Synthesis, Molecular Structure, and NMR Spectra of Trimesitylaluminum, a Novel Molecule with Three Coordinate Aluminum

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Trimesitylaluminum, 1, was prepared by metal exchange between dimesitylmercury and aluminum. The crystal structure of 1 was determined by single-crystal X-ray diffraction methods. 1 was found to be trigonal of space group $P\bar{3}$ with $a = b = 13.409$ (4) Å and $c = 7.664$ (3) Å, and ρ(calcd) = 1.070 g cm^{-3} for M_r 384.54 and $Z = 2$. The molecule is monomeric and essentially planar around the Al center with the three mesityl groups disposed in a propeller-like fashion about the trigonal axis with a dihedral angle of 56° between the aromatic rings and the plane containing the Al atom and the ipso carbons of the aromatic rings. The Al–C distance of 1.995 (8) Å is normal for a terminal Al–C bond distance. ^{1}H, ^{13}C, and ^{27}Al NMR spectra are reported. The ^{13}C CP/MAS spectra show that the ortho methyl groups are magnetically nonequivalent in the solid state as a result of crystal packing but become equivalent in solution when these constraints are removed.

Introduction

All simple organoaluminum compounds which have been characterized by single-crystal X-ray diffraction methods have been shown to be dimeric in the solid state with three-centered, two-electron carbon bridge bonds[2] or have chain structures as exhibited by Me_2AlCp[3] and $Al(CH_2Ph)_3$.[4] The only monomeric structure described in detail is that of $AlMe_3$ monomer determined in the gas phase by electron diffraction.[5] In solution the majority of these derivatives remain largely dimeric but are typically involved in monomer–dimer equilibria and in bridge terminal exchange.[6] Since it has been shown that this equilibrium is shifted toward monomer by increasing the bulk of the substituent,[6] we have prepared trimesitylaluminum to determine if steric interactions in this molecule would force it exclusively into the monomeric form and then to determine if this alteration in the coordination of the Al atom alters the C⋯Al bond distance. We now report NMR and single-crystal X-ray structural studies on trimesitylaluminum which is monomeric both in the solid state and in solution.

Experimental Section

Preparation of Trimesitylaluminum. An aluminum–mercury couple was prepared by stirring 8–20 mesh aluminum (5 g) with 0.5% $HgCl_2$/THF (100 mL) until the solution turned cloudy. The couple was rinsed several times with THF. The THF was removed by evacuation on a Schlenk line. Dimesitylmercury[7] (1.2 g, 0.003 mol) was placed in a reaction tube with the Al–Hg couple (1.5 g) and 30 mL of xylene. The reaction mixture was refluxed with stirring for 4 h under an Ar atmosphere. The solution was cooled to room temperature and decanted into an H-vessel, the xylene removed by vacuum distillation, and the solid trimesitylaluminum, 1, recrystallized from pentane (yield 0.8 g, 61%).

Table I. Physical Constants and Experimental Crystal Data for the Structure Determination of Trimesitylaluminum

compd	$AlC_{27}H_{33}$
mol wt	384.54
cryst system	trigonal
space group	$P\bar{3}$
Z	2
a, Å	13.409 (4)
b, Å	13.409 (4)
c, Å	7.664 (3)
V, Å^3	1193.4 (7)
F(000)	416
d(calcd), g/cm^3	1.070
cryst dimens, mm^3	0.25 × 0.37 × 0.34
2θ scan range, deg	3–45
max dev of stds during data collection, %	7
no. of unique data collected	1290
no. of data used, $\sigma(I) > 2.5$	361
linear abs coeff μ, cm^{-1}	1.27
$R_F = \sum\|\|F_o\| - \|F_o\|\|/\sum\|F_o\|$	5.2%
$R_{WF} = \{\sum w(\|F_o\| - \|F_c\|)^2/\sum w(\|F_o\|^2\}^{1/2}$	5.7%

Table II. Positonal Coordinates for the Non-Hydrogen Atoms in Trimesitylaluminum

atom	x	y	z
Al	0.3333	0.6667	0.3394 (7)
C1	0.2255 (9)	0.7246 (9)	0.3313 (17)
C2	0.2265 (9)	0.7948 (9)	0.1949 (15)
C3	0.1396 (12)	0.8221 (8)	0.1821 (14)
C4	0.0526 (10)	0.7845 (10)	0.2981 (19)
C5	0.0493 (9)	0.7156 (9)	0.4329 (15)
C6	0.1359 (11)	0.6878 (7)	0.4508 (15)
C21	0.3190 (9)	0.8369 (8)	0.0547 (12)
C41	−0.0408 (9)	0.8169 (8)	0.2767 (12)
C61	0.1330 (8)	0.6191 (9)	0.6085 (13)

Collection of X-ray Diffraction Data. A colorless single crystal of 1 of dimensions 0.25 × 0.37 × 0.34 mm^3 suitable for X-ray diffraction studies was wedged into a thin-walled capillary tube under an Ar atmosphere in a drybox. The sample was then sealed and mounted on the goniometer head, and the data were collected on a Syntex P2$_1$ automated diffractometer with use of Mo K$\bar{\alpha}$ radiation diffracted from a highly oriented graphite crystal in the parallel mode with a θ–2θ scan in the bisecting mode. The specific conditions, unit cell, and other experimental crystallo-

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[7] Dimesitylmercury was prepared by a standard Grignard reaction and characterized by its NMR and Mass spectra.

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Table III. A Complete Listing of Bond Distances (Å) and Bond Angles (deg) for Trimesitylaluminum

	Bond Distances		
Al-C(1)	1.995 (8)	C(3)-C(4)	1.348 (11)
C(1)-C(2)	1.402 (11)	C(4)-C(41)	1.525 (12)
C(1)-C(6)	1.390 (11)	C(4)-C(5)	1.372 (11)
C(2)-C(3)	1.390 (11)	C(5)-C(6)	1.392 (11)
C(2)-C(21)	1.520 (11)	C(6)-C(61)	1.509 (11)
	Bond Angles		
C(1)-Al-C(1)	120.15 (5)	C(2)-C(3)-C(4)	122.5 (11)
Al-C(1)-C(2)	122.1 (11)	C(3)-C(4)-C(5)	118.6 (11)
Al-C(1)-C(6)	121.1 (11)	C(3)-C(4)-C(41)	120.1 (14)
C(6)-C(1)-C(2)	116.4 (9)	C(5)-C(4)-C(41)	121.3 (14)
C(1)-C(2)-C(3)	120.2 (9)	C(4)-C(5)-C(6)	120.3 (11)
C(1)-C(2)-C(21)	120.6 (12)	C(1)-C(6)-C(61)	119.9 (13)
C(3)-C(2)-C(21)	119.2 (13)	C(5)-C(6)-C(61)	118.1 (13)

graphic data are given in Table I.

Solution and Refinement of the Structure. The crystal was found to be trigonal in the space group $P3$ or $P\bar{3}$. The structure was solved by light atom techniques through the use of MULTAN[8] which gave positions for all 10 non-hydrogen atoms. Final refinement was based on the space group $P\bar{3}$ which gave the best fit to the experimental data. The hydrogen atom positions were calculated by using HFINDR[9] and were adjusted on every other cycle of least-squares refinement. Full-matrix least-squares refinement on the positional and anisotropic thermal parameters for the non-hydrogen atoms with the hydrogen atoms in fixed positions as indicated on 361 data gave $R_F = 5.2\%$ and $R_{wF} = 5.7\%$. Final atomic coordinates are given in Table II with the pertinent distances and angles listed in Table III. Thermal parameters and observed and calculated structure factors are available.[10]

NMR Spectral Studies. The solution NMR spectra were collected on a General Electric QE-300 NMR spectrometer (^{1}H and ^{13}C), solution ^{27}Al on a Nicolet NT-300 spectrometer, and the CP/MAS spectra on a General Electric GN-300 spectrometer equipped for CP/MAS NMR spectroscopy. The solutions were prepared by adding 1 to the NMR tube in an Ar-filled drybox which were then capped by a stopcocks and transferred to a vacuum system where solvent was distilled into the tubes which were then sealed. The CP/MAS NMR samples were prepared by packing the trimesitylaluminum into Kel-F rotors in the drybox under an Ar atmosphere. Each sample was then stored in a tightly closed vessel under argon until the spectrum was to be recorded. It was then removed and quickly placed into the probe where it was immediately blanketed with N_2 gas used for spinning. Spinning rates were of the order of 2500 Hz and were determined by the spacing of the spinning side bands. All samples were measured at least two spinning rates to make assignment more certain. On completion of the NMR run the samples were carefully examined to determine the extent of decomposition. In most instances the seals were adequate to prevent any significant deterioration of the sample during the course of the NMR experiment. If deterioration was detected, the sample was rejected.

Results and Discussion

Description of the Structure. The unit cell contains two molecules related by a center of inversion. A diagram of the molecule is shown in Figure 1 with selected bond distances and angles. The Al–C distance, 1.995 (8) Å, is normal for terminal Al–C distances in the solid state for all known aromatic derivatives[2,11-14] and corresponds to that observed for $AlMe_3$ monomer in the gas phase.[5] The central AlC_3 unit is essentially planar with the Al atom on the threefold axis. The mesityl groups are arranged in a propeller like fashion with each ring forming an angle of 56° between the ring plane and the plane described by the central AlC_3 unit. Since the two molecules in the unit cell are related by a center of inversion, one takes the form of a right-handed screw and the other is in the left-handed form. It should be noted that the three methyl groups on the mesityl moiety are all nonequivalent in the solid state. This is of importance in interpretation of the CP/MAS NMR studies reported. The Al–Al distance is 7.664 (3) Å with the closest intermolecular interaction to the Al atom 4.67 Å to a hydrogen in an adjacent molecule, thus establishing the fact that the molecule is monomeric.

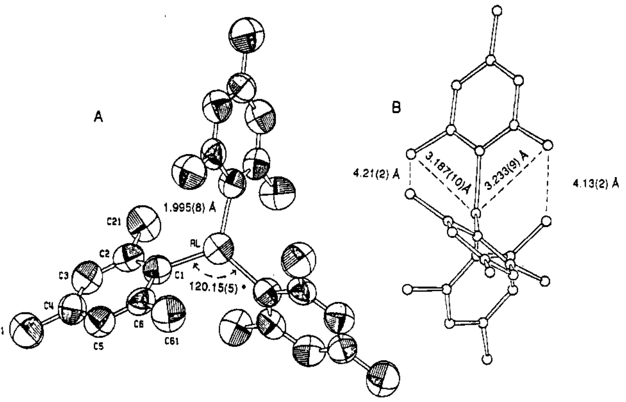

Figure 1. A: the molecular structure of trimesitylaluminum projected along the threefold axis (50% thermal ellipsoids) with the atoms labeled. B: a projection perpendicular to the threefold axis showing the nonequivalence of the ortho methyl groups C21 and C61.

NMR Spectra. The proton NMR spectrum consists of broad lines at $\delta\ 2.38_6$ ($\nu_{1/2}$ = 2.2 Hz) and at $\delta\ 2.12_2$ ($\nu_{1/2}$ = 2.2 Hz) corresponding to the ortho and para methyl groups and at $\delta\ 6.69_7$ ($\nu_{1/2}$ = 3.1 Hz) arising from the two aromatic protons. The solution ^{13}C NMR spectrum shows two types of methyl groups with δ values of 21.83 (^1J = 125.3 Hz) and 24.23 (^1J = 123.9 Hz) corresponding to the para and ortho groups. The assignments are confirmed by the long-range coupling to the ring protons which give rise to a triplet for the para methyl carbon with coupling of 4.9 Hz and to unsymmetrical splitting of the ortho methyl groups with splittings of 2.1–3.1 Hz. The aromatic resonances are at δ 127.13 (C3, ^1J = 157.4 Hz, long-range coupling gives rise to a 7-line multiplet with 5-Hz splitting), δ 138.92 (C4, multiplet, long-range coupling of 5.8 Hz), δ 144.42 (C2, multiplet, long-range coupling of 5.5 Hz), and a broad resonance centered at 143.52 ppm corresponding C1, the ipso carbon broadened by the ^{27}Al quadrupolar relaxation, as well as coupling to the other protons. These values are all within the expected range for the aromatic group.

The ^{13}C CP/MAS spectra gave similar chemical shifts for the aromatic region (three clearly resolved lines at 127.79, 137.77, and 143.71 ppm), but examination of the methyl region shows quite a different result with three resonance lines at 22.16, 23.52, and 24.82 ppm, rather than

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[9] Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for data reduction; (2) FORDAP, A. Zalkin's Fourier program; (3) HFINDR, A. Zalkin's idealized hydrogen program; (4) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levey's full-matrix least-squares program and function error program; (5) ORTEP, C. K. Johnson's program for drawing crystal models. Scattering factors were taken from: Ibers, J. A.; Hamilton, W. C. *International Tables for X-ray Crystallography*; Knoch Press: Birmingham, England, 1974; Vol. IV.

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two as observed in solution. This shows that the equivalence of the ortho methyl groups (δ 24.23 ppm in solution) has been removed in the solid state as a result of the crystal packing. This is shown in Figure 1B. The equivalence also may have been removed for the ring carbon atoms but is not observable because of the line widths. The ^{27}Al chemical shifts obtained in solution and by CP/MAS on a solid sample were centered at 108 and 101 ppm (relative to 1 M $Al(NO_3)_3$), respectively, and were extremely broad ($\nu_{1/2} \geq 10\,000$ Hz) consistent with the planar structure.[15]

Conclusions. In trimesitylaluminum the structural data indicates that the reason for the formation of monomer rather than dimer is the result of steric interference between the ortho methyl groups which prevent the molecule from forming a stable dimer. This was suggested by our earlier studies on tri-*o*-tolylaluminum dimer which showed that the C–Al–C–Al ring was distorted from that observed in aromatic compounds in which there were no substituents in the ortho positions.[13] The fact that the Al–C distance observed is nearly identical with that observed in a variety of other derivatives including monomeric trimethylaluminum shows that the steric interference does not significantly alter the Al–C bond. The steric hindrance, and not alteration in bonding, therefore appears to accounts for the limited reactivity of this molecule toward Lewis bases and likely toward other reagents since many of these reactions proceed via initial complex formation. Thus, by prevention of the initial complex formation through the steric crowding around the vacant orbital on aluminum atom, the reactivity of the Al–C bond is reduced.

Preliminary studies have been carried out on this compound which indicate that its reactivity is also altered from that of other compounds because of the structural effects of the mesityl group which take the form of reduced reactivity toward hydrolysis, complex formation, and oxidation. These studies are now being pursued further.

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Registry No. Trimesitylaluminum, 58336-22-4; aluminum, 7429-90-5; dimesitylmercury, 26562-17-4.

Supplementary Material Available: Listings of anisotropic thermal parameters and atomic positional parameters, (2 pages); a listing of observed and calculated structure amplitudes (4 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Crystal and Molecular Structure of Trimesitylgallium(III)

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The compound trimesitylgallium(III) ($GaMes_3$) has been prepared and fully characterized by elemental analysis, IR and ^{1}H NMR data, Lewis acid–base studies, and an X-ray structural study. Trimesitylgallium(III) crystallizes in the centrosymmetric trigonal space group $P\bar{3}$ (No. 147) with a = 13.415 (4) Å, c = 7.628 (2) Å, and ρ(calcd) = 1.19 g cm^{-3} for M_r 427.3 and Z = 2. Single-crystal X-ray diffraction data (Mo Kα, 2θ = 4.0–40.0°) were collected with a Syntex P2$_1$ automated four-circle diffractometer. All atoms (including hydrogen atoms) were located, and the structure was refined to R_F = 3.9% and R_{wF} = 3.3% for all 743 unique reflections (none rejected). The gallium(III) atom lies on a site of crystallographically imposed C_3 symmetry (and approximate D_3 symmetry) and has a trigonal-planar stereochemistry (C(1)–Ga–C(1′) = 119.93 (16)°) with a gallium–carbon bond length of 1.968 (4) Å. The aromatic rings of the mesityl ligands form a propeller-like arrangement about gallium with an angle of 55.9° between each ring and the metal coordination plane.

Introduction

Bulky substituents have been used in main-group chemistry to stabilize a variety of unusual compounds. Of the possible groups with large steric demands, aromatic rings with alkyl groups in the 2- and 6-positions have been frequently employed. Mesityl (Mes) groups have been used to stabilize Si_2Mes_4, the first fully characterized compound with a silicon–silicon double bond.[1] The 2,6-diethylphenyl substituent stabilized a compound with a germanium–germanium double bond,[2] whereas the 2,6-diisopropylphenyl group provided sufficient steric effects to provide a tin–tin derivative.[3] The 2,4,6-tri-*tert*-butylphenyl substituent was used as a substituent in compounds with phosphorus–phosphorus[4] and arsenic–arsenic double bonds.[5]

In group 13 chemistry in general and gallium chemistry in particular, very few typical compounds with bulky substituents are known. The derivative $Ga(CH_2SiMe_3)_3$, a pyrophoric liquid at room temperature, has been fully

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