reflections. The crystal density was determined by the flotation method in a mixed solution of carbon tetrachloride and *n*-hexane. Intensity measurements were carried out at room temperature by using the ω–2θ scan technique with a β-filter. The scan range, $\Delta(2\theta)$ of each reflection was computed by this equation:

$$\Delta(2\theta) = 2.0^\circ + 0.7^\circ \tan\theta_c.$$

The starting angle of the scan is $(2\theta_c - 1.0^\circ)$, where θ_c is the calculated value of the Bragg angle using the $\lambda(\text{Mo}K\alpha_1)$ (=0.70926 Å), and the scanning speed of the scintillation counter was 4.0°/min. Sheets of nickel foil with graded thicknesses were used as intensity attenuators. Before scanning a reflection, a short, fixed-time (one second) intensity measurement was taken at the $2\theta_c$ position, and an appropriate attenuator was selected and was inserted in order to control the intensity in the optimum range (below 7000 cps in this experiment). The background scattering was measured for five seconds at both ends of the scan range by means of the stationary-crystal stationary-counter technique. The intensities were corrected for the background scattering and for the usual Lorentz and polarization effects. Each structure factor, along with its standard deviation, as estimated by the counting statistics, was calculated and printed out before the measurement of the next reflection. The absorption correction was ignored (μ=1.3 cm^{-1} for Mo$K\alpha$). The intensity of the 300 reflection was chosen as the standard and was measured every 25 reflections. The crystal used had dimensions of about 0.5×0.3×0.3 mm. The collimator was 1.0 mm in diameter. During the intensity measurements, the intensity of the standard reflection gradually decreased. The structure factor magnitudes, therefore, decreased approximately linearly up to $(\sin\theta)/\lambda=0.458$. After this, they showed a sudden decrease. Probably the crystal decomposed completely. Then another crystal of an approximately equal size was chosen and further intensity measurements were carried out up to $(\sin\theta)/\lambda=0.539$. The intensities of about 200 reflections ($(\sin\theta)/\lambda=0.235$) were also remeasured for the second crystal, and the structure factor magnitudes were compared with those obtained from the first crystal. No special anisotropy due to the absorption was found. Then the scalings of the two kinds of data, including the intra- and inter-crystal scaling, were undertaken linearly based on the observed changes in the structure factor magnitudes of the standard reflection. A total of 2399 independent reflections were obtained, among which 2048 were non-zero reflections.

Table 1. Crystal data of [$(CH_3)_2Al\cdot O\cdot C(C_6H_5):N(C_6H_5), ON(CH_3)_3$]

Triclinic		$C_{18}H_{25}N_2O_2Al$
a= 8.517	±0.004Å	M=328.4
b= 10.096	±0.005Å	Z=2
c= 12.256	±0.005Å	d_m=1.14 g·cm^{-3}
α=104.67	±0.04°	d_x=1.149 g·cm^{-3}
β=106.97	±0.04°	Space group $P\bar{1}$
γ= 98.10	±0.04°	μ=1.3 cm^{-1} (for Mo$K\alpha$)
V=948.5 Å^3		

Structure Determination and Refinement

The crystal structure was solved by obtaining phases directly from the structure factor magnitudes by means of the symbolic addition procedure.[12)] The structure factors reduced previously were placed on an absolute scale by means of a three-dimensional Wilson plot, and the structure factor magnitudes, $|F|$, and the normalized structure factor magnitudes, $|E|$, were computed by means of SIGMA program[13)] on a FACOM 230-60 computer at Kyoto University. The distribution of the normalized structure factor magnitudes, $|E|$, and their statistical averages are given in Table 2. On the basis of these statistics, the space group was determined to be $P\bar{1}$, which was confirmed at the later stage of the structure determination. The SIGMA program was also utilized to list the $\sum_2$ relationships for each reflection and to calculate the associated probabilities. The probabilities were determined by

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11) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).

12) J. Karle and I. L. Karle, *ibid.*, **21**, 849 (1966).

13) T. Ashida, SIGMA, The Universal Crystallographic Computing System (I), edited by T. Sakurai, p. 43, Japanese Crystallographic Association, 1967.

means of the equation:

$$P_+(E_h) = \frac{1}{2} + \frac{1}{2} \tanh\,(\sigma_3\sigma_2{}^{-3/2}|E_h|\textstyle\sum E_k E_{h-k}),$$

and their lower limit was set at 0.97.

Positive signs were assigned to three linearly-independent reflections in order to define the origin of the unit cell. The signs of the five other reflections were then all determined to be + from the $\sum_2$ relationships among the origin-defining reflections. Four additional reflections were chosen, and their phases were designated by the letters a, b, c, and d in order to facilitate the symbolic addition procedure. Starting from the phases of these 12 reflections (Table 3), 99 signs out of 103 reflections whose $|E|$ values are greater than 2.0 were determined as functions of a, b, c, and d by using the SORT-SIGMA 2 program.[14] Through the application of the $\sum_2$ formula, it was found, from the relationships among the symbols, that $a=c=d$ and $b=+$.

As the + signs were assumed for the three origin-fixing reflections, the − sign was never introduced into these reflections in the course of the application of the $\sum_2$ formula for the space group $P\bar{1}$. It was then necessarily concluded that the signs of a, c, and d are all −; otherwise, a trivial solution would have resulted. On the basis of these 99 phases, the application of the $\sum_2$ relationship was extended over 303 reflections with $|E|\geqq 1.50$ and the phases of 203 additional reflections were determined. At this stage, one of the 99 phases changed its sign to the correct one.

From the E-map (Fig. 1), the locations of all of the 23 nonhydrogen atoms were found easily. On the basis of these atomic locations, block-diagonal least-squares refinement was carried out by means of the HBLS IV program.[15] The atomic scattering factors used in the calculation were taken from those of Hanson and his co-workers.[16] After 5 cycles refinement using the isotropic temperature factors, the R index was found to be 0.17 for non-zero reflections. This rather large R value was considered to have resulted from the large differences between $|F_o|$ and $|F_c|$ values, especially for small $|F_o|$'s. Therefore, all the $|F_o|$'s smaller than $3\sigma(F_o)$ were excluded from the further refinement. Anisotropic temperature factors were then introduced for all the nonhydrogen atoms and the refinement was continued. After 4 cycles, the R value was reduced to 0.097 for 1359 non-zero reflections. From the difference Fourier map computed by means of SFFR program[17] and from the model examination, all of the hydrogen atoms were located. Considering these hydrogen atoms and using a weighting scheme to be described later, the final refinement was undertaken and the R index decreased to 0.068 for non-zero reflections. The weighting scheme applied was;

$$|F_o| < F_{\min}:\ w = F_{\mathrm{wt}}$$
$$F_{\min} \leqq |F_o| \leqq F_{\max}:\ w = 1.0$$
$$F_{\max} < |F_o|:\ w = F_{\max}/|F_o|$$

where $F_{\max}=20.0$, $F_{\min}=0.0$, and $F_{\mathrm{wt}}=0.0$. The weighted R index defined as $\{\sum w\cdot(|F_o|-|F_c|)^2/\sum w\cdot(F_o)^2\}^{1/2}$ is 0.082.

TABLE 2. DISTRIBUTION OF THE NORMALIZED STRUCTURE FACTOR MAGNITUDE AND STATISTICAL AVERAGES

	Distribution of $\lvert E\rvert$ %		Number of reflections
	Theoretical (Centrosymmetric)	Experimental	
$\lvert E\rvert\geqq 3.0$	0.3	0.38	9
$\lvert E\rvert\geqq 2.0$	5.0	4.3	103
$\lvert E\rvert\geqq 1.0$	32.0	33.0	792
			2399 (total)

	Experimental	Theoretical	
		Centrosymmetric	Noncentrosymmetric
$<\lvert E^2\rvert>$	1.000	1.000	1.000
$<\lvert E\rvert>$	0.790	0.798	0.886
$<\lvert E^2-1\rvert>$	0.946	0.968	0.739

TABLE 3. STARTING SET OF APPLICATION OF $\sum_2$ FORMULA

h	k	l	$\lvert E\rvert$	Phase	
1	$\bar{1}$	2	3.39	+	for origin definition
5	$\bar{5}$	$\bar{5}$	3.48	+	
7	2	$\bar{6}$	4.10	+	
1	8	$\bar{3}$	2.13	+	
2	7	$\bar{1}$	2.75	+	
5	4	$\overline{10}$	2.19	+	
6	3	$\bar{8}$	2.78	+	
6	$\bar{6}$	$\bar{3}$	2.23	+	
2	$\bar{1}$	6	2.75	a	
8	$\bar{2}$	$\bar{6}$	3.18	b	
5	3	$\bar{9}$	3.21	c	
1	$\bar{2}$	$\bar{1}$	2.33	d	

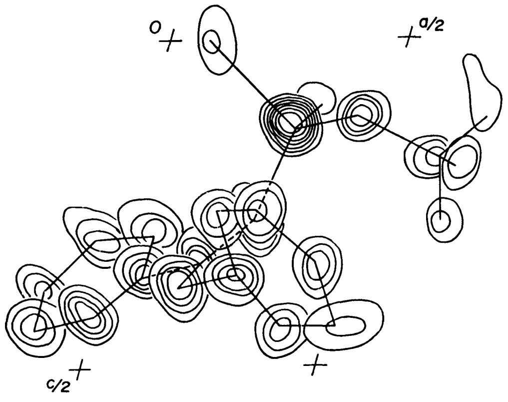

Fig. 1. E-map. Contours in an arbitrary scale.

The final atomic co-ordinates of the heavy atoms, along with their estimated standard deviations and the anisotropic temperature factors, are shown in Tables 4 and 5 respectively. The atomic co-ordinates and the

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[14] N. Yasuoka, SORT-SIGMA2, unpublished program.

[15] T. Ashida, HBLS IV, Ref. 13, p. 65.

[16] H. P. Hanson, F. Herman, J. D. Lea, and S. S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

[17] T. Ashida, SFFR, Ref. 13, p. 74.

Table 4. Atomic co-ordinates of the heavy atoms (in fraction of cell edges) along with their estimated standard deviations (in 10^{-3} Å)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Al	0.3060	3	−0.2250	3	0.1332	3
O(1)	0.2983	5	−0.1692	5	0.2802	5
O(2)	0.4574	5	−0.0861	6	0.1222	5
N(1)	0.1638	7	−0.0155	6	0.3675	7
N(2)	0.6329	6	−0.0455	7	0.1803	7
C(1)	0.3755	12	−0.4042	10	0.1077	12
C(2)	0.0934	9	−0.2192	11	0.0183	9
C(3)	0.1848	7	−0.1384	8	0.3316	7
C(4)	0.0786	7	−0.2588	7	0.3461	7
C(5)	−0.0156	8	−0.2337	8	0.4208	8
C(6)	−0.1160	9	−0.3460	9	0.4333	10
C(7)	−0.1207	10	−0.4819	9	0.3733	11
C(8)	−0.0236	11	−0.5068	10	0.2998	12
C(9)	0.0753	11	−0.3955	9	0.2867	10
C(10)	0.2654	8	0.1010	7	0.3564	9
C(11)	0.4180	8	0.1738	8	0.4468	9
C(12)	0.5030	8	0.2971	9	0.4403	9
C(13)	0.4441	8	0.3490	9	0.3461	10
C(14)	0.2939	9	0.2738	9	0.2563	10
C(15)	0.2073	8	0.1516	8	0.2613	9
C(16)	0.7134	10	−0.1264	12	0.1033	12
C(17)	0.6806	10	0.1069	10	0.1903	11
C(18)	0.6830	9	−0.0629	12	0.3010	10

Table 5. Anisotropic temperature factors of the heavy atoms expressed in the form of $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	0.0149	0.0122	0.0087	0.0058	0.0125	0.0063
O(1)	0.0147	0.0151	0.0082	0.0071	0.0127	0.0079
O(2)	0.0139	0.0183	0.0098	0.0066	.00098	0.0137
N(1)	0.0212	0.0122	0.0127	0.0069	0.0195	0.0108
N(2)	0.0128	0.0172	0.0116	0.0049	0.0122	0.0124
C(1)	0.0387	0.0159	0.0185	0.0146	0.0327	0.0126
C(2)	0.0201	0.0255	0.0084	0.0012	0.0086	0.0075
C(3)	0.0132	0.0141	0.0065	0.0062	0.0068	0.0080
C(4)	0.0151	0.0107	0.0067	0.0029	0.0099	0.0045
C(5)	0.0192	0.0134	0.0086	0.0093	0.0154	0.0074
C(6)	0.0219	0.0158	0.0155	0.0085	0.0242	0.0153
C(7)	0.0234	0.0157	0.0180	0.0045	0.0249	0.0150
C(8)	0.0348	0.0133	0.0195	0.0023	0.0337	0.0071
C(9)	0.0346	0.0117	0.0142	0.0044	0.0319	0.0033
C(10)	0.0202	0.0090	0.0117	0.0083	0.0209	0.0083
C(11)	0.0160	0.0149	0.0103	0.0048	0.0093	0.0096
C(12)	0.0166	0.0156	0.0113	0.0001	0.0077	0.0045
C(13)	0.0168	0.0131	0.0163	0.0045	0.0139	0.0125
C(14)	0.0232	0.0138	0.0158	0.0083	0.0184	0.0171
C(15)	0.0174	0.0114	0.0114	0.0034	0.0085	0.0087
C(16)	0.0191	0.0272	0.0195	0.0098	0.0230	−0.0020
C(17)	0.0231	0.0189	0.0154	0.0028	0.0128	0.0130
C(18)	0.0187	0.0319	0.0130	0.0108	0.0062	0.0268

isotropic temperature factors of hydrogen atoms are listed in Table 6. The observed and calculated structure factors are given in Table 7.

Table 6. Atomic co-ordinates (in fraction of cell edges) along with their estimated standard deviations (in 10^{-2}Å) and isotropic temperature factors for the hydrogen atoms (in Å^2)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
H(1)	0.460	8	−0.411	8	0.190	8	3.6
H(2)	0.440	8	−0.415	8	0.044	8	3.9
H(3)	0.263	8	−0.496	8	0.072	9	4.3
H(4)	0.001	8	−0.261	8	0.043	8	3.1
H(5)	0.076	8	−0.278	8	−0.072	8	3.9
H(6)	0.087	8	−0.114	8	0.019	8	3.9
H(7)	−0.009	8	−0.125	8	0.471	8	3.1
H(8)	−0.192	8	−0.326	7	0.491	8	3.0
H(9)	−0.199	8	−0.568	8	0.384	8	3.2
H(10)	−0.019	8	−0.614	8	0.255	8	3.9
H(11)	0.155	8	−0.417	8	0.231	8	3.4
H(12)	0.470	8	0.133	8	0.523	8	3.1
H(13)	0.621	8	0.356	8	0.512	8	3.5
H(14)	0.512	7	0.446	7	0.341	8	2.8
H(15)	0.244	8	0.314	8	0.182	8	3.5
H(16)	0.088	8	0.093	7	0.189	8	3.0
H(17)	0.681	8	−0.239	8	0.101	8	3.7
H(18)	0.858	8	−0.098	8	0.128	8	3.5
H(19)	0.658	8	−0.125	8	0.014	8	3.8
H(20)	0.664	8	0.128	8	0.100	8	3.5
H(21)	0.601	8	0.163	8	0.232	8	3.8
H(22)	0.809	8	0.151	8	0.249	8	3.9
H(23)	0.823	8	−0.036	8	0.332	8	3.5
H(24)	0.643	8	0.022	8	0.354	8	4.3
H(25)	0.659	8	−0.169	8	0.317	8	4.0

Results and Discussion

The molecular structure, with the numbering of atoms, as viewed along the *b* axis is shown in Fig. 2. The interatomic bond distances and angles calculated using the DAPH program[18] are listed in Tables 8 and 9 respectively.

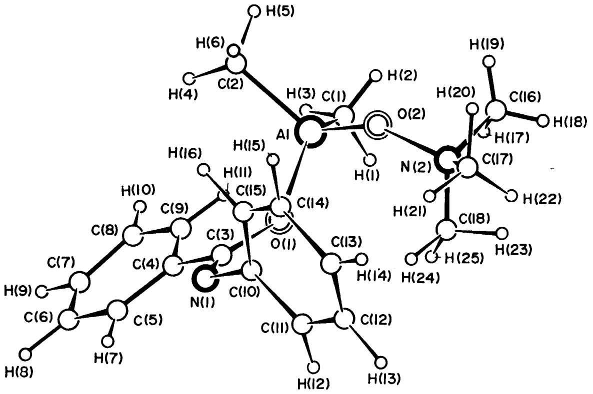

Fig. 2. Molecular structure.

Molecular Structure. The molecule is monomeric. The amide and $ONMe_3$ groups are both connected to the aluminum atom through oxygen atoms. The aluminum atom has a slightly distorted tetrahedral

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18) T. Ashida, DAPH, Ref. 13, p. 76.

TABLE 7. THE OBSERVED AND CALCULATED STRUCTURE FACTORS (each multiplied by the factor of 5.0)

K	FO	FC
H,L=	0	-12
5	21	-14
H,L=	0	-11
3	18	-8
4	19	-19
6	20	21
H,L=	0	-10
1	49	-50
7	37	32
8	24	22
H,L=	0	-9
2	57	-52
3	43	39
5	42	-46
6	32	-33
8	36	37
9	31	22
H,L=	0	-8
1	36	-31
2	39	-42
3	27	-20
4	57	53
6	83	-81
8	51	54
9	36	34
H,L=	0	-7
2	113	-110
3	52	-54
5	49	53
7	58	-57
8	72	-69
9	30	-30
H,L=	0	-6
1	165	168
2	129	126
3	95	92
4	22	18
5	27	-27
6	26	21
7	92	-96
8	38	-43
H,L=	0	-5
1	109	109
2	110	115
4	72	66
5	82	84
8	34	40
9	43	41
H,L=	0	-4
1	174	-174
2	210	-200
3	87	-82
5	43	43
6	124	118
7	76	77
8	82	-87
9	44	-41
H,L=	0	-3
1	236	-239
2	37	35
4	27	25
5	83	-83
6	72	67
7	93	92
8	72	77
9	58	-53
H,L=	0	-2
1	243	-230
2	172	-165
4	41	35
6	45	-47
8	31	29
9	68	67
H,L=	0	-1
1	110	-98
2	84	-89
3	131	-130
4	50	51
5	65	-69
6	210	-209
7	24	-22
8	29	-13
H,L=	0	0
1	242	255
2	113	-121
3	138	-142
4	21	-21
7	24	-26
8	48	47
H,L=	0	1
0	141	-133
1	283	273
2	82	78
3	22	-25
4	68	-63
5	113	113
7	34	-37
9	28	22
H,L=	0	2
0	243	-230
1	40	36
2	62	-58
3	98	89
4	38	34
5	36	33
6	21	22
7	29	-32
8	49	-48
H,L=	0	3
0	112	113
1	96	98
2	91	91
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1	25	17
3	38	-43
4	28	-23
H,L=	5	-11
0	20	-5
1	44	44
3	27	-25
5	51	51
6	27	-1[illegible]
H,L=	5	-10
-4	24	20
-3	30	28
-1	35	-32
4	62	65
6	23	19
H,L=	5	-9
-5	42	-35
-2	34	-23
-1	47	-50
1	29	29
2	38	34
3	114	-124
4	52	-56
H,L=	5	-8
-6	23	19
-5	28	21
-4	24	-23
-3	44	41
-2	36	26
-1	37	-43
0	46	-63
2	106	109
3	72	87
4	106	-116
7	43	39
H,L=	5	-7
-4	28	-23
-3	27	-23
-2	73	82
0	43	-43
3	42	56
4	53	54
5	22	-18
H,L=	5	-6
-6	43	43
-5	58	-65

Table 7. (continued)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
-4	43	-36	-7	41	37	-4	67	-67	H,L=	5	8	2	53	62	3	91	94	H,L=	6	4	-2	43	44	1	40	41	H,L=	8	-5
-2	78	77	-4	32	35	-1	27	-31	-4	22	-21	3	98	-101	5	49	-50	-5	59	-59	0	70	-77	2	29	20	-4	34	-33
-1	51	45	-3	69	65	0	119	-113	-3	28	23	5	19	-14	H,L=	6	-1	-4	59	-65	1	79	-77	H,L=	7	1	-3	54	-56
1	126	-131	-2	24	-22	1	102	-103	H,L=	6	-11	H,L=	6	-5	-8	37	-29	-1	28	-29	3	37	40	-6	43	-41	-1	61	58
2	52	-54	-1	34	31	2	35	30	-2	26	26	-7	26	-24	-6	49	42	H,L=	6	5	H,L=	7	-4	-5	31	-36	0	55	56
H,L=	5	-5	0	26	21	3	66	68	-1	30	-29	-6	26	-33	-4	44	-41	-7	27	26	-7	42	42	-1	31	-38	H,L=	8	-4
-8	28	-25	1	126	133	4	53	57	0	41	-39	-3	58	61	-2	76	70	-3	28	18	-2	52	66	0	26	-32	-5	30	29
-7	27	-22	2	64	70	H,L=	5	2	2	37	34	0	35	35	-1	35	40	0	29	-26	0	44	-49	H,L=	7	2	-3	41	-44
-5	137	149	3	64	-63	-5	64	63	3	25	29	1	70	66	0	57	-62	H,L=	6	6	1	32	-27	-7	35	38	-2	80	-86
-4	43	44	6	27	-23	-4	30	-22	H,L=	6	-10	3	46	47	1	87	-90	-6	35	35	2	92	-89	-6	34	35	H,L=	8	-3
-3	95	-102	H,L=	5	-1	-3	64	-62	-2	22	16	H,L=	6	-4	2	35	-27	-5	23	22	3	29	-30	-5	19	5	-3	26	-28
-2	72	-78	-9	32	-30	1	73	-67	-1	27	23	-7	34	33	4	47	-42	-4	28	-29	H,L=	7	-3	-4	35	-30	-2	32	-30
-1	82	79	-6	45	-44	2	62	-65	4	26	-32	-6	71	-75	5	23	-17	-2	37	36	-7	33	-38	-2	34	27	-1	19	-20
0	23	21	-5	60	-60	H,L=	5	3	5	20	-10	-5	105	-109	H,L=	6	0	H,L=	7	-10	-6	48	49	2	24	16	H,L=	8	-2
2	24	-18	-3	81	82	-9	31	29	H,L=	6	-9	-3	73	73	-6	39	40	-2	22	-16	-5	36	35	H,L=	7	3	-3	28	29
3	70	71	-2	20	-16	-5	34	40	-2	24	22	1	32	33	-5	40	43	-1	45	37	-4	34	30	-7	27	24	0	24	20
H,L=	5	-4	-1	116	-119	-4	61	58	-1	33	-38	2	30	19	-2	84	81	1	24	-25	-2	46	53	-6	42	40	2	67	-66
-6	43	-49	0	25	22	H,L=	5	4	0	51	-47	3	64	-64	-1	70	74	H,L=	7	-9	-1	59	64	-4	24	-17	H,L=	8	-1
-4	27	26	1	64	67	-5	32	32	2	38	42	4	33	-25	0	40	40	0	48	46	0	27	18	-3	23	13	-3	38	39
-3	38	-49	2	113	118	-4	32	38	5	36	-34	5	39	43	2	40	-49	1	25	28	1	51	-53	-2	34	33	1	36	36
-2	73	-72	4	77	-76	0	27	24	H,L=	6	-8	H,L=	6	-3	4	42	36	4	29	35	2	68	69	0	24	-16	2	22	27
-1	78	-77	5	63	-59	H,L=	5	5	-5	34	31	-7	41	39	H,L=	6	1	H,L=	7	-8	3	57	61	H,L=	7	4	H,L=	8	0
0	34	31	6	22	21	-6	50	-43	0	39	-48	-6	73	73	-8	25	-23	-5	25	-21	H,L=	7	-2	-1	27	19	-3	30	29
1	34	42	H,L=	5	0	-5	46	-50	1	49	-47	-5	32	-32	-7	48	-51	-2	20	-16	-7	53	-54	0	27	-17	-2	37	40
2	49	-47	-8	20	-7	-3	69	70	3	92	95	-4	54	-71	-4	43	38	-1	35	42	-6	48	-49	H,L=	7	5	0	43	-42
3	33	-32	-7	34	25	-2	35	37	H,L=	6	-7	-3	23	-17	-2	55	-60	0	48	45	-1	86	86	-4	22	-18	1	36	-30
4	27	28	-6	40	38	0	33	31	-6	23	-27	-2	54	54	-1	29	30	H,L=	7	-7	2	44	-41	-3	25	-22	H,L=	8	1
6	20	-15	-5	32	-23	1	31	26	-5	27	-26	-1	52	-51	0	54	48	-4	22	28	H,L=	7	-1	H,L=	8	-9	-2	39	39
H,L=	5	-3	-4	69	-67	2	30	-28	-1	69	69	0	39	-30	H,L=	6	2	-2	63	-72	-8	19	10	-1	28	-23	H,L=	8	2
-9	22	19	-2	97	96	3	30	-28	1	36	-43	2	69	69	-7	35	-32	-1	57	-65	-7	24	21	H,L=	8	-8	-4	47	-49
-8	30	29	-1	22	13	H,L=	5	6	2	135	-148	5	22	19	-6	46	-43	1	56	62	-5	33	-26	-2	34	32	-3	35	-27
-5	64	-67	0	124	-122	-5	31	-36	4	58	61	6	54	51	-4	59	55	3	26	-29	0	35	37	0	32	-36	-1	38	40
-4	34	35	1	19	-22	-1	27	-21	5	21	-22	H,L=	6	-2	-3	44	42	H,L=	7	-6	2	48	-46	H,L=	8	-7			
-3	46	49	2	70	68	1	32	33	6	47	-49	-5	45	42	1	34	10	-6	31	28	4	33	35	-3	27	28			
-1	19	-20	3	27	23	2	44	41	H,L=	6	-6	-3	29	-32	H,L=	6	3	-3	43	43	H,L=	7	0	-2	24	17			
2	30	-33	6	39	34	H,L=	5	7	-7	26	-19	-2	77	-81	-8	33	23	-1	102	-106	-8	27	21	0	22	-20			
3	100	-97	7	22	19	-5	20	-8	-4	67	68	-1	64	-62	-7	21	18	0	56	-58	-7	22	-22	H,L=	8	-6			
4	47	-50	H,L=	5	1	-4	27	-26	-2	41	-49	0	83	-85	-5	32	-26	1	31	15	-3	46	-48	-4	24	-29			
H,L=	5	-2	-7	47	45	-3	43	-43	0	37	39	1	38	-40	1	51	57	2	132	127	-2	62	-63	-2	82	81			
-8	30	30	-6	52	54	0	35	-32	1	41	43	2	59	64	2	35	36	H,L=	7	-5	0	43	38	-1	66	59			

TABLE 8. INTERATOMIC DISTANCES ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS

Atoms	Distance (Å)	σ (Å)	Atoms	Distance (Å)	σ (Å)
Al–O(1)	1.770	0.006	O(1)–C(3)	1.330	0.009
Al–O(2)	1.826	0.006	C(3)–C(4)	1.490	0.011
Al–C(1)	1.962	0.012	C(3)–N(1)	1.263	0.011
Al–C(2)	1.962	0.011	N(1)–C(10)	1.419	0.011
O(2)–N(2)	1.402	0.009	N(2)–C(17)	1.499	0.013
N(2)–C(16)	1.474	0.014	N(2)–C(18)	1.477	0.014
C(4)–C(5)	1.383	0.011	C(10)–C(11)	1.391	0.012
C(5)–C(6)	1.390	0.013	C(11)–C(12)	1.382	0.013
C(6)–C(7)	1.372	0.015	C(12)–C(13)	1.378	0.014
C(7)–C(8)	1.393	0.016	C(13)–C(14)	1.380	0.014
C(8)–C(9)	1.379	0.016	C(14)–C(15)	1.371	0.013
C(4)–C(9)	1.379	0.013	C(10)–C(15)	1.378	0.012
C(1)–H(1)	1.08	0.08	C(17)–H(20)	1.15	0.08
C(1)–H(2)	1.07	0.08	C(17)–H(21)	1.10	0.09
C(1)–H(3)	1.13	0.09	C(17)–H(22)	1.08	0.08
C(2)–H(4)	1.00	0.08	C(18)–H(23)	1.11	0.08
C(2)–H(5)	1.07	0.08	C(18)–H(24)	1.09	0.09
C(2)–H(6)	1.07	0.08	C(18)–H(25)	1.14	0.08
C(16)–H(17)	1.13	0.08			
C(16)–H(18)	1.15	0.08			
C(16)–H(19)	1.06	0.08			
C(5)–H(7)	1.10	0.08	C(11)–H(12)	1.11	0.08
C(6)–H(8)	1.09	0.08	C(12)–H(13)	1.09	0.08
C(7)–H(9)	1.08	0.08	C(13)–H(14)	1.09	0.08
C(8)–H(10)	1.09	0.09	C(14)–H(15)	1.09	0.08
C(9)–H(11)	1.09	0.08	C(15)–H(16)	1.10	0.08

geometry. The C(1)–Al–C(2) bond angle (117.3(0.5)°) is equal to that of the polymerization catalyst [$Me_2Al\cdot O\cdot CPh{:}NPh$]$_2$ (117.6(0.5)°), but it shows a large deviation from the typical tetrahedral bond angle of 109.5°. Such a rather large bond angle of C(methyl)–Al–C(methyl) is often found associated with tetrahedrally co-ordinated aluminum atoms in some organoaluminum compounds.[19–22]

The interatomic bond distances between the aluminum atom and the oxygen of the amide moiety, Al–O(1), is 1.770(6) Å, which is a little shorter than the corresponding distances of the related complexes: 1.805(6) Å in [$Me_2Al\cdot O\cdot CPh{:}NPh$]$_2$, 2.045(7) Å in [$Me_2Al\cdot O\cdot CPh{:}NPh, MeCHO$]$_2$, and 1.846(7) Å in [$Me_2Al\cdot O\cdot CPh{:}NPh, MeCHO, AlMe_3$]. The O(1)–C(3) bond distance of 1.330(9) Å is intermediate between typical single and double bond distances. The C(3)–N(1) distance is 1.263(11) Å. The carbon and nitrogen double bond distance has been given as 1.265 Å by Pauling[23] and as 1.28 Å by Cox and his co-workers.[24] The C–N bond in oximes, >C=N–OH, is generally assumed to be a localized double bond, the distance of which lies between 1.225 and 1.33 Å.[25] From these facts, it can be concluded that the C(3)–N(1) in the present complex is an almost-localized double bond. Five atoms, O(1), C(3), N(1), C(4), and C(10), are co-planar within a deviation of 0.01 Å. The most interesting feature is that, unlike those in [$Me_2Al\cdot O\cdot CPh{:}NPh, MeCHO$]$_2$ and [$Me_2Al\cdot O\cdot CPh{:}NPh, MeCHO, AlMe_3$], the two adjacent benzene rings take the more stable, *trans* configuration about the C(3)–N(1) bond, the internal rotation angle being 178.9°. The dihedral angle between the best plane

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TABLE 9. INTERATOMIC ANGLES ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS

Atoms	Angle(°)	σ(°)	Atoms	Angle(°)	σ(°)
O (1)-Al-C (1)	109.0	0.4	Al-O (2)-N (2)	128.3	0.5
O (1)-Al-C (2)	109.2	0.4	O (2)-N (2)-C (16)	108.8	0.7
O (1)-Al-O (2)	106.7	0.3	O (2)-N (2)-C (17)	105.1	0.7
C (1)-Al-C (2)	117.3	0.5	O (2)-N (2)-C (18)	112.0	0.7
C (1)-Al-O (2)	111.8	0.4	C (16)-N (2)-C (17)	108.8	0.8
C (2)-Al-O (2)	102.2	0.4	C (16)-N (2)-C (18)	111.8	0.8
Al-O (1)-C (3)	137.7	0.5	C (17)-N (2)-C (18)	110.1	0.8
O (1)-C (3)-C (4)	116.3	0.7	C (3)-N (1)-C (10)	120.7	0.7
O (1)-C (3)-N (1)	123.9	0.7			
N (1)-C (3)-C (4)	119.8	0.7			
C (3)-C (4)-C (5)	119.9	0.7	N (1)-C (10)-C (11)	120.4	0.8
C (3)-C (4)-C (9)	120.4	0.7	N (1)-C (10)-C (15)	120.4	0.8
C (9)-C (4)-C (5)	119.7	0.8	C (11)-C (10)-C (15)	118.9	0.8
C (4)-C (5)-C (6)	119.9	0.8	C (10)-C (11)-C (12)	118.8	0.8
C (5)-C (6)-C (7)	120.4	0.9	C (11)-C (12)-C (13)	122.4	0.9
C (6)-C (7)-C (8)	119.5	1.0	C (12)-C (13)-C (14)	117.8	0.9
C (7)-C (8)-C (9)	120.1	1.1	C (13)-C (14)-C (15)	120.7	0.9
C (8)-C (9)-C (4)	120.4	1.0	C (14)-C (15)-C (10)	121.3	0.8
Al-C (1)-H (1)	111	4	Al-C (2)-H (4)	106	5
Al-C (1)-H (2)	111	5	Al-C (2)-H (5)	112	5
Al-C (1)-H (3)	111	4	Al-C (2)-H (6)	112	5
H (1)-C (1)-H (2)	107	6	H (4)-C (2)-H (5)	110	6
H (1)-C (1)-H (3)	108	6	H (4)-C (2)-H (6)	110	6
H (2)-C (1)-H (3)	108	6	H (5)-C (2)-H (6)	107	6
N (2)-C (16)-H (17)	107	4	N (2)-C (17)-H (20)	115	4
N (2)-C (16)-H (18)	120	4	N (2)-C (17)-H (21)	108	4
N (2)-C (16)-H (19)	109	5	N (2)-C (17)-H (22)	110	5
H (17)-C (16)-H (18)	106	6	H (20)-C (17)-H (21)	108	6
H (17)-C (16)-H (19)	106	6	H (20)-C (17)-H (22)	109	6
H (18)-C (16)-H (19)	108	6	H (21)-C (17)-H (22)	107	6
N (2)-C (18)-H (23)	104	4			
N (2)-C (18)-H (24)	104	5			
N (2)-C (18)-H (25)	123	4			
H (23)-C (18)-H (24)	108	6			
H (23)-C (18)-H (25)	100	6			
H (24)-C (18)-H (25)	117	6			
C (4)-C (5)-H (7)	120	4	C (10)-C (11)-H (12)	120	4
C (6)-C (5)-H (7)	120	4	C (12)-C (11)-H (12)	121	4
C (5)-C (6)-H (8)	120	4	C (11)-C (12)-H (13)	119	4
C (7)-C (6)-H (8)	120	4	C (13)-C (12)-H (13)	119	4
C (6)-C (7)-H (9)	120	4	C (12)-C (13)-H (14)	122	4
C (8)-C (7)-H (9)	121	4	C (14)-C (13)-H (14)	120	4
C (7)-C (8)-H (10)	121	5	C (13)-C (14)-H (15)	119	4
C (9)-C (8)-H (10)	119	5	C (15)-C (14)-H (15)	120	4
C (8)-C (9)-H (11)	119	4	C (14)-C (15)-H (16)	120	4
C (4)-C (9)-H (11)	120	4	C (10)-C (15)-H (16)	119	4

of the two benzene rings is 80.5°. The average values of the C–C and C–H distances in benzene rings are 1.381 and 1.09 Å respectively.

The $ONMe_3$ moiety is attached to the aluminum atom by the co-ordination of the oxygen atom. The Al–O(2) bond distance, 1.826(6) Å, takes a reasonable value compared with those found in the related organoaluminum compounds.[1–4] The crystal structure of $[Me_3NO,HCl]$ was determined by Rérat[26] and had since been refined by Caron and his co-workers[27] in the course of the crystal structure analysis of $ONMe_3$.[28] The corresponding bond distances and angles in these complexes are compared with those in the $ONMe_3$ moiety of the present complex (Table 10). The O(2)–N(2) bond distance (1.402(9) Å) is intermediate between those in $[Me_3N^+–O^-]$ and $[Me_3N^+OH\cdot Cl^-]$.

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[27] A. Caron and J. Donohue, *ibid.*, **15**, 1052 (1962).

[28] A. Caron, G. J. Palenik, E. Goldish, and J. Donohue, *ibid.*, **17**, 102 (1964).

Caron and his co-workers considered that the opposite formal charge affects the O–N bond distance in the structure of $ONMe_3$. According to this theory, the negative formal charge on the oxygen atom of the $ONMe_3$ moiety in the present complex may be weakened by the co-ordination to the electron-deficient aluminum atom. The aluminum atom is not so strong a Lewis acid as the proton; however, it may be that the co-ordination of oxygen does not completely cancel the charge on the oxygen atom, as in the case of the proton in [$Me_3N^+OH \cdot Cl^-$]. This can reasonably explain the fact that the O(2)–N(2) distance lies between the corresponding distances in [$Me_3N^+{-}O^-$] and [Me_3N^+-$OH \cdot Cl^-$]. The average values of the two C–N bond distances are 1.478 ± 0.011 Å in [$Me_3N^+OH \cdot Cl^-$] and 1.477 ± 0.006 Å in [$Me_3N^+{-}O^-$]. The N(2)–C(16) and N(2)–C(18) bond distances have values equal to those found in the above two compounds. The N(2)–C(17) bond is slightly longer than the other N(2)–C bonds, though the difference is not very significant. The geometry around the N(2) atom is a little distorted tetrahedron. Such a geometry around the nitrogen atom is also found in [$Me_3N^+{-}O^-$].

TABLE 10. COMPARISON OF THE INTERATOMIC DISTANCES AND ANGLES IN THE $ONMe_3$ GROUPS

Atoms	[Me_3N^+-OH, Cl^-]$^{a)}$ (Ref. 26)	[$Me_3N^+{-}O^-$]$^{a)}$ (Ref. 27)	Me_3NO moiety in the present complex	
N–O	1.425 Å (11)	1.388 Å (5)	1.402 Å (9)	
N–C(1)	1.475 (10)	1.470 (8)	1.474 (14)	N(2)–C(16)
	1.480 (11)	1.484 (4)	1.499 (13)	N(2)–C(17)
			1.477 (14)	N(2)–C(18)
O–N–C(1)	103.9° (1.1)	110.4° (0.6)	108.8° (0.7)	O(2)–N(2)–C(16)
O–N–C(2)	109.1 (1.3)	109.6 (0.4)	105.1 (0.7)	O(2)–N(2)–C(17)
C(1)–N–C(2)	111.0 (1.5)	109.2 (0.7)	112.0 (0.7)	O(2)–N(2)–C(18)
C(2)–N–C(2′)	112.3 (1.4)	108.9 (0.4)	108.8 (0.8)	C(16)–N(2)–C(17)
			111.8 (0.8)	C(16)–N(2)–C(18)
			110.1 (0.8)	C(17)–N(2)–C(18)

a) The crystal structure of these compounds has a mirror symmetry and only two carbon atoms of three methyl carbons are independent.

The molecular structures of the polymerization catalyst I and of the present complex IV are compared in Fig. 3 and Table 11. In Fig. 3 both molecules are projected onto the O–C–N plane of the amide moiety, which is present in both compounds. The amide moiety is connected to the electron-deficient aluminum atom by both oxygen and nitrogen atoms in I, but only by oxygen in IV. The nitrogen atom in IV is, therefore, liberated from bonding to the aluminum. The C(3)–N(1) bond distance in IV is a little shorter than that in I. The C(3)–O(1) distance in IV is, on the contrary, a little longer than that in I. Such differences in the C–N and C–O bond distances are probably due to the difference in C–N bond character: that is, there a delocalized double bond in I, but an

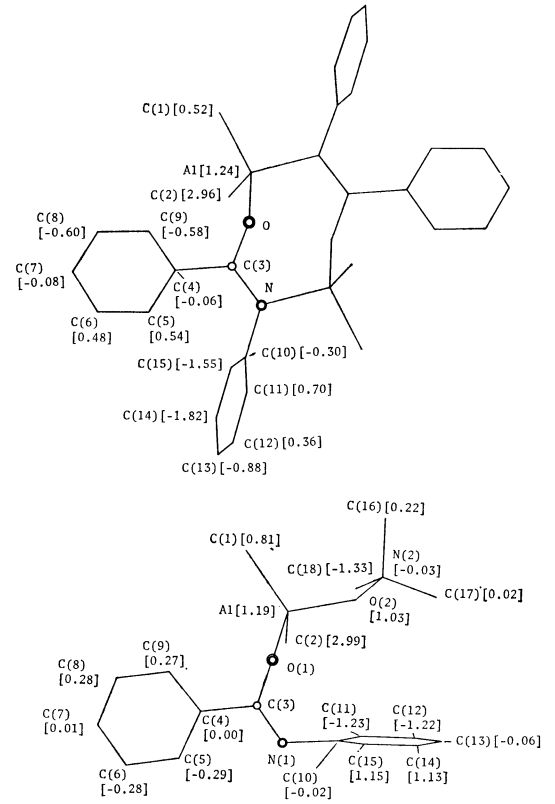


Fig. 3. Comparison of the molecular structure of [$Me_2Al \cdot O \cdot CPh{:}\ NPh$]$_2$ (*top*) and [$Me_2Al \cdot O \cdot CPh{:}\ NPh$, $ONMe_3$] (*bottom*). Both are projected onto the plane of the –O–C–N– skeletons which are contained commonly in both molecules. Deviations from the plane (in Å) are given in brackets.

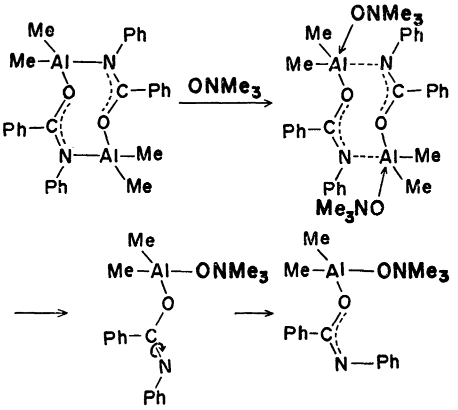
TABLE 11. COMPARISON OF THE SELECTED INTERATOMIC DISTANCES AND ANGLES AND DIHEDRAL ANGLES BETWEEN SOME PLANES$^{a)}$ IN THE AMIDE MOIETIES OF COMPLEXES (I) AND (IV)

	(I)	(IV)
Al–O(1)	1.805(6) Å	1.770(6) Å
O(1)–C(3)	1.277(10)	1.330(9)
C(3)–N(1)	1.305(11)	1.263(11)
C(3)–C(4)	1.501(12)	1.490(11)
N(1)–C(10)	1.447(12)	1.419(11)
Al–O(1)–C(3)	133.6(0.6)°	137.7(0.5)°
Plane 1–Plane 2	2.9°	0.03°
Plane 1–Plane 3	14.3	1.0
Plane 1–Plane 4	27.6	13.5
Plane 1–Plane 5	75.5	86.2
Plane 2–Plane 3	11.4	1.1
Plane 4–Plane 5	70.3	80.5

a) These planes are consisted of the atoms of;
Plane 1; O(1), C(3), N(1)
Plane 2; N(1), C(3), C(4)
Plane 3; C(3), N(1), C(10)
Plane 4; Least-squares plane of benzene ring (C(4)-C(9))
Plane 5; Least-squares plane of benzene ring (C(10)-C(15))

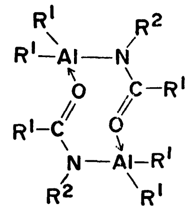
almost localized double bond in IV. The most remarkable configurational difference in the amide moieties is that the two benzene rings are *cis* in I, but *trans* in IV.

The isolation of the present complex [$Me_2Al\cdot O\cdot CPh:NPh,ONMe_3$] in a stable crystalline form and its molecular structure throw some interesting aspects on the chemical reactions of this catalytic system. One is concerned with the reaction from I to IV, the reaction which has been formulated before. When the dimeric complex of I is treated with a strong Lewis base, $ONMe_3$, an nucleophilic attack of the oxygen of $ONMe_3$ on the aluminum occurs. This promotes the cleavage of the Al–N bond, but not that of the Al–O bond. After the bond fission, the benzene ring attached to the nitrogen atom takes the more stable *trans* configuration. This is schematically shown below.

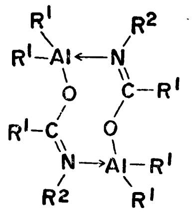


The second is related to the co-ordination scheme in the molecular structure of [$Me_2Al\cdot O\cdot CPh:NPh$]$_2$. The reaction of trialkylaluminum, R^1_3Al, and related compounds with isocyanate, R^2NCO, has been reported;[29,30] the products of this reaction gave *N*-substituted acid amides, R^1CONHR^2, on hydrolysis. Two intermediate compounds have been proposed in this reaction, depending on whether the insertion of isocyanate to an R^1–Al bond occurs by means of the C=N or C=O bond. In the insertion of isocyanate into the Et–Al bond,[31] the reaction products have been proposed to have the eight-membered ring structures of (iii) and (iv), which correspond to the dimeric structures of (i) and (ii) respectively.

$$\begin{tikzcd}
& {[R^1_2Al\cdot NR^2\cdot CO\cdot R^1]} \arrow[r, "H_2O"] & R^1CO\cdot NHR^2 \\
R^2NCO \arrow[ur, "R^1_3Al"] \arrow[dr] & \text{(i)} & \\
& {[R^1_2Al\cdot O\cdot CR^1:NR^2]} \arrow[r, "H_2O"] & R^1C(OH):NR^2 \arrow[uu] \\
& \text{(ii)} &
\end{tikzcd}$$



(iii)



(iv)

Jennings and his co-workers studied the reaction between trialkylaluminum and various *N*-substituted acid amides,[32] and they proposed that the reaction products had eight-membered ring structures like (iii) and (iv). We recently determined the molecular structure of [$Me_2Al\cdot O\cdot CPh:NPh$]$_2$.[1,2] The molecule has a centrosymmetrical eight-membered ring structure, and the bond distances show the molecule to have a hybrid structure of the two canonical forms, (iii) and (iv). On the other hand, the molecular structure of the present complex, [$Me_2Al\cdot O\cdot CPh:NPh,ONMe_3$], shows that the Al–O bond is more stable than the Al–N bond towards attack by a strong Lewis base on the aluminum atom. In other words, this result shows that the Al–N bond has much more of a co-ordination-bond character than the Al–O bond. On the basis of this fact, we can assume that the canonical form, (iv), is predominant in the dimeric structure of [$R_2Al\cdot O\cdot CR':NR''$]$_2$.

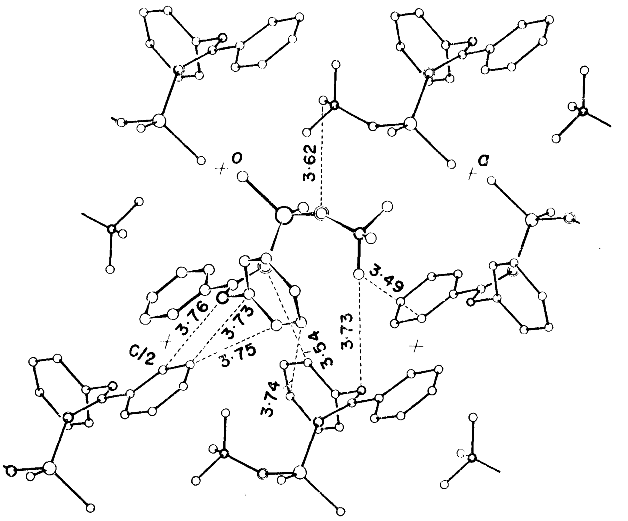


Fig. 4. Crystal structure viewed along the *b* axis.

Crystal Structure. Figure 4 shows the molecular packing projected along the *b* axis. The intermolecular atomic contacts less than 3.8 Å are shown by broken lines. None of them is significantly shorter than the normal van der Waals' contact.

The authors wish to express their deep thanks to Professor Hisaya Tani and Dr. Hajime Yasuda of Osaka University for their kindness in supplying the sample and for their helpful discussions.

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