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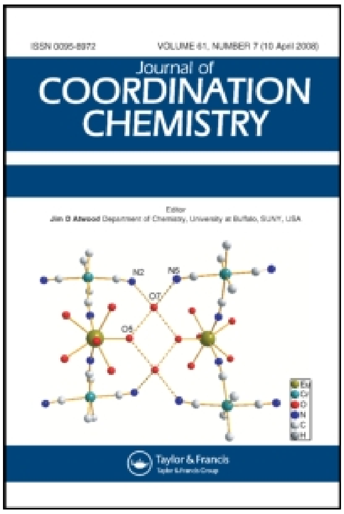

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Synthesis and Structural Characterization of *o*-Tol_3GaOEt_2

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NOTE

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF o-Tol$_3$Ga·OEt$_2$

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INTRODUCTION

Trialkyl gallium compounds have come under widespread scrutiny as likely reagents for the OMCVD of semiconducting materials.[1] Part of our work in this area involves the isolation and structural characterization of trialkyl gallium species that have varying degrees of steric bulk. Often, the trialkyl galium species are liquids and can be isolated as Lewis base adducts. Past work has focused on derivatives of t-Bu$_3$Ga.[2] More recently, we have prepared gallium compounds utilizing moderately bulky aryl groups such as 2-CH_3–C_6H_5 (*o*-Tolyl). Since *o*-Tol$_3$Ga is a liquid[3] we chose to isolate the solid diethylether adduct in order to effect an X-ray crystallographic study. To our knowledge, *o*-Tol$_3$Ga·OEt$_2$ (1) represents the first instance where the *o*-Tol-Ga fragment has been structurally characterized.

EXPERIMENTAL

Standard Schlenk-line techniques were employed in conjunction with an inert atmosphere glove box. Diethylether and toluene were distilled from sodium metal under purified N_2 prior to use. $GaCl_3$ was used as received from Alpha and stored at −15°C. ^{1}H and ^{13}C NMR specta were recorded on a General Electrics QE-300 spectrometer. X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer.

Synthesis of o-Tol$_3$Ga·OEt$_2$ (1)

A solution of *o*-TolMgBr was prepared by the reaction of *o*-TolBr with magnesium metal in the presence of a trace amount of I_2. Three molar equivalents of this solution (34.08 mmol, 17.04 cm^3, 2.00 M) in diethylether (50 cm^3) was added dropwise to a stirred diethylether solution of $GaCl_3$ (11.36 mmol, 2.00 g) at −78°C. The reaction mixture was allowed to warm (25°C) and then stirred for 12 h before volatile materials

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* Present address: Footnote.

were removed *in vacuo*. The residue was extracted with hexane and filtered. The filtrate was then cooled (−20°C) for 2 days to yield colourless, cubic, X-ray quality crystals of *o*-$Tol_3Ga{\cdot}OEt_2$ (**1**); Mp 98–100°C (rev.), yield 80% based on $GaCl_3$. ^1H NMR (C_6D_6): δ1.95 (s, 9H, *CH₃*-Ph-Ga), 2.20 (b, 6H, O-CH_2-*CH₃*), 3.09 (m, 4H, O-*CH₂*-CH_3), 6.55–6.68 (m, 12H, CH_3-*Ph*-Ga). Anal: Calcd: C, 71.97; H, 7.49%. Found: C, 70.86; H, 7.41%.

Structural solution and refinement

Crystals of **1** were sealed in Lindemann capillaries under an atmosphere of dry argon. Intensities were collected on an Enraf-Nonius CAD-4 diffractometer at 25°C using the $\theta/2\theta$ scan technique. Reflections were measured in the range $2<2\theta<50°$. Of 4489 independent reflections collected, 2195, having $I>3\sigma(I)$ were used for the structure analysis. The intensities were corrected for Lorentz and polarization effects. No empirical absorption correction was applied. Details of the data collection are given in Table I. Positional and equivalent isotropic thermal parameters are listed in Table II and selected bond lengths and angles are given in Table III.

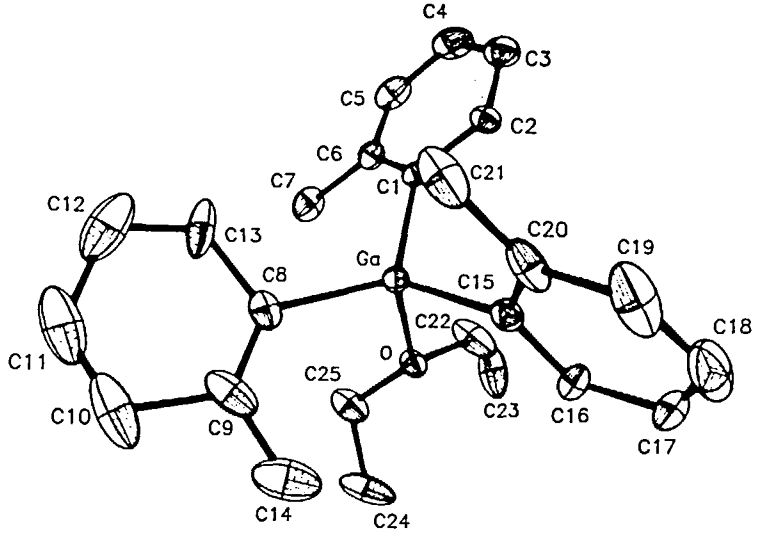
All calculations were performed on a MICROVAX 3100 computer, using the SHELX software package.[4] The structure was solved by Patterson and fourier methods. The hydrogen atoms were placed in their geometrically calculated positions and included in the final structure factor calculations with fixed isotropic thermal parameters. The final R value was 0.0647 ($R_w=0.0744$). Full lists of anisotropic thermal parameters, H atom positions, bond lengths and angles and observed and calculated structure factors are available from R.J. upon request.

TABLE I
Data collection and processing parameters

Formula	$C_{25}H_{31}OGa$
MW	417.28
Space group	$P2_1/n$
a	9.173(1)
b	20.789(1)
c	12.037(1) Å
β	98.93(1)°
V	2267(4) Å^3
Z	4
D_c	1.227 g cm^{-3}
$F(000)$	743.90
μ	12.23 cm^{-1}
Radiation	MoK_α
2θ range	2–50°
Unique reflections	4489
Reflections with $I>3\sigma(I)$	2195
Refined parameters	244
R	0.0647
R_w	0.0744

TABLE II
Positional and equivalent isotropic thermal parameters.

Atom	x/a	y/b	z/c	U(eqv)
Ga	−0.1387(1)	0.16327(5)	0.51741(9)	0.057(6)
O	0.0896(6)	0.1526(3)	0.5719(6)	0.074(27)
C(1)	−0.217(1)	0.1090(5)	0.6318(9)	0.069(9)
C(2)	−0.303(1)	0.0574(5)	0.588(1)	0.076(8)
C(3)	−0.364(1)	0.0166(7)	0.659(1)	0.112(24)
C(4)	−0.338(2)	0.261(9)	0.774(2)	0.146(7)
C(5)	−0.252(2)	0.0771(9)	0.818(1)	0.123(32)
C(6)	−0.191(1)	0.1202(6)	0.749(1)	0.082(12)
C(7)	−0.098(1)	0.1751(7)	0.802(1)	0.115(32)
C(8)	−0.167(1)	0.2584(5)	0.517(1)	0.075(9)
C(9)	−0.114(2)	0.2993(9)	0.453(2)	0.124(7)
C(10)	−0.157(3)	0.368(1)	0.451(2)	0.172(64)
C(11)	−0.252(4)	0.381(2)	0.519(2)	0.191(86)
C(12)	−0.321(2)	0.336(1)	0.592(2)	0.204(64)
C(13)	−0.275(2)	0.2791(7)	0.588(1)	0.133(22)
C(14)	−0.016(2)	0.286(1)	0.382(1)	0.173(57)
C(15)	−0.161(1)	0.1227(5)	0.3655(9)	0.076(15)
C(16)	−0.043(2)	0.0911(7)	0.328(1)	0.135(14)
C(17)	−0.071(3)	0.063(1)	0.219(2)	0.213(62)
C(18)	−0.202(4)	0.064(2)	0.155(2)	0.258(162)
C(19)	−0.308(3)	0.0965(9)	0.189(1)	0.160(111)
C(20)	−0.297(2)	0.1242(6)	0.297(1)	0.100(41)
C(21)	−0.426(1)	0.1587(7)	0.333(1)	0.128(51)
C(22)	0.136(2)	0.0857(7)	0.616(2)	0.189(153)
C(23)	0.260(2)	0.0676(7)	0.642(2)	0.187(60)
C(24)	0.309(2)	0.2153(9)	0.563(2)	0.195(75)
C(25)	0.181(1)	0.2054(7)	0.621(1)	0.116(42)



URE 1 A perspective view of the molecular unit showing atom labelling. H atoms have been omitted
larity.

TABLE III
Selected bond lengths and angles (Å and degrees).

Atoms		Distance	Atoms		Distance
Ga	—O	2.107(6)	Ga	—C(1)	2.00(1)
Ga	—C(8)	2.00(1)	Ga	—C(15)	1.99(1)
O	—C(22)	1.49(1)	O	—C(25)	1.45(1)
C(1)	—C(2)	1.39(1)	C(1)	—C(6)	1.41(1)
C(2)	—C(3)	1.38(2)	C(3)	—C(4)	1.38(2)
C(4)	—C(5)	1.38(2)	C(5)	—C(6)	1.40(2)
C(6)	—C(7)	1.51(2)	C(8)	—C(9)	1.30(2)
C(8)	—C(13)	1.47(2)	C(9)	—C(10)	1.49(3)
C(9)	—C(14)	1.37(2)	C(10)	—C(11)	1.30(4)
C(11)	—C(12)	1.49(4)	C(12)	—C(13)	1.25(3)
C(15)	—C(16)	1.39(2)	C(15)	—C(20)	1.39(2)
C(16)	—C(17)	1.42(2)	C(17)	—C(18)	1.33(4)
C(18)	—C(19)	1.30(4)	C(19)	—C(20)	1.41(2)
C(20)	—C(21)	1.51(2)	C(22)	—C(23)	1.20(2)
C(24)	—C(25)	1.47(2)			

Atoms			Angle	Atoms			Angle
O	—Ga	—C(1)	99.8(3)	O	—Ga	—C(8)	103.3(3)
C(1)	—Ga	—C(8)	119.9(5)	O	—Ga	—C(15)	101.2(4)
C(1)	—Ga	—C(15)	113.4(4)	C(8)	—Ga	—C(15)	115.1(5)
Ga	—O	—C(22)	115.1(7)	Ga	—O	—C(25)	122.1(7)
C(22)	—O	—C(25)	115.1(9)	Ga	—C(1)	—C(2)	115.0(8)
Ga	—C(1)	—C(6)	125.1(9)	C(2)	—C(1)	—C(6)	120(1)
C(1)	—C(2)	—C(3)	120(1)	C(2)	—C(3)	—C(4)	120(1)
C(3)	—C(4)	—C(5)	120(2)	C(4)	—C(5)	—C(6)	122(2)
C(1)	—C(6)	—C(5)	118(1)	C(1)	—C(6)	—C(7)	123(1)
C(5)	—C(6)	—C(7)	119(1)	Ga	—C(8)	—C(9)	126(1)
Ga	—C(8)	—C(13)	113(1)	C(9)	—C(8)	—C(13)	120(2)
C(8)	—C(9)	—C(10)	121(2)	C(8)	—C(9)	—C(14)	126(2)
C(10)	—C(9)	—C(14)	113(2)	C(9)	—C(10)	—C(11)	113(4)
C(10)	—C(11)	—C(12)	129(4)	C(11)	—C(12)	—C(13)	113(3)
C(8)	—C(13)	—C(12)	124(2)	Ga	—C(15)	—C(16)	121(1)
Ga	—C(15)	—C(20)	119(1)	C(16)	—C(15)	—C(20)	119(1)
C(15)	—C(16)	—C(17)	117(2)	C(16)	—C(17)	—C(18)	123(2)
C(17)	—C(18)	—C(19)	118(2)	C(18)	—C(19)	—C(20)	124(3)
C(15)	—C(20)	—C(19)	118(2)	C(15)	—C(20)	—C(21)	121(1)
C(19)	—C(20)	—C(21)	121(2)	O	—C(22)	—C(23)	128(2)
O	—C(25)	—C(24)	111(1)				

RESULTS AND DISCUSSION

A view of the molecule is shown in Figure 1. The coordination geometry about the gallium atom is that of a distorted tetrahedron. The methyl groups of the *o*-tolyl units clearly adopt positions which minimize steric repulsions. The ethyl groups of the diethylether moiety are directed away from the gallium atom. Rather than adopt “propeller” geometry which is observed in Ph$_3$AlPPh$_3$,[5] the phenyl rings in the resent case are oriented with two of the groups being roughly planar while the third rojects its methyl group above the plane. Steric repulsions between the in plane ngs result in a slight increase in the bond angle between them (C(1)-Ga-C(8) 119.9(5)) mpared to the same angles formed with the group projecting above the plane (1)-Ga-C(15) 113.4(4), C(8)-Ga-C(15) 115.1(5)). The Ga-C bond lengths (2.00(1) Å flect a slight steric effect, falling between the mean values for other trialkyl gallium lducts that are sterically hindered to a greater, (t-Bu$_3$GaNH$_2$Ph, Ga-C 2-01(3) Å[2] d lesser, (Me$_3$GaNH$_2$(t-Bu), Ga-C 1.98(3) Å[6] degree.

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