The Crystal Structures of Dimeric Di(*tert*-butyl)aluminium and -gallium Iodides

Xin Tian[a], Roland Fröhlich[b], and Norbert W. Mitzel[a]

[a] Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster,
Corrensstr. 30, D-48149 Münster, Germany
[b] Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster,
Corrensstr. 40, D-48149 Münster, Germany

Reprint requests to Prof. Dr. N.W. Mitzel. Fax: +49 (0)251 83 36007.
E-mail: mitzel@uni-muenster.de

The syntheses of di^{t}butylaluminium and -gallium iodide *via* metathesis reactions of the respective chlorides with lithium iodide are reported. The compounds were identified by elemental analyses, multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{27}Al) and mass spectra (EI). The structures obtained by single crystal X-ray diffraction reveal that the new compound ^{t}Bu$_2$AlI crystallizes in the monoclinic crystal system, space group $P2_1/n$, as a dimer with a planar Al$_2$I$_2$ four-membered ring. The crystal structure of the monoclinic structure of ^{t}Bu$_2$GaI was redetermined. Its mass spectra reveal the existence of trimers and dimers in addition to the predominant monomeric species in gas phase.

Key words: Aluminium, Gallium, Organometallic Compounds, Crystal Structure

Introduction

The alkyl-aluminium halides have been widely used in inorganic synthesis and as catalysts or co-catalysts in the isomerization and polymerization of olefins [1], as well as in many other reactions. A large number of investigations on their synthesis, properties, structures and also their applications have been reported [2]. Among these organometallic aluminium halide compounds the most reactive are alkyl-aluminium iodides, such as Me$_n$AlI$_{3-n}$ ($n = 1, 2$) [3] or Et$_n$AlI$_{3-n}$ [4]. In contrast to the established butyl-substituted organoaluminium systems ^{i}Bu$_n$AlI$_{3-n}$ and ^{n}Bu$_n$AlI$_{3-n}$ [5], to the best of our knowledge, ^{t}Bu$_2$AlI has not been reported so far.

Result and Discussion

Synthesis of ^{t}Bu$_2$AlI (**1**) and ^{t}Bu$_2$GaI (**2**)

The metathesis reactions between ^{t}Bu$_2$MCl (M = Al, Ga) and LiI in hexane give the corresponding di^{t}butyl-metal iodides.

$$^t\text{Bu}_2\text{MCl} + \text{LiI} \xrightarrow{\text{hexane}} t\text{Bu}_2\text{MI} + \text{LiCl} \text{ (M = Al, Ga)}$$
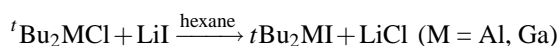
Both compounds are sensitive to oxygen and moisture. They dissolve well in non-polar solvents such as pentane and hexane, but even better in toluene or ethers, and were isolated as colourless crystalline materials upon cooling hexane solutions to -25 °C. Compound **2** has a melting point at 124 °C and is thermally more stable than **1**, which decomposes before the onset of melting. Compounds **1** and **2** have been identified by elemental analyses, by NMR spectroscopy of the nuclei ^{1}H, ^{13}C (and ^{27}Al for **1**) in C$_6$D$_6$, by mass-spectra (EI) and by single crystal X-ray crystallography. In the mass spectra of compound **1**, the predominant mass peaks correspond to the dimer cations, but mass peaks corresponding to the monomer cations are also observed. These can be formed either by the ionization of monomers present in the gas phase and/or by decay upon ionization of the dimers. In the mass spectra of compound **2**, the predominant mass peaks correspond to the monomer cations. Additionally there are also peaks with higher masses than that of the dimer, the largest being at $m/z = 635$ (3.33 %), which corresponds to the (Bu$_2$Ga$_2$I$_3$)$^+$ cation. However, no mass peaks were found beyond $m/z = 700$. This indicates the existence of trimeric aggregates of compound **2** in addition to dimers and the predominance of the monomers in the gas phase.

Crystal structures of ^{t}Bu$_2$AlI (**1**) and ^{t}Bu$_2$GaI (**2**)

Compound **1** crystallizes as a dimer in the a monoclinic space group $P2_1/n$. The dimeric molecule in

Table 1. Selected bond lengths and angles of **1** and **2**, together with the values of ^{t}Bu$_2$GaI from [11] [Å, °]. Symmetry transformations used to generate equivalent atoms (denoted with *): **1** $(-x, -y+2, -z+1)$ and **2** $(-x, -y, -z+1.)$.

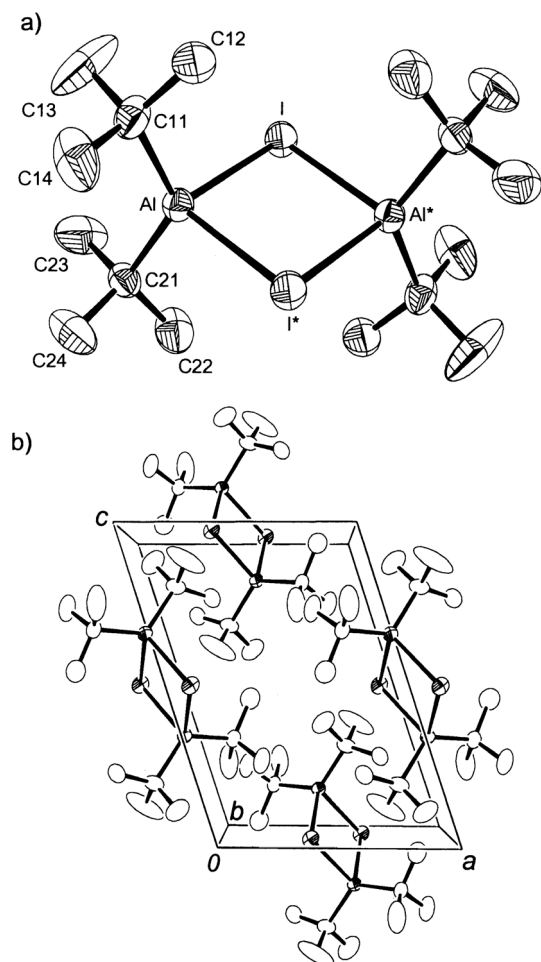|	^{t}Bu$_2$AlI (**1**)	^{t}Bu$_2$GaI (**2**)	^{t}Bu$_2$GaI [11]
I-M	2.717(1)	2.758(1)	2.758(1)
M-C21	1.985(2)	2.001(3)	2.027(9)
M-C11	1.986(2)	1.999(3)	2.010(10)
M-I*	2.711(1)	2.765(1)	2.753(1)
M*-I-M	86.9(1)	88.0(1)	88.3(1)
I*-M-I	93.1(1)	92.0(1)	91.8(1)
C21-M-C11	124.2(1)	127.4(1)	126.8(4)
C21-M-I	109.4(1)	108.3(1)	108.6(3)
C11-M-I	108.6(1)	107.0(1)	108.0(3)
C21-M-I*	108.9(1)	108.3(1)	108.5(3)
C11-M-I*	108.2(1)	108.0(1)	107.4(3)
C14-C11-M	108.9(2)	107.9(2)	108.1(9)
C12-C11-M	114.3(2)	113.9(2)	113.4(8)
C13-C11-M	108.6(2)	107.2(2)	106.3(8)
C24-C21-M	109.3(2)	108.0(2)	108.0(8)
C23-C21-M	109.2(2)	107.6(2)	107.6(8)
C22-C21-M	113.5(2)	113.2(2)	113.6(8)

Fig. 1. Crystal structure of **1**. a) ORTEP drawing with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. b) The cell contents of **1** projected on (010) (only the front half components are depicted for clarity). Symmetry transformation used to generate equivalent atoms: $-x$, $-y+2$, $-z+1$.

the crystal has a centre of inversion in the middle of the planar four-membered Al$_2$I$_2$ ring. As it is shown in Fig. 1, the dimeric structure has two four-coordinated Al centres, one of the dominating coordination modes of organometallic compounds of Group 13 metals in the oxidation state +3 [2]. Selected bond lengths and angles are listed in Table 1.

As expected all the *endo*-cyclic angles in the four-membered Al$_2$I$_2$ ring of compound **1** are close to 90°: the Al-I-Al angles at the bridging I atoms are 86.9(2)° and the I-Al-I angles 93.1(2)°. These values are quite similar to the corresponding angles in

solid [AlI$_3$]$_2$ [Al-I-Al 83.9(7) and 84.9(7)°, I-Al-I 95.2(7) and 95.9(7)°] [6] and in [^{t}Bu$_2$AlCl]$_2$ [Al-Cl-Al 87.2(1)°, Cl-Al-Cl 92.8(1)°] [7]. Thus the coordination geometry of the Al atom can be described as distorted tetrahedral with the most acute angle associated with the Al$_2$I$_2$ ring. The Al-I bonds at 2.711(1) and 2.717(1) Å are much longer than the average Al-I (bridging) bonds in [AlI$_3$]$_2$, in the solid phase 2.62 Å [6] and also in the gas phase 2.64 Å [8], and also much longer than the average terminal Al-I bonds in [AlI$_3$]$_2$, in the solid phase at 2.48 Å [6] and in the gas phase at 2.45 Å [8]. The C-Al-C angle at the Al atom at 124.2(1)° is only slightly larger than in [^{t}Bu$_2$AlCl]$_2$ [123.6(3)°] [7] and in dimeric [Me$_3$Al]$_2$ in the solid phase [123.2(1)] [9], and more than 15° larger than the ideal tetrahedral angles due to the steric repulsion of the bulky ^{t}Bu groups. The Al-C bond lengths at 1.985(2) and 1.986(2) Å are only slightly longer than those in [^{t}Bu$_2$AlCl]$_2$ [1.982(9) and 1.966(6) Å] [7] and much longer than the corresponding Al-C bonds in dimeric [Me$_3$Al]$_2$ [1.949(2) and 1.956(2) Å] [9], but shorter than the Al-C bond lengths in ^{t}Bu$_3$Al (between 2.003 and 2.007 Å) [10].

The crystal structure of ^{t}Bu$_2$GaI was redetermined and data of improved quality and better defined atomic positions were obtained ($R_1 = 0.0265$ compared with the earlier work $R_1 = 0.036$ [11]). Selected bond lengths and angles of **2** together with the values from the earlier structure determination [11] are listed in Table 1 for comparison with the data of **1**. The Ga-C

Table 2. Crystal and refinement data of **1** and **2**.

	[^{t}Bu$_2$AlI]$_2$ (**1**)	[^{t}Bu$_2$GaI]$_2$ (**2**)
Cryst. system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	8.646(1)	8.648(1)
b [Å]	12.392(1)	12.418(1)
c [Å]	11.442(1)	11.418(1)
β [°]	109.12(1)	109.02(1)
V [Å^3]	1158.3(2)	1159.2(2)
ρ_{calc} [g cm^{-3}]	1.537	1.781
Z	2	2
μ [mm^{-1}]	2.784	4.980
Temp. [K]	198(2)	198(2)
λ [Å]	0.71073	0.71073
$T_{min/max}$	0.4424/0.5428	0.3690/0.6358
$2\theta_{max}$ [°]	56.54	56.56
Measd. refl.	7076	6889
Unique refl.	2806	2807
Observed refl.	2654	2555
R_{int}	0.021	0.036
Parameters	97	97
$R_1[I > 2\sigma(I)]$	0.0226	0.0265
wR_2 (all data)	0.0549	0.0686
ρ_{fin} (min/max) [eÅ^3]	−0.603/0.351	−0.603/0.500
CCDC-No.	255452	255453

bonds at 1.999(3) and 2.001(3) Å in **2** are only slightly longer than the Ga-C bonds at 1.983(3) Å in the trimeric [^{t}Bu$_2$GaCl]$_3$ [12], and the average Ga-C bond length at 1.985 Å in Me$_3$Ga in solid state [13]. The C-Ga-C angles in **2** at 127.4(1)° are 4° smaller than the corresponding angles in [^{t}Bu$_2$GaCl]$_3$ at 131.6(2)° [12].

Experimental Section

General remarks

All reactions and manipulations were carried out under a dry nitrogen atmosphere with standard Schlenk and high vacuum techniques using double manifolds or in a glove box under argon. Solvents were purified and dried by standard methods immediately prior to use. NMR data were collected on a Varian Inova 500 (499.8 MHz for ^{1}H, 125.7 MHz for ^{13}C, 130 MHz for ^{27}Al) in C$_6$D$_6$ as solvent. Chemical shifts are quoted relative to TMS or 1 M Al(NO$_3$)$_3$ aqueous solution. A Nonius Kappa-CCD X-ray diffractometer was used to collect the reflections for single crystal structure determination. Electronic ionization (EI) mass spectra were obtained by a Varian MAT 212 mass spectrometer (70 eV). ^{t}Bu$_2$AlCl [14] and ^{t}Bu$_2$GaCl [15] were prepared by literature methods.

*General procedure for the preparation of ^{t}Bu$_2$AlI (**1**) and ^{t}Bu$_2$GaI (**2**)*

A solution of ^{t}Bu$_2$MCl in 20 ml of hexane was added dropwise to a suspension of LiI in hexane (20 ml) at −78 °C with vigorous stirring. The reaction mixture was stirred overnight and allowed to warm up to ambient temperature. The mixture was filtered through a sintered glass filter (porosity no. 4), the resulting clear solution was concentrated under vacuum until it became slightly cloudy and then was cooled slowly to −25 °C overnight. In this way, colourless, well formed crystals were obtained.

^{t}Bu$_2$AlI (**1**): ^{t}Bu$_2$AlCl (0.35 g, 2.0 mmol) and LiI (0.27 g, 2.0 mmol). Yield: 0.28 g, 53%. – ^{1}H NMR (C$_6$D$_6$): δ = 1.16 (s, $^1J_{CH}$ = 136.5 Hz). – ^{13}C NMR (C$_6$D$_6$): δ = 1.4 (Al*C*CH$_3$), 29.4 (AlC*C*H$_3$). – ^{27}Al NMR (C$_6$D$_6$): δ = 149 ($v_{1/2}$ = 6500 Hz). – MS [EI, 70 eV] m/z (%) = 536 (2.73) [2M$^+$], 479 (76.59) [2M$^+$-Bu], 268 (27.06) [M$^+$], 211 (70.04) [M$^+$-Bu], 128 (17.86) [I$^+$], 57 (100) [Bu$^+$]. C$_8$H$_{18}$AlI (268.12): calcd. C 35.84, H 6.77; found C 35.30, H 6.70.

^{t}Bu$_2$GaI (**2**): ^{t}Bu$_2$GaCl (0.35 g, 1.6 mmol) and LiI (0.21 g, 1.6 mmol). Yield: 0.24 g, 49%. – M.p. 124 °C. – ^{1}H NMR (C$_6$D$_6$): δ = 1.25 (s, $^1J_{CH}$ = 125.2 Hz). – ^{13}C NMR (C$_6$D$_6$): δ = 1.4 (Ga*C*CH$_3$), 29.6 (GaC*C*H$_3$). – MS (EI, 70 eV) m/z (%) = 635 (3.33) [(Bu$_2$Ga$_2$I$_3$)$^+$], 565 (1.26) [(Bu$_3$Ga$_2$I$_2$)$^+$], 451 (2.03) [(BuGa$_2$I$_2$)$^+$], 380 (5.04) [(BuGaI$_2$)$^+$], 310 (27.19) [M$^+$], 253 (100) [M$^+$-Bu], 196 (36.32) [M$^+$-2Bu], 126 (22.56) [M$^+$-2Bu-I]. – C$_8$H$_{18}$GaI (310.86): calcd. C 30.91, H 5.84; found C 30.29, H 5.75.

Crystal structure analyses

Structure solutions were carried out using direct methods and the refinements of the structures were undertaken with the program SHELXTL 6.10 [16]. Further details of data collections and refinements are listed in Table 2. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications (Table 2). Copies of the data can be obtained freely from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk].

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