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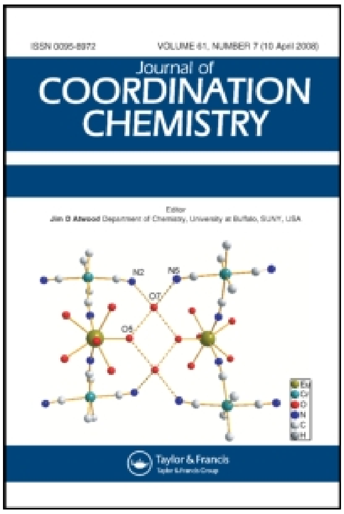

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SYNTHESIS AND STRUCTURES OF TWO BULKY GALLIUM CHLORIDES

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The bulky gallium chlorides, $(t\text{-BuGaCl}_2)_2$ (**1**) and $(\text{Cy}_2\text{GaCl})_2$ ($\text{Cy} = \text{C}_6\text{H}_{11}$) have been prepared *via* the reaction of GaCl_3 with *t*-BuLi and CyMgCl, respectively. The structures of **1** and **2** have been determined by X-ray methods. Crystals of **1** are monoclinic, space group $P2_1/c$, with $a = 6.937(4)$, $b = 6.877(5)$, $c = 17.11(1)$ Å, $\beta = 95.65(6)°$, $Z = 2$; crystals of **2** are monoclinic, space group $P2_1/c$, with $a = 10.389(2)$, $b = 11.580(3)$, $c = 11.198(2)$ Å, $\beta = 95.96(2)°$, $Z = 2$. The R values for **1** and **2** are 0.0617 and 0.0681, respectively. The solid state structures of **1** and **2** consist of chloride-bridged dimers.

Keywords: Gallium(III), *t*-butyl, cyclohexyl, synthesis, X-ray structure

INTRODUCTION

Gallium halides with bulky alkyl or aryl substituents play an important role as starting materials for the preparation of a wide range of mono- and polymetallic derivatives, some of which are useful as precursors to compound semiconductors.[1] In the present paper, we describe the syntheses and X-ray crystal structures of two such gallium halides, namely *t*-butylgallium dichloride (**1**) and dicyclohexylgallium chloride (**2**). Previous examples of structurally characterized bulky alkyl or aryl gallium halides are restricted to $[(\text{Me}_5\text{C}_5)\text{GaCl}_2]_2$,[2] $[(\text{Me}_5\text{C}_5)_2\text{GaCl}]_2$,[2] and the polymer $[(\text{Mes})\text{GaCl}_2]_\infty$ ($\text{Mes} = 1,3,5\text{-Me}_3\text{C}_6\text{H}_2$).[3]

EXPERIMENTAL

Both compounds were prepared under dry nitrogen with use of standard vacuum-line and dry-box techniques. All solvents were dried and distilled prior to use. Instruments: (^{1}H and ^{13}C), General Electric QE 300. NMR spectra were recorded in C_6D_6 and THF-d_8, at ambient temperature and are referenced to Me_4Si; EI–MS, Bell and Howell CEC 24-491; 70·eV CI–MS, Finnigan MAT 4023; CAD-4 diffractometer.

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Preparation of [t-BuGaCl$_2$]$_2$ (1)

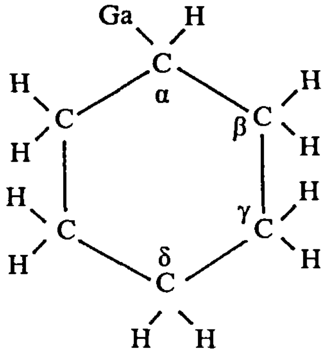
A pentane solution of *t*-BuLi (1.7 *M*, 5.67 mmol 33.4 cm^3) was added dropwise to a stirred solution of $GaCl_3$ (10 g, 5.67 mmol) in 150 cm^3 of dry benzene at room temperature. After completion of the addition, the resulting white suspension was refluxed for 12 h. Filtration afforded a white residue (12 g) which was washed with pentane and dried under vacuum. This solid, which is insoluble in pentane, hexane, benzene and toluene was sublimed under vacuum (10^{-4} Torr, 125°C) to produce 5.6 g (50%) of colourless crystals suitable for X-ray diffraction. The sublimed material (mp 85–86°C) is soluble in pentane, hexane, benzene, toluene and diethyl ether.

^1H NMR (300.15 MHz, THF-d_8, 295K, TMS ext.): $\delta = 1.02$ (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR (75.48 MHz, THF-d_8, 295K, TMS ext.): $\delta = 28.78$ (CH_3), 27.54 (broad s, C-Ga). MS(CI, CH_4): 161(*t*-BuGaCl$^+$), 57(100%, *t*-Bu).

Preparation of [Cy$_2$GaCl]$_2$ (2)

An Et_2O solution of CyMgCl (0.95 *M*, 32.94 mmol, 34.67 cm^3) was added dropwise to a stirred solution of $GaCl_3$ (2.90 g, 16.47 mmol) in 40 cm^3 of Et_2O at −78°C. The reaction mixture was allowed to warm to 25°C over 1 h, then heated to 60°C for 4 h prior to solvent removal (10^{-3} Torr) and hexane extraction. Filtration of the resulting colourless solution followed by solvent removal afforded an 85% yield of colourless **2**. X-ray quality crystals of **2** (mp 121–3°C) were produced by dissolution in Et_2O (40 cm^3) and cooling to −30°C for two weeks. Compound **2** is moderately air sensitive (decomposition in air occurs in 2 h); it does not sublime under vacuum (0–150°C, 10^{-3} Torr).

^1H NMR (300.15 MHz, C_6D_6, 295K, TMS ext.): $\delta = 1.71$ (m, 2H, δ CH_2) $\delta = 1.38$ (m, 4H, γ-CH_2) $\delta = 1.02$ (q, 4H, β-CH_2) $\delta = 0.88$ (t, 2H, α-CH) $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 295K, TMS ext.): $\delta = 33.82$ (δ-*C*), $\delta = 29.27$ (γ-*C*), $\delta = 28.36$ (β-*C*), $\delta = 26.77$ (α-*C*)



MS(EI): 506 (M$^+$-Cl), 340 (M$^+$-Cl−2Cy), 272 (Cy_2GaCl^+), 235 (100%, Cy_2Ga^+), 187 (CyGaCl$^+$), 152, (CyGa$^+$).

X-Ray Crystal Structure Analyses of (t-BuGaCl(μ-Cl))$_2$ (1) and (Cy$_2$Ga(μ-Cl))$_2$ (2)

Crystals of **1** and **2** were sealed in Lindemann capillaries under an atmosphere of dry argon. Intensities were collected on an Enraf-Nonius CAD-4 diffractometer at 25°C

TABLE I
Atomic coordinates for $(t\text{-BuGaCl}(\mu\text{-Cl}))_2$ (**1**).

atom	x/a	y/b	z/c
Ga	0.8262(2)	0.1555(2)	0.46858(9)
Cl(1)	0.8366(5)	0.8239(6)	0.5002(2)
Cl(2)	0.7045(6)	0.2904(6)	0.5648(2)
C(1)	0.750(2)	0.207(2)	0.3549(8)
C(2)	0.800(3)	0.423(3)	0.342(1)
C(3)	0.527(3)	0.187(3)	0.3389(9)
C(4)	0.875(4)	0.083(3)	0.310(1)

TABLE II
Atomic coordinates for $(\text{Cy}_2\text{Ga}(\mu\text{-Cl}))_2$ (**2**).

atom	x/a	y/b	z/c
Ga	0.47192(9)	0.85851(8)	0.47156(9)
Cl	0.5304(2)	0.0199(2)	0.3559(2)
C(1)	0.2915(8)	0.8252(6)	0.4148(7)
C(2)	0.1992(8)	0.9276(9)	0.412(1)
C(3)	0.0605(9)	0.893(1)	0.369(1)
C(4)	0.050(1)	0.831(1)	0.253(1)
C(5)	0.1399(9)	0.729(1)	0.2543(9)
C(6)	0.2787(8)	0.7657(8)	0.2952(8)
C(11)	0.6234(7)	0.7605(7)	0.5021(7)
C(12)	0.6939(9)	0.7327(8)	0.3929(8)
C(13)	0.804(1)	0.6502(8)	0.421(1)
C(14)	0.766(1)	0.5412(8)	0.4788(8)
C(15)	0.6989(8)	0.5652(8)	0.5888(9)
C(16)	0.5870(8)	0.6484(7)	0.5617(8)

using the $\theta/2\theta$ scan technique. Reflections were measured in the ranges $2 < 2\theta < 40°$ and $2 < 2\theta < 55°$ for **1** and **2** respectively. Of 1302 (**1**) and 1869 (**2**) independent reflections collected, 989 (**1**) and 1366 (**2**), having $I > 3\sigma(I)$ were used for the structure analyses. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to **1**, but not to **2**.

Crystal Data

Compound **1**: $C_8H_{18}Cl_4Ga_2$, $M = 395.48$, monoclinic, $P2_1/c$, $a = 6.937(4)$, $b = 6.877(5)$, $c = 17.11(1)$ Å, $\beta = 95.65(6)°$, $V = 812(5)$ Å^3, $Z = 2$, $Dc = 1.623$ gcm^{-3}, $F(000) = 392$, $\mu(\text{MoK}\alpha) = 39.57$ cm^{-1}.

Compound **2**: $C_{24}H_{44}Cl_2$, $M = 542.35$, monoclinic, $P2_1/c$, $a = 10.389(2)$, $b = 11.580(3)$, $c = 11.198(2)$ Å, $\beta = 95.96(2)°$, $V = 1340(2)$ Å^3, $Z = 2$, $Dc = 1.351$ gcm^{-3}, $F(000) = 568$, $\mu(\text{MoK}\alpha) = 43.89$ cm^{-1}.

All calculations were performed on a MICROVAX 3100 computer, using the SHELX software package.[4] Both structures were 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 isotropic thermal parameters. The final R values were 0.0617 and 0.0681 for **1** and **2** respectively. Atomic coordinates for **1** and **2** are listed in Tables I and II, respectively.

RESULTS AND DISCUSSION

Compounds **1** and **2** were made by metathetical reactions from $GaCl_3$ (eq. *1* and *2*, respectively).

$$GaCl_3 + t\text{-BuLi} \longrightarrow 1/2(t\text{-BuGaCl}_2)_2 \qquad (1)$$

$$GaCl_3 + 2CyMgCl \longrightarrow 1/2(Cy_2GaCl)_2 \qquad (2)$$

$$Cy = C_6H_{11}$$

The yields of **1** and **2** are 50 and 85%, respectively. Both compounds are moderately air sensitive. In the case of **1**, the initially formed product is apparently polymeric since it is insoluble in pentane, hexane, benzene, and toluene.[5] However, vacuum sublimation results in conversion to the soluble, dimeric (in the solid state) form. These results contrast with those in an earlier report[6] in which it was noted that **1** is a pale yellow liquid.

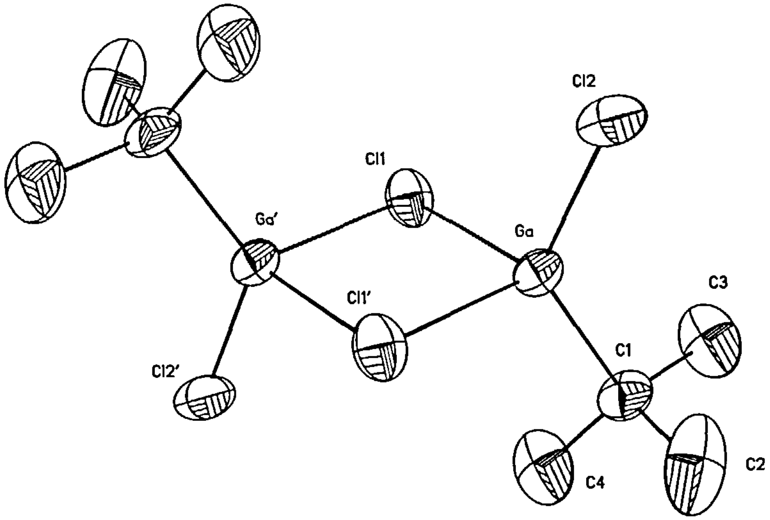


FIGURE 1 Structure of $(t\text{-BuGaCl}(\mu\text{-Cl}))_2$ (**1**) showing the atom numbering scheme.

Compounds **1** (Figure 1) and **2** (Figure 2) both exist as chloride-bridged dimers in the solid state. Key bond distances and angles for **1** and **2** are given in Tables III and IV, respectively. The Ga_2Cl_2 moieties of both compounds are close to square planar. However, the Ga–Cl bond lengths for **2** (average 2.390(2) Å) are somewhat longer than those for **1** (average 2.347(4) Å). Doubtless, this arises from the fact that **2** features two bulky alkyl groups. In fact, it has been noted previously[2] that increasing the steric bulk of the substituents in terminal positions results in increases in the bridging Ga–Cl bond distances. Moreover, these changes are accompanied by increases and decreases in the Ga–Cl–Ga bond and Cl–Ga–Cl bond angles, respectively. It can be seen from Table V that, in general, the metric parameters for **1** and **2** follow these trends. However, note that the Ga–Cl–Ga and Cl–Ga–Cl bond angles

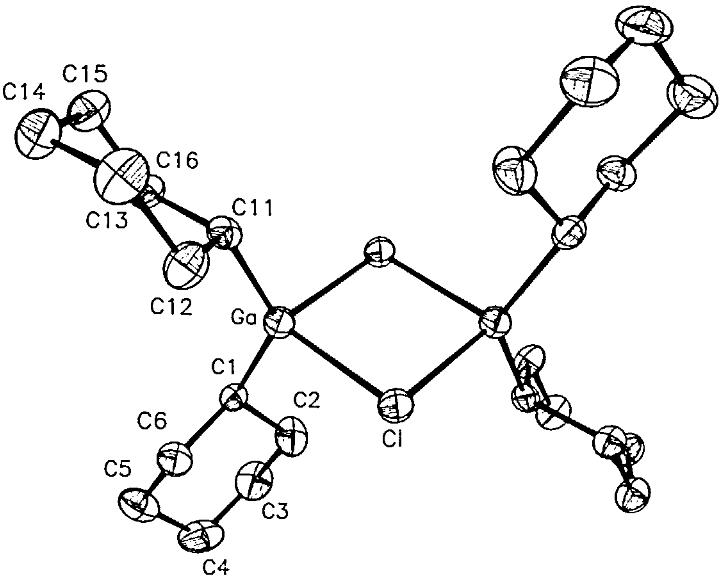


FIGURE 2 Structure of (Cy$_2$Ga(μ-Cl))$_2$ (2) showing the atom numbering scheme.

TABLE III
Key bond distances (Å) and bond angles (°) for (*t*-BuGaCl(μ-Cl))$_2$ (2).

Bond distances

Ga-Cl(1)	2.343(4)	Ga-Cl(1)′	2.352(4)
Ga-Cl(2)	2.136(4)	Ga-C(1)	2.00(1)
C(1)-C(2)	1.54(2)	C(1)-C(3)	1.55(2)
C(1)-C(4)	1.49(2)	Ga-Ga	3.56

Bond angles

Cl(1)-Ga-Cl(1)′	89.9(2)	Cl(1)-Ga-Cl(2)	104.5(2)
Cl(1)-Ga-Cl(1)	113.4(5)	Cl(2)-Ga-C(1)	125.9(5)
Ga-Cl(1)-Ga′	89.3(2)	Ga-C(1)-C(2)	105(1)
Ga-C(1)-C(3)	109(1)	C(2)-C(1)-C(3)	107(2)
Ga-C(1)-C(4)	107(1)	C(2)-C(1)-C(4)	109(2)
C(3)-C(1)-C(4)	119(2)		

for **2** are out of sequence. Steric hindrance is also responsible for the observation that the C–Ga–C angle in **2** (132.4(3)°) is appreciably wider than the Cl–Ga–C angle in **1** (125.9(5)°). The fact that the terminal Ga–Cl bonds (2.136(4) Å) of **1** are shorter than the bridge bonds (average 2.347(4) Å) is expected and consistent with other structures (Table V). Finally, the Ga–C bond distances in **1** [2.00(1)] and **2** [av. 1.948(8)] are similar to the average bond distances in e.g. Ga(C$_6$H$_5$)$_3$ [1.947(1)],[8] MeGa(O$_2$CMe)$_2$ [1.946],[8] and [(Me$_5$C$_5$)GaCl$_2$]$_2$ [1.97(1)].[2]

TABLE IV
Key bond distances (Å) and bond angles (°) for $(Cy_2Ga(\mu\text{-}Cl))_2$ (**2**).

Bond distances

Ga-Cl	2.388(2)	Ga-Cl′	2.393(2)
Ga-C(1)	1.954(8)	Ga-C(11)	1.942(8)
C(1)-C(2)	1.52(1)	C(1)-C(6)	1.50(1)
C(2)-C(3)	1.52(1)	C(3)-C(4)	1.48(2)
C(4)-C(5)	1.50(1)	C(5)-C(6)	1.53(1)
C(11)-C(12)	1.52(1)	C(11)-C(16)	1.52(1)
C(12)-C(13)	1.50(1)	C(13-C(14)	1.49(1)
C(14)-C(15)	1.50(1)	C(15)-C(16)	1.52(1)
Ga-Ga	3.63		

Bond angles

Cl′-Ga-Cl	90.1(2)	Cl-Ga-C(1)	105.5(2)
Cl′-Ga-C(1)	106.8(2)	Cl-Ga-C(11)	107.8(2)
Cl′-Ga-C(11)	106.1(2)	C(1)-Ga-C(11)	132.4(3)
Ga′-Cl-Ga	89.9(1)	Ga-C(1)-C(2)	115.6(6)
Ga-C(1)-C(6)	112.0(6)	C(2)-C(1)-C(6)	110.0(7)
C(1)-C(2)-C(3)	112.1(8)	C(2)-C(3)-C(4)	112.5(8)
C(3)-C(4)-C(5)	113.0(9)	C(4)-C(5)-C(6)	110.2(9)
C(1)-C(6)-C(5)	113.0(7)	Ga-C(11)-C(12)	115.5(6)
Ga-C(11)-C(16)	110.0(5)	C(12)-C(11)-C(16)	109.4(7)
C(11)-C(12)-C(13)	112.9(8)	C(12)-C(13)-C(14)	113.3(8)
C(13)-C(14)-C(15)	111.6(8)	C(14)-C(15)-C(16)	111.4(8)
C(11)-C(16)-C(15)	114.1(7)		

TABLE V
Trends in bond distances (Å) and bond angles (°) for gallium chlorides.

Compound	Ga-Cl(t)[a]	Ga-Cl(b)[a]	Cl(b)-Ga-Cl(b)	Ga-Cl(b)-Ga	Reference
$(GaCl_3)_2$	2.06(3)	2.29(9)	94(2)	86(2)	7
$(t\text{-}BuGaCl_2)_2$ (**1**)	2.136(4)	2.347(4)	89.9(2)	89.3(2)	this work
$[(Me_5C_5)GaCl_2]_2$	2.124(4)	2.362(3)	88.6(1)	91.4(1)	2
$(Cy_2GaCl)_2$ (**2**)		2.390(2)	90.1(2)	89.9(1)	this work
$[(Me_5C_5)GaCl]_2$		2.447(8)	82.6(2)	97.4(2)	2

[a] t = terminal; b = bridge.

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