

X-RAY CRYSTAL STRUCTURE OF TRIBENZYLALUMINUM · DIETHYL ETHERATE

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Summary

The crystal structure of tribenzylaluminum · diethyl etherate has been determined by single crystal X-ray diffraction techniques. It crystallizes in the monoclinic system, space group $P2_1$, with unit cell dimensions of a 8.106(1), b 15.098(2), c 10.037(1) Å, β 111.02(1)°, V 1146.6(3) Å³, and $Z=2$. The final full matrix least-squares refinement on 1139 data gave R_F 3.8 and R_{wF} 5.2%. The compound is similar to other organoaluminum adducts yielding a four coordinate aluminum atom with average Al–C distances of 1.986 and an Al–O distance of 1.901(4) Å which is significantly shorter than the Al–O distance observed in other ether adducts. The average C–Al–C and C–Al–O angles are 113 and 106°, respectively.

Introduction

Structural and spectroscopic studies on organoaluminum compounds and their adducts have been of great interest because of the unusual modes of bonding observed and the ability of suitable Lewis bases to disrupt these modes of bonding [1]. Many of the structural data have been reviewed [2] and several reviews have appeared which deal with the NMR spectral studies on these compounds [3–5]. In the earlier work two modes of bonding were reported for the dimeric aluminum species. The first of these, best represented by the studies of trimethylaluminum, can be described in terms of a three-centered molecular orbital arising from the interaction of a C sp^3 orbital with two sp^3 hybrid orbitals, one from each of the Al atoms. This has been extended to include secondary interactions between π electron systems or p orbitals on the bridging group, as in the cyclopropyl derivatives or in the vinyl bridged derivatives, which provide additional stabilization to the bridge bond. The second type of interaction which has been described, is observed when an ethynyl moiety serves as the bridging group. In this dimer the bridging group is bonded to one Al atom by a σ interaction and to the second by a π interaction giving rise to an unsymmetrically bridged molecule both in the solid state [6,7] and in the gas phase [8]. An alternative mode of bonding is exhibited for the cyclopentadienyl derivative, $CpAlMe_2$, which forms an infinite chain in the solid state

with unsymmetrical C_5H_5 bridging units with the bonding occurring through the π system of the C_5H_5 unit in an alternating η^3 and η^2 fashion [9]. In the gas phase, this molecule has been shown to be monomeric with the Al atom bonded to the C_5H_5 ring in an η^2 fashion and appears to undergo rapid fluxional motion under these conditions [10].

We reported a second variation for the formation of an infinite chain in tribenzylaluminum with the interaction occurring between the vacant orbital on the aluminum atom with the C(2) carbon atom of a benzyl group in an adjacent molecule [11]. We now have shown that the extended bonding observed in the unsolvated tribenzylaluminum is disrupted by ether, giving a normal tribenzylaluminum · diethyl ether adduct.

Experimental

Preparation of compounds

Tribenzylaluminum was prepared by reaction of excess (10-fold) aluminum granules with dibenzylmercury. The reaction was carried out in either toluene, as

TABLE 1

EXPERIMENTAL DATA FROM THE X-RAY DIFFRACTION STUDY ON TRIBENZYLALUMINUM · DIETHYL ETHERATE

Molecular formula	$AlC_{25}H_{31}O$
Molecular weight	374.5
Crystal system	monoclinic
Space group	$P2_1$
Cell dimensions	a 8.106(1) Å b 15.098(2) Å c 10.037(1) Å β 111.02(1)°
V	1146.6(3) Å ³
Z	2
D_{calc}	1.085 g cm ⁻³
Radiation	Mo- K_{α} (λ 0.71069 Å)
Monochromator	graphite crystal
Reflections measured	+ h , + k , $\pm l$
2θ range	4–45°
Scan type	θ – 2θ ; moving crystal, moving counter
Scan speed	variable, 2.0–5.0° min ⁻¹
Unique data	1781
Unique data with $F^2 \geq 2.5\sigma(F_o^2)$	1139
Abs. coeff., μ	0.946 cm ⁻¹
F(000)	404
Max shift/error for last	
Least-squares cycle:	0.0010
$R_F = \Sigma F_o - F_c / \Sigma F_o $	0.038
$R_{wF} = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o ^2]^{1/2}$	0.052

Background measurements: the ratio of the background to scan time was 0.5 standard reflections; 3 standard reflections were measured every 97 reflections; no significant deviation from the mean was observed for either crystal

described by Eisch and Biedermann [13], or xylene solvent maintained at 140°C for 4 h in an oil bath. The resulting product contained yellow decomposition product which was removed by recrystallization from pentane or hexane and gave colorless crystals. These were dissolved in a mixed benzene-ether solvent system and crystals suitable for X-ray diffraction studies were obtained from this solution upon slow removal of a portion of the solvent on the vacuum system.

X-Ray data collection

A crystal suitable for X-ray diffraction was mounted in a thin-walled capillary tube in the drybox, plugged with grease, removed from the drybox, flame sealed, and then mounted on a goniometer head. X-ray diffraction data were collected on a Syntex P2₁ diffractometer using Mo-K α radiation diffracted from a highly oriented graphite crystal in the parallel mode. The data were collected with a θ - 2θ scan. The specific conditions, unit cell, and unit cell dimensions are given in Table 1.

Solution and refinement of structure

The tribenzylaluminum · diethyl ether adduct was found to be monoclinic and was assigned to the space group $P2_1$ on the basis of systematic absences. The aluminum atom was located by the analysis of the three-dimensional Patterson

TABLE 2

ATOMIC COORDINATES FOR TRIBENZYLALUMINUM · DIETHYL ETHERATE

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Al	0.3710(2)	0.4999	0.3985(2)
C(1)	0.5001(8)	0.5078(5)	0.6079(6)
C(2)	0.3502(10)	0.3780(5)	0.3198(7)
C(3)	0.1488(8)	0.5686(6)	0.3518(6)
O	0.5166(5)	0.5604(3)	0.3161(4)
C(11)	0.3825(9)	0.4876(5)	0.6866(5)
C(12)	0.2901(12)	0.5528(5)	0.7248(7)
C(13)	0.1678(14)	0.5325(8)	0.7879(9)
C(14)	0.1382(12)	0.4478(10)	0.8153(9)
C(15)	0.2318(15)	0.3828(7)	0.7818(9)
C(16)	0.3466(12)	0.4020(5)	0.7158(7)
C(21)	0.5215(10)	0.3450(4)	0.3108(8)
C(22)	0.5473(12)	0.3433(5)	0.1825(8)
C(23)	0.7112(16)	0.3216(6)	0.1748(10)
C(24)	0.8483(13)	0.3023(6)	0.2975(15)
C(25)	0.8241(14)	0.3012(6)	0.4246(12)
C(26)	0.6605(13)	0.3225(6)	0.4301(8)
C(31)	0.0428(8)	0.5975(5)	0.2046(6)
C(32)	-0.0720(9)	0.5406(5)	0.1080(8)
C(33)	-0.1749(11)	0.5681(9)	-0.0281(9)
C(34)	-0.1652(14)	0.6511(10)	-0.0714(9)
C(35)	-0.0558(13)	0.7083(6)	0.0191(10)
C(36)	0.0476(10)	0.6824(6)	0.1578(8)
C(41)	0.4568(9)	0.5694(6)	0.1606(7)
C(42)	0.4893(12)	0.6598(6)	0.1166(8)
C(43)	0.7090(10)	0.5640(5)	0.3886(7)
C(44)	0.7688(10)	0.6478(6)	0.4639(8)

synthesis. The carbon and oxygen positions were determined from subsequent Fourier maps. The hydrogen atom positions were then calculated by using HFINDR [14]. Two additional cycles of refinement were carried out on all non-hydrogen atoms with the hydrogen atoms in fixed positions to give the final parameters listed. In the final least-squares, the number of variables was 243, the number of observed data was 1139, and the error in observation unit weight was 1.53. The largest peak on the final difference map was 0.18 electrons/ \AA^3 , 1.244 \AA away from the Al atom. Neutral atom scattering factors, including anomalous dispersion, were used for all the atoms [14]. Final positional parameters are presented in Table 2. The errors were estimated by the variance-covariance method. Lattice errors were not included. Additional details for the structure is available [15].

Results and discussion

A diagram showing the molecular unit with the atoms labeled is given in Fig. 1. Selected bond distances and angles are collected in Table 3. A comparison of the pertinent values with a variety of other organoaluminum compounds and adducts is given in Table 4. These data show that the gross features of the tribenzylaluminum adduct are similar in all respects to those of other aluminum addition compounds. A more detailed inspection of the data reveals that the Al–O bond distance in this derivative is significantly shorter than in the other known structures, 0.027 \AA shorter than that in the (*o*-Tol) $_3$ Al·OEt $_2$ adduct and a full 0.1 \AA less than the reported distance in several of the Me $_3$ Al adducts given in Table 4. These observations are

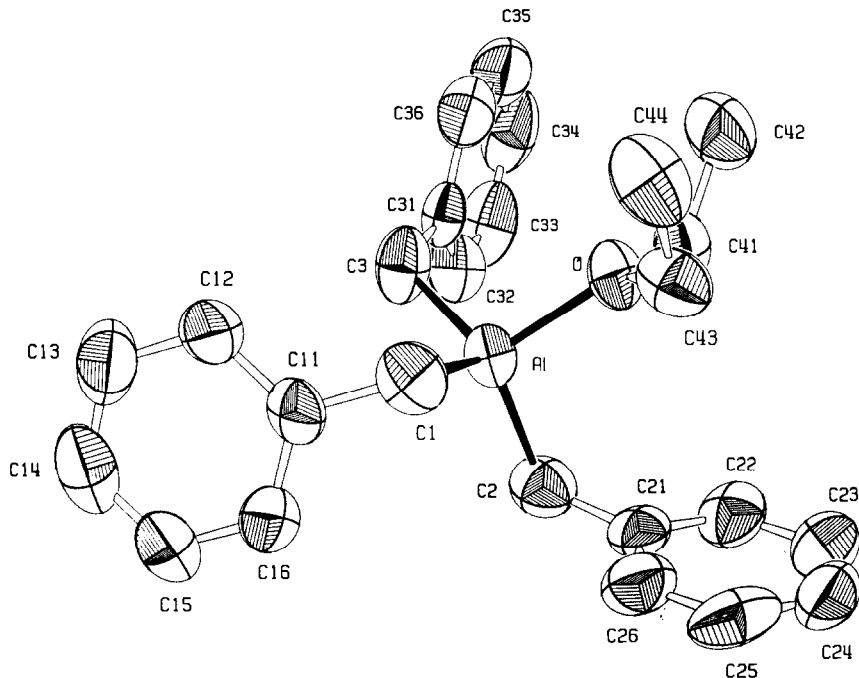


Fig. 1. A perspective view of the tribenzylaluminum·diethyl etherate molecule with the atoms labeled.

TABLE 3

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR TRIBENZYLALUMINUM · DIETHYL ETHERATE

Al-C(1)	1.987(6)	C(1)-Al-C(2)	114.5(3)
Al-C(2)	1.986(6)	C(2)-Al-C(3)	116.7(3)
Al-C(3)	1.984(7)	C(1)-Al-C(3)	107.9(3)
C(1)-C(11)	1.472(9)	Al-C(1)-C(11)	111.0(4)
C(2)-C(21)	1.509(10)	Al-C(2)-C(21)	112.4(5)
C(3)-C(31)	1.484(9)	Al-C(3)-C(31)	122.8(4)
Al-O	1.901(4)	C(1)-Al-O	104.9(3)
O-C(41)	1.464(7)	C(2)-Al-O	104.5(3)
O-C(43)	1.466(8)	C(3)-Al-O	107.4(3)

consistent with the fact that the aromatic substituents on aluminum can better delocalize the negative charge on the organic group and, thus, increase the positive charge on the Al atom. This would tend to increase the Al-O bond energy and lead

TABLE 4

A COMPARISON OF AVERAGE BOND DISTANCES AND ANGLES IN SELECTED ORGANOALUMINUM DERIVATIVES AND OF ORGANOALUMINUM · ETHER ADDUCTS

Compound	Al-C distances (Å)		C-Al-C angles (°)		Adducts	
	terminal	bridge	terminal	bridge	Al-O distance (Å)	C-Al-O angle (°)
Al ₂ Me ₆ ^a	1.95	2.12	123.1	105.3		
Al ₂ ∇ ₆ ^b	1.944	2.074	115.5	97.1		
Al ₂ (μ- <i>trans</i> -CH=CH- <i>t</i> -Bu)(<i>i</i> -Bu) ₄ ^c	1.969	2.118	127.8	78.4		
Al ₂ Ph ₆ ^d	1.960	2.184	115.4	103.5		
Al ₂ (<i>o</i> -Tol) ₆ ^e	1.997	2.128	108.7	98.1		
(Me ₂ Al-μ-C ₃ H ₅) _n ^f	1.953	2.248	121.8			
		2.203				
Al ₂ (μ-C≡CPh) ₂ Ph ₄ ^g	1.956	2.05				
		2.15				
[Al(CH ₂ Ph) ₃] _n ^h	1.989	2.453	114.5			
Me ₃ Al·OMe ₂ (gas) ⁱ	1.973		117.8		2.014	98.7
(AlMe ₃) ₂ ·(dibenzo-18-crown-6) ^j	1.960		115.5		1.967	102.4
(AlMe ₃) ₄ ·(15-crown-5) ^j (Al(1))	1.93		115.9		2.005	101.8
	1.95		116.2		2.005	101.4
(Me ₃ Al) ₂ · <i>p</i> -dioxane ^k	1.96		116.8		2.02	100.4
(<i>o</i> -Tol) ₃ Al·OEt ₂ ^e	1.990		114.4		1.928	103.8
(PhCH ₂) ₃ Al·OEt ₂	1.986		113.0		1.901	105.6

^a P.H. Lewis and R.E. Rundle, *J. Chem. Phys.*, 21 (1953) 987; R.G. Vranka and E.L. Amma, *J. Am. Chem. Soc.*, 89 (1967) 3121; J.C. Huffman and W.E. Streib, *J. Chem. Soc. D*, (1971) 911. ^b Parameters determined from -67° data, W.H. Ilesley, M.D. Glick, J.P. Oliver and J.W. Moore, *Inorg. Chem.*, 19 (1980) 3572. ^c M.J. Albright, W.M. Butler, T.J. Anderson, M.D. Glick, and J.P. Oliver, *J. Am. Chem. Soc.*, 98 (1976) 3995; revised values, B. Teclé, Ph.D. Dissertation, Wayne State University, Detroit, MI, (1983). ^d J.F. Malone and W.S. McDonald, *J. Chem. Soc., Dalton Trans.*, (1972) 2646. ^e M. Barber, D. Liptak, and J.P. Oliver, *Organometallics*, 1 (1982) 1307. ^f Ref. 9. ^g Ref. 6. ^h Ref. 11. ⁱ A. Haaland, S. Samdal, and O. Stokkeland, *J. Organomet. Chem.*, 134 (1977) 165. ^j J.L. Atwood, D.C. Hrnčir, R. Shakir, M.S. Dalton, R.D. Priester, and R.D. Rogers, *Organometallics*, 1 (1982) 1021. ^k J.L. Atwood and G.D. Stucky, *J. Am. Chem. Soc.*, 89 (1967) 5362.

to the bond shortening observed. To further substantiate this proposal additional cases need to be examined in which both the Lewis base and the substituent on the aluminum atom are varied.

Examination of the data in Table 3 reveals that the three sets of angles involving the aluminum atom, C–Al–C, C–Al–O, and Al–C–C, show significant variations. Further, in each case where the angle deviates by a significant amount from the value that might be expected, the third benzyl group is involved. The molecular packing shows that the individual tribenzylaluminum·diethyl etherate molecules are separated in the lattice with no unusual interactions. This leaves the most probable explanation for the large variations observed in these angles, the interaction of the diethyl ether molecule with benzyl group 3 resulting in the angular deformation.

In contrast to the rather normal behavior of the addition compound, the structure of the parent molecule was shown to behave in an unusual manner with the aluminum atom in a pseudo-tetrahedral environment surrounded by the three methylene carbon atoms with the fourth position occupied by an *ortho*-carbon atom from a phenyl ring on an adjacent tribenzylaluminum molecule. The extended array is disrupted on addition of ether and the adduct formed behaves in a completely normal fashion for an aluminum addition compound.

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- 14 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: J.A. Ibers and W.C. Hamilton, *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, England, 1974, Vol. IV.
- 15 Tables containing a listing of bond lengths and bond angles, hydrogen atom positional parameters, anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen and observed and calculated structure amplitudes are available on request from J.P.O.