Journal of Organometallic Chemistry, 51 (1973) 105–111

THERMAL DECOMPOSITION OF ANIONIC ORGANOALUMINUM COMPOUNDS

III*. THE PREPARATION AND STRUCTURE OF THE NEUTRAL ADDITION COMPLEX OF ACETONITRILE AND TRIMETHYLALUMINUM

J. L. ATWOOD, S. K. SEALE and D. H. ROBERTS

Department of Chemistry, The University of Alabama, University, Alabama 35486 (U.S.A.)

(Received August 15th, 1972)

SUMMARY

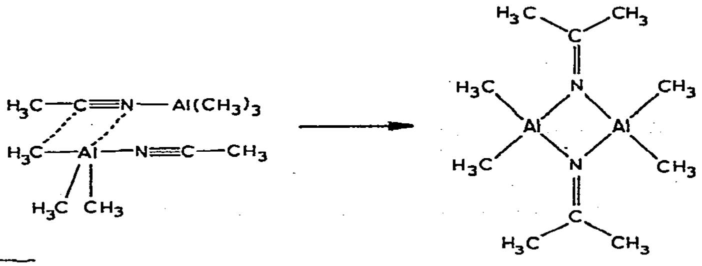
Tetraisocyanatogermanium reacts with trimethylaluminum upon heating to 50° to form the acetonitrile adduct of trimethylaluminum, $(CH_3)_3Al \cdot NCCH_3$. The crystal structure of acetonitriletrimethylaluminum has been determined from three-dimensional X-ray data measured by counter methods. $(CH_3)_3Al \cdot NCCH_3$ crystallizes in the orthorhombic space group *Pnma* with cell dimensions $a = 6.617(3)$, $b = 7.821(4)$, $c = 16.135(7)$ Å, and $\rho_{calc} = 1.05$ g/cm³ for $Z = 4$. Least-squares refinement gave a final weighted R value of 9.5% for 430 independent reflections. The behavior of the $Ge(NCO)_4/Al(CH_3)_3$ system is related to that of KSCN and $Al(CH_3)_3$.

INTRODUCTION

The thermolysis of anionic organoaluminum complexes has been previously investigated for two systems, $K[Al_2(CH_3)_6SCN]$[1] and $[N(CH_3)_4][Al(CH_3)_3I]$[2]. The potassium salt decomposes under relatively mild conditions to form (isopropylideneamino)dimethylaluminum:

$$K[Al_2(CH_3)_6SCN] \xrightarrow{120^\circ} [(CH_3)_2CNAl(CH_3)_2]_2 + \text{unidentified decomposition products}$$

For this reaction several mechanistic possibilities exist. One of the most reasonable involves the intermediate production of the acetonitrile adduct of trimethylaluminum followed by the thermal nitrile rearrangement to (isopropylideneamino)dimethylaluminum[3]:



---

* For Part I, II, see ref. 1, 2.

TABLE 1

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES FOR ACETONITRILETRIMETHYLALUMINUM

Reflections for which a slow scan was carried out, but $F_{obs} < \sigma(F_{obs})$, are indicated by an asterisk.

K	L	OBS	CAL
*******H= 0********			
1	1	23.8	25.8
1	3	26.4	25.2
1	5	0.8	7.2*
1	7	19.2	19.1
1	9	4.9	4.8
1	11	15.5	15.1
1	13	9.4	9.4
1	17	1.7	2.0*
1	19	1.2	3.1*
2	2	58.3	57.2
2	4	15.5	15.0
2	6	24.6	24.5
2	8	26.1	26.7
2	10	14.6	13.1
2	12	12.2	12.1
2	14	4.0	0.9
2	16	2.8	7.1*
3	3	21.9	19.7
3	7	25.9	23.5
3	9	1.4	0.4*
3	11	15.1	13.5
3	13	4.2	3.6
4	0	53.9	57.3
4	6	2.3	0.2
4	8	12.5	11.2
4	10	4.8	3.4
4	14	1.4	1.6*
5	13	1.9	4.7*
6	0	19.7	17.7
6	2	8.1	8.2
6	4	7.1	4.5
6	6	3.7	3.5
6	10	4.4	4.0
6	12	0.9	2.4*
7	3	4.4	3.8
7	7	1.4	5.4*
8	4	1.0	1.9*
9	5	1.6	1.2*
*******H= 1********			
0	1	40.9	44.3
0	2	10.6	11.4
0	3	29.9	28.4
0	4	42.5	38.6
0	5	2.1	2.2*
0	6	8.1	7.0
0	7	12.5	14.3
0	8	5.4	7.0
0	9	14.6	12.8
5	1	10.7	9.7
5	2	19.0	18.2
5	4	1.3	0.0*
5	5	5.0	4.9
5	6	10.3	9.2
5	7	5.4	5.0
5	8	2.1	2.1*
5	9	2.3	0.1*
5	10	5.5	4.1
5	12	4.0	4.2
5	14	2.0	1.8*
6	1	7.1	6.0
6	2	3.2	3.4
6	4	3.5	3.2
6	5	5.7	4.3
6	9	6.6	6.0
6	10	1.9	1.5*
6	15	1.9	0.3*
7	2	5.3	4.1
7	4	2.8	2.8
7	6	4.5	3.9
8	6	1.1	1.1*
8	8	1.4	0.0*
9	2	1.3	1.9*
9	4	1.5	0.1*
9	6	1.4	1.0*
*******H= 2********			
0	0	5.5	3.0
0	1	48.4	42.2
0	2	28.4	26.3
0	3	22.5	20.7
0	4	38.5	39.1
0	5	23.5	21.2
0	6	5.9	4.6
0	7	2.5	4.2*
0	8	24.0	21.4
0	9	8.2	5.2
0	10	13.3	13.2
0	12	8.9	9.2
0	14	7.9	10.4
1	0	14.4	14.3
1	1	16.4	17.8
1	2	11.9	10.9
1	3	17.0	19.2
1	4	11.5	11.8
1	5	10.5	9.5
1	6	6.4	7.1
1	7	15.6	14.9
1	8	3.2	3.1
0	1	11.6	11.4
0	2	25.6	24.2
0	3	17.9	17.3
0	4	7.4	4.5
0	5	29.7	32.0
0	6	5.2	6.8
0	7	3.4	5.3
0	8	2.3	2.0*
0	9	11.3	9.9
0	10	5.3	7.5
0	11	5.4	4.6
0	13	8.8	8.1
0	15	1.6	0.4*
0	17	1.0	1.5*
1	1	9.8	10.7
1	2	16.4	17.4
1	3	13.2	14.4
1	4	7.4	7.4
1	5	11.7	12.3
1	6	14.8	17.1
1	7	2.8	3.2
1	8	12.8	13.2
1	9	6.9	6.7
1	10	6.0	7.2
1	12	5.7	7.9
1	14	2.9	3.2*
1	16	3.2	5.1
2	1	16.0	15.9
2	2	4.0	2.5
2	3	25.1	24.6
2	4	18.1	19.4
2	5	22.4	24.0
2	6	4.8	3.6
2	7	2.0	0.7*
2	8	6.2	6.5
2	9	5.3	3.8
2	11	3.5	3.7
2	13	6.7	4.7
2	14	1.9	2.3*
2	16	0.8	0.9*
3	1	2.7	3.9
3	2	15.5	16.9
3	3	4.0	3.9
3	5	11.1	11.8
3	6	11.6	12.4
3	8	7.3	6.9
3	9	6.8	7.1
3	12	4.6	5.7
3	16	3.1	4.3
2	3	2.4	2.7*
2	4	13.4	13.2
2	5	3.7	8.9
2	6	5.8	5.7
2	7	8.2	8.5
2	14	3.2	4.4
3	0	1.5	0.1*
3	1	12.2	12.3
3	2	2.3	2.5*
3	3	11.0	10.4
3	4	7.7	7.0
3	5	8.6	8.0
3	6	4.8	3.8
3	7	8.5	7.4
3	11	4.6	3.7
3	12	2.7	2.0
4	0	9.1	8.9
4	2	4.5	4.6
4	3	1.7	1.1*
4	4	5.7	5.2
4	5	3.7	4.8
4	6	7.3	7.6
4	7	3.7	2.8
4	12	2.5	2.9*
5	1	3.5	2.7
5	3	5.8	5.5
5	4	4.6	3.5
5	7	6.9	6.7
6	0	6.1	5.5
6	2	2.1	1.8*
*******H= 5********			
0	1	7.1	6.0
0	2	2.9	1.9
0	3	1.1	0.8*
0	4	2.9	3.2
0	5	8.1	7.1
0	6	9.3	7.5
0	7	4.7	6.5
0	8	4.1	2.9
0	9	11.6	11.3
0	10	4.1	3.6
0	13	0.7	4.6*
1	1	1.3	1.4*
1	2	8.2	6.6
1	3	3.2	3.8
1	4	4.1	3.6
1	5	6.0	5.9
1	6	4.9	4.2
1	8	2.5	2.5

0	11	6.7	8.2
0	12	8.0	8.5
0	13	7.4	7.4
0	14	6.2	5.9
0	15	4.4	5.1
0	17	1.4	4.9*
1	1	29.7	34.6
1	2	53.2	57.1
1	3	2.0	7.4*
1	4	4.3	6.1
1	5	15.0	14.1
1	6	30.3	30.3
1	7	16.1	17.2
1	8	7.4	8.2
1	9	4.6	5.1
1	10	16.2	16.4
1	12	10.9	9.4
1	14	5.6	6.5
1	15	1.1	2.7*
1	19	0.9	0.6*
2	1	9.9	13.8
2	2	42.2	35.0
2	3	17.1	13.7
2	4	4.5	6.4
2	5	19.0	18.9
2	6	4.4	5.0
2	7	2.7	3.5
2	8	6.7	6.3
2	9	23.6	24.4
2	10	7.7	8.2
2	11	3.4	1.7
2	12	7.4	7.7
2	13	9.8	8.4
2	14	2.5	1.7*
3	1	14.5	14.8
3	2	25.4	25.4
3	3	16.5	18.5
3	4	14.0	13.4
3	5	3.0	3.5
3	6	21.7	22.7
3	7	8.5	8.8
3	8	10.2	9.1
3	9	7.5	7.1
3	10	14.3	15.0
3	11	2.8	3.1*
3	12	6.9	5.3
3	14	5.1	5.0
4	1	17.9	17.5
4	2	4.9	4.6
4	3	8.9	9.5
4	4	10.3	10.8
4	5	8.6	7.1
4	6	4.5	4.8
4	7	6.4	7.7
4	8	2.4	2.2*
4	9	10.3	8.7
4	10	2.4	2.3*
4	12	1.7	1.6
4	13	4.4	3.6
4	14	2.7	3.3*
4	15	1.4	2.4*

1	9	4.1	3.3
1	10	7.5	8.7
1	11	11.3	9.9
1	12	4.1	4.8
1	15	6.8	6.9
1	17	1.6	2.8*
2	0	5.7	3.6
2	1	2.8	1.5
2	2	16.5	15.0
2	3	14.7	15.6
2	4	30.9	30.8
2	5	6.5	7.0
2	6	7.9	8.6
2	7	10.9	13.3
2	8	20.2	21.5
2	9	3.8	3.8
2	10	11.5	10.4
2	11	8.7	7.3
2	12	8.2	9.1
2	13	1.9	4.2*
2	14	7.9	7.3
3	1	13.8	11.8
3	2	12.8	13.1
3	3	15.7	15.4
3	4	8.1	9.0
3	5	6.6	6.8
3	6	2.6	2.6
3	7	12.0	12.0
3	8	6.8	7.8
3	9	3.2	3.5
3	10	7.2	6.2
3	11	9.4	6.8
3	15	4.2	4.7
4	0	3.8	4.6
4	1	9.7	11.1
4	2	8.1	9.2
4	3	7.4	8.6
4	4	16.8	18.6
4	5	5.2	6.0
4	6	3.1	2.7
4	8	10.3	10.9
4	10	6.7	6.5
4	12	4.5	4.4
4	13	1.0	0.1*
4	14	5.3	5.5
5	0	7.1	8.9
5	1	6.7	7.4
5	3	7.9	7.9
5	5	2.7	3.3
5	7	4.8	5.6
5	11	3.3	4.1
5	15	3.4	3.3
6	4	5.2	7.4
6	8	5.4	5.5
6	10	2.2	3.3*
6	11	1.0	1.6*
7	3	3.7	3.6*
7	12	1.6	0.4*
8	0	0.8	0.6*
8	5	1.0	0.1*
9	2	1.8	0.2*

*******L= 3*******

3	17	1.0	0.2*
4	1	6.6	7.0
4	2	9.6	10.2
4	3	9.8	10.0
4	4	4.8	3.8
4	5	14.1	14.6
4	7	1.5	2.5*
4	9	5.6	4.3
4	10	1.7	2.6*
4	13	5.6	4.6
4	16	1.5	1.7*
5	1	3.1	3.6
5	2	5.3	5.8
5	3	5.9	6.4
5	4	2.0	3.3
5	5	3.4	2.5
5	6	5.9	6.6
5	8	6.2	5.6
5	9	1.7	1.3*
5	12	1.7	3.1*
5	15	1.1	0.3*
6	1	4.4	3.5
6	3	5.3	4.7
6	4	3.8	3.5
6	5	6.1	7.1
6	7	1.0	0.4*
6	10	1.3	0.1*
7	2	1.6	3.6*
7	7	2.5	0.2
8	2	0.7	1.3*
8	4	1.4	1.2*
8	7	1.1	0.4*

*******L= 4*******

0	0	13.2	12.3
0	1	6.5	6.6
0	2	11.9	11.7
0	4	7.2	8.2
0	5	8.3	8.9
0	6	16.6	17.5
0	7	7.5	5.7
0	8	2.5	2.8*
0	10	4.9	5.3
0	12	5.1	5.6
0	13	1.2	0.6*
0	14	3.2	4.1
0	15	2.3	4.5
1	1	12.3	12.2
1	2	5.3	5.0
1	3	15.6	15.8
1	4	11.1	8.8
1	5	8.0	7.4
1	6	5.5	4.6
1	7	15.4	14.5
1	11	7.6	6.6
1	12	3.6	2.7
1	13	1.0	1.1*
1	14	2.9	1.5
1	15	1.1	1.9*
2	0	23.6	23.6
2	1	2.2	0.8*
2	2	4.6	3.7

1	9	1.8	3.6*
1	10	4.4	3.0
1	11	1.0	1.2*
2	1	10.0	8.4
2	2	4.8	3.8
2	3	7.2	7.3
2	4	3.8	3.9
2	5	4.3	2.6
2	6	8.4	7.9
2	7	6.5	7.4
2	8	1.3	0.7*
2	9	6.2	5.8
3	1	1.5	1.9*
3	2	8.1	6.7
3	3	3.8	4.2
3	5	3.5	3.9
3	6	3.2	2.3
3	13	0.5	2.8*
4	1	4.9	3.3
4	2	2.9	1.5
4	4	1.9	2.2*
4	5	3.5	3.0
4	6	3.6	3.9*
5	6	0.9	2.1*
6	2	1.4	0.6*

*******L= 6*******

0	0	3.4	2.6
0	2	0.8	0.9*
0	3	5.0	5.9
0	4	3.7	3.1
0	5	2.5	2.4*
0	6	0.7	0.2*
0	8	0.8	5.8*
0	10	1.2	3.3*
1	0	6.2	6.0
1	1	3.9	3.5
1	2	1.4	1.3*
1	3	5.1	4.5
1	4	5.0	4.6
1	5	2.1	2.3*
1	8	0.9	4.0*
2	0	5.0	4.4
2	1	4.3	4.5
2	3	4.7	5.3
2	4	3.6	3.1
2	8	1.8	3.6*
3	0	6.1	5.6
3	1	3.7	2.9
3	3	1.7	3.0*
3	5	1.1	1.6*
4	3	0.7	3.1*
4	7	1.7	1.9*
4	8	0.8	3.2*
5	7	1.1	1.7*

*******L= 7*******

0	1	1.5	4.1*
0	4	0.8	0.9*
1	3	0.9	0.2*

We wish now to report the isolation and crystal structure of the acetonitrile adduct of trimethylaluminum from the related reaction of $Ge(NCO)_4$ and $(CH_3)_3Al$.

EXPERIMENTAL

Germanium tetraisocyanate, prepared by the method of Miller and Carlson[4], was purified and diluted with toluene in an inert atmosphere box. Trimethylaluminum was then added drop-wise such that the mole ratio of $Ge(NCO)_4$ to $Al(CH_3)_3$ was 1/1. The reaction took place vigorously and upon removal of the solvent a mass of yellow-brown residue was obtained. The material was dried under vacuum, and then heated to 50°. A colorless crystalline sublimate was isolated in approximately 20% yield. The nuclear magnetic resonance spectrum and melting point were used to characterize[3] the substance as $(CH_3)_3Al \cdot NCCH_3$.

Single crystals of acetonitriletrimethylaluminum were grown by slow sublimation and sealed in thin-walled glass capillaries. Preliminary unit cell parameters were determined by precession (Cu-K_α) photographs. The crystal system is orthorhombic. Systematic absences allow the space group to be *Pnma* or *Pna*2_1. The lattice parameters as determined from a least-squares refinement of $(\sin \theta/\lambda)^2$ values of 10 reflections with 2θ values $>70°$ are: $a = 6.617(3)$, $b = 7.821(4)$ and $c = 16.135(7)$ Å. The calculated density is 1.05 g/cm^3 with $Z = 4$. Data were taken on an ENRAF-NONIUS CAD-4 diffractometer with Ni-filtered copper radiation. The crystal, an irregular polyhedron of approximate dimensions 0.25 mm × 0.40 mm × 0.30 mm, was aligned on the diffractometer such that no symmetry axis was coincident with the φ axis of the diffractometer.

The diffracted intensities were collected by the ω-2θ scan technique with a take-off angle of 1.5°. The scan rate was variable and was determined by a fast (20°/min) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 1.0°/min. Background counts were collected for 25% of the total scan time at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where $A = 0.8°$ and $B = 0.45°$. Aperture settings were determined in a like manner with $A = 4$ mm and $B = 4$ mm. The crystal-to-source and crystal-to-detector distances were 21.6 and 20.8 cm, respectively. The lower level and upper level discriminators of the pulse height analyzer were set to obtain a 95% window centered on the Cu-K_α peak. As a check on the stability of the diffractometer and the crystal, two standard peaks were measured periodically during data collection. An 11% decrease was noted during the course of the data collection process: the intensities were broken into groups and scaled up appropriately.

The standard deviations of the intensities, σ_I, were estimated from the formula

$$\sigma = \{[C_N + (T_C/2T_B)^2 \cdot (B_1 + B_2)] + 0.03\,[C_N + (T_C/2T_B)^2 \cdot (B_1 + B_2)]^2\}^{\frac{1}{2}}$$

where C_N is the counts collected during scan time T_C, and B_1 and B_2 are background intensities, each collected during the background time T_B. Four symmetry related octants of data were measured out to $2\theta = 100°$, and one octant to $2\theta = 140°$. A total of 2480 reflections were collected of which 430 were unique and had intensities of

50 counts over background during the prescan. Of this group 105 were later judged to be unobserved on the criterion that $I > \sigma_I$.

The intensities were corrected in the usual manner for Lorentz and polarization effects but not for absorption (μ 15.8 cm^{-1}).

Fourier calculations were made with the ALFF[5] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy Program ORFLS[6]. The function $\Sigma[W\cdot(|F_o|-|F_c|)^2]$ was minimized. No corrections were made for extinction or anomalous dispersion. Neutral atom scattering factors were taken from the compilations of Ibers[7] for Al, N, C, and H. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE[8] program. Crystal structure illustrations were obtained with the program ORTEP[9].

STRUCTURE DETERMINATION AND REFINEMENT

Statistical tests based on normalized structure factors clearly indicated the space group to be the centric *Pnma*. Structure solution was accomplished by means of the symbolic addition procedure. Several cycles of isotropic refinement on the initial model produced a reliability index of $R=\Sigma(|F_o|-|F_c|)/(\Sigma|F_o|)\times 100=15.3\%$. Conversion to anisotropic temperature factors, the inclusion of a weighting scheme ($W=1/\sigma^2$), and additional cycles of refinement produced a final $R_1=10.0\%$ and $R_2=[\Sigma\, W(|F_o|-|F_c|)^2/\Sigma(F_o)^2]^{\frac{1}{2}}\times 100=9.5\%$. The largest parameter shifts in the final cycle of refinement were less than 0.05 of their estimated standard deviations. A final difference Fourier map showed several peaks of approximately 0.8 e$^-$/Å^3; however, no attempt was made to assign hydrogen atom positions. The value of ERF was 2.33. Final observed and calculated structure factor amplitudes are listed in Table 1. The final positional and thermal parameters are given in Table 2.

TABLE 2

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS[a,b] FOR ACETONITRILETRIMETHYLALUMINUM

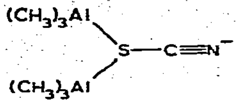
Atom	*x/a*	*y/b*	*z/c*
Al	0.4817(6)	0.2500	0.1138(2)
N	0.3240(16)	0.2500	0.0063(6)
C1	0.2292(23)	0.2500	−0.0556(10)
C2	0.1078(20)	0.2500	−0.1305(8)
C3	0.7697(17)	0.2500	0.0719(9)
C4	0.3895(12)	0.0339(13)	0.1678(5)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	0.0333(11)	0.0315(10)	0.0051(2)	0.0000	−0.0005(5)	0.0000
N	0.0451(41)	0.0290(30)	0.0057(7)	0.0000	−0.0010(13)	0.0000
C1	0.0434(53)	0.0277(36)	0.0063(9)	0.0000	0.0057(17)	0.0000
C2	0.0540(52)	0.0514(52)	0.0046(8)	0.0000	−0.0099(15)	0.0000
C3	0.0298(53)	0.0362(36)	0.0100(10)	0.0000	0.0054(14)	0.0000
C4	0.0499(32)	0.0377(34)	0.0073(6)	−0.0062(26)	0.0045(10)	0.0054(10)

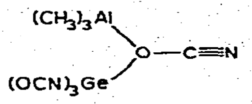
[a] Standard deviations in parentheses refer to last digit quoted. [b] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+2\,\beta_{12}\cdot h\cdot k+2\,\beta_{13}\cdot h\cdot l+2\,\beta_{23}\cdot k\cdot l)]$.

DISCUSSION

From the data presented here it is apparent that the OCN^- group may be split in a manner reminiscent[1] of that of the SCN^- group in $K[Al_2(CH_3)_6SCN]$. One can indeed view the two situations as being quite analogous if the intitial structures[10] are written as:



(I)



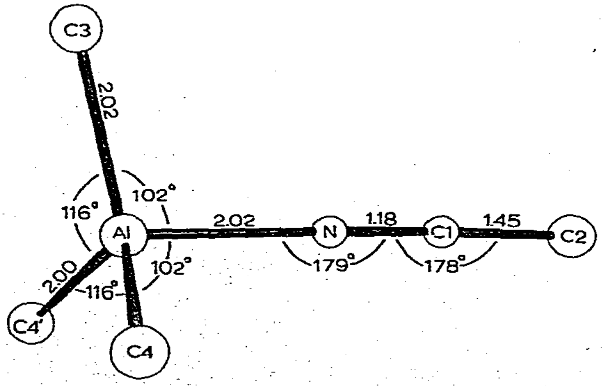
(II)

For the thiocyanate the parent complex (I) has a stable existence, and it thermally decomposes at 120° to yield (isopropylideneamino)dimethylaluminum. In the case of the cyanate, the proposed parent compound (II) has not been isolated; however, thermolysis (≈50°) produces the acetonitrile adduct of trimethylaluminum. Two reaction sequences may be proposed to correlate these observations:

$$\begin{array}{l} \qquad\mathrm{KSCN+2\,Al(CH_3)_3 \longrightarrow K[Al_2(CH_3)_6SCN]} \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow 120^\circ \\ \mathrm{[(H_3C)_2AlNC(CH_3)_2]_2 \longleftarrow \{(H_3C)_3Al{-}NC{-}CH_3\}} \end{array} \tag{1}$$

$$\begin{array}{l} \mathrm{Ge(NCO)_4+Al(CH_3)_3 \longrightarrow \{(OCN)_3GeOCNAl(CH_3)_3\}} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow 50^\circ \\ \quad\mathrm{[(H_3C)_2AlNC(CH_3)_2]_2 \longleftarrow (H_3C)_3Al{-}NC{-}CH_3} \end{array} \tag{2}$$

where the substances not as yet isolated are given in braces. With the thiocyanate, $(H_3C)_3Al{-}NC{-}CH_3$ is not obtained because at the time of generation, the melt



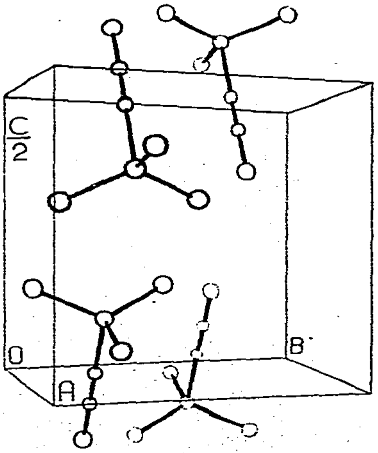


Fig. 1. Molecular structure of $(CH_3)_3Al\cdot NCCH_3$. The standard deviations for the distances and angles about the aluminum atom are 0.01 Å and 0.5°, respectively; for the remaining values they are 0.02 Å and 1.0°.

Fig. 2. Packing of $(CH_3)_3Al\cdot NCCH_3$ molecules in one half of the unit cell.

temperature is already far above the 80° Wade[3] had reported to be necessary for the rearrangement to (isopropylideneamino)dimethylaluminum. On the other hand, for the cyanate, $(H_3C)_3Al{-}NC{-}CH_3$ is found since the temperature did not reach the 80° mark. Although one cannot at present rule out other possible mechanisms for the thermal decomposition of $K[Al_2(CH_3)_6SCN]$, the results on the tetraisocyanatogermanium/trimethylaluminum system lend support to reaction sequence (1).

In the structure of acetonitriletrimethylaluminum (Fig. 1), the acetonitrile molecule, the aluminum atom, and one of the methyl carbon atoms all lie in a crystallographic mirror plane. The two independent aluminum–carbon bond lengths (2.00 and 2.02 Å) are quite normal for the situation in which the hydrogen atoms of the methyl group have not been located[11]. There exist no other aluminum-*sp*-hybridized nitrogen distances for comparison, but the value of 2.02(1) Å falls well within the overall range of aluminum–nitrogen lengths: 1.93(3) Å in $[(CH_3)_2Al{\cdot}N(CH_2)_2]_3$[12] to 2.06(1) Å in $(CH_3)_3Al{\cdot}NC_7H_{13}$[13]. The bond angles about the aluminum atom (C–Al–C, 116°; C–Al–N, 102°) are typical for compounds of this type[14], and may be explained by either classical electrostatic or second-order rehybridization arguments. As Fig. 2 illustrates, the intermolecular contacts are normal for a low melting molecular complex such as this. The only approaches less than 4.0 Å are between aluminum-methyl-carbon and cyano-carbon atoms (3.82(2) Å), and aluminum-methyl-carbon and acetonitrile-methyl-carbon atoms (3.94(3) Å).

ACKNOWLEDGEMENTS

We are grateful to the National Science Foundation for support of this work under Grant GP-24852, and for departmental assistance in the purchase of the X-ray diffractometer. The authors also thank Mr. W. J. Cook for aid in obtaining the crystal structure illustrations.

REFERENCES

1 J. L. Atwood, P. A. Milton and S. K. Seale, *J. Organometal. Chem.*, 28 (1971) C29.
2 J. L. Atwood and P. A. Milton, *J. Organometal Chem.*, 36 (1972) C1.
3 J. R. Jennings, J. E. Lloyd and K. Wade, *J. Chem. Soc.*, (1965) 5083.
4 F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, 17 (1961) 977.
5 C. R. Hubbard, C. O. Quicksall and R. A. Jacobson, *USAEC Report IS*-2625, Ames Laboratory, Iowa State University, Ames, Iowa, 1971.
6 W. R. Busing, K. O. Martin and H. A. Levy, *Report No. ORNL-TM*-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
7 J. A. Ibers, *International Tables for X-ray Crystallography*, Vol. III, Kynoch Press, Birmingham, England, 1962, pp. 202, 203.
8 W. R. Busing, K. O. Martin and H. A. Levy, *Report No. ORNL-TM*-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
9 C. K. Johnson, *Report No. ORNL*-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
10 J. L. Atwood and W. R. Newberry, *J. Organometal. Chem.*, 42 (1972) C77.
11 J. L. Atwood and G. D. Stucky, *J. Organometal. Chem.*, 13 (1968) 53.
12 J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, 92 (1970) 285.
13 C. D. Whitt, L. M. Parker and J. L. Atwood, *J. Organometal. Chem.*, 32 (1971) 291.
14 J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, 89 (1967) 5362.