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Binuclear alkylmetallane dioldiates ${}^t\text{Bu}_4\text{M}_2(\text{diol}-(\text{H}))_2$ ($\text{M} = \text{Al}, \text{Ga}$) and their reactions with aluminium- and gallium trialkyls

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Abstract

Reactions of 1,2-di(hydroxymethyl)benzene with ${}^t\text{Bu}_3\text{M}$ ($\text{M} = \text{Al}, \text{Ga}$) yield binuclear compounds [${}^t\text{Bu}_4\text{M}_2(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH})_2$], $\text{M} = \text{Al}$ (**1**) and $\text{M} = \text{Ga}$ (**2**) respectively. Compounds **1** and **2** as bifunctional (two OH groups), tetradentate (4O) ligands react with aluminium- and gallium trialkyls with formation of trinuclear products [${}^t\text{Bu}_4\text{XM}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$] [$\text{M} = \text{Al}$, $\text{X} = {}^t\text{Bu}$ (**3**); $\text{M} = \text{Ga}$, $\text{X} = {}^t\text{Bu}$ (**4**); $\text{M} = \text{Ga}$, $\text{X} = \text{Me}$ (**6**)]. The transmetalation reaction of the compound **6** with one equivalent of Me_3Ga causes the exchange of ${}^t\text{Bu}_2\text{Ga}$ unit and formation of the new mixed-ligand compound ${}^t\text{Bu}_2\text{Me}_3\text{Ga}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**7**). The transmetalation reaction is considered as a method of synthesis of mixed-ligand and mixed-metal complexes of Group 13 alkyls with multidentate ligands. The molecular structures of $\text{Me}_3\text{Al}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**5**), **6** and **7** have been determined by X-ray crystallography.

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Keywords: Aluminium; Gallium; Diols; 1,2-Di(hydroxymethyl)benzene; Transmetalation

1. Introduction

The reactions of aluminium-, gallium- and indium-trialkyls with one equivalent of alcohol afford mainly dimeric complexes [$(\text{R}_2\text{MOR}^1)_2$] containing a M_2O_2 four-membered ring core [1]. Dimethylmetallane methoxides are trimeric due to the sterically non-demanding alkoxide and alkyl ligands [2]. The interaction of bifunctional alcohols (diols) with R_3M ($\text{M} = \text{Al}, \text{Ga}$; $\text{R} = \text{alkyl}$ group) leads to the formation of a number of binuclear and trinuclear metal diolate complexes of the type **A** and **B**, respectively (Scheme 1) [3].

The compounds **A** were described as bifunctional tetradentate ligands, which can react with Group 13 hydrides and alkyls. One equivalent of R_3M (where $\text{M} = \text{Al}, \text{Ga}$; $\text{R} = \text{H}, \text{Cl}, \text{alkyl}$) reacts with the two acidic protons of the dimer **A**, which results in the introduction

of the central metal. Therefore the complexes **A** have been considered as intermediate products in the formation of the trimetallic diolates of the type **B** [4]. The examples of trinuclear mixed-metal and mixed-ligand diolates have been reported [3], however we have recently found, that some of the dimers of **A** type are inactive toward the reaction with R_3M [5]. In an effort to gain a deeper understanding of the reaction mechanism of Group 13 trialkyls with diols an investigation of the reactions of 1,2-di(hydroxymethyl)benzene with trialkylalanes and gallanes has been undertaken.

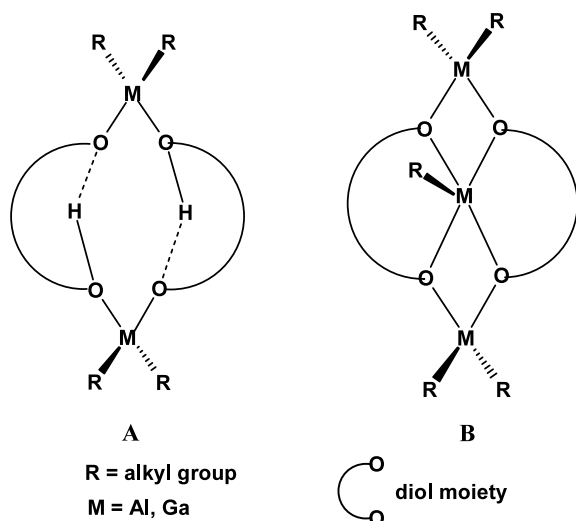
2. Results and discussion

The binuclear complexes [${}^t\text{Bu}_4\text{M}_2(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH})_2$] [$\text{M} = \text{Al}$ (**1**); $\text{M} = \text{Ga}$ (**2**)] are formed by reaction of ${}^t\text{Bu}_3\text{M}$ [$\text{M} = \text{Al}, \text{Ga}$] with 1,2-di(hydroxymethyl)benzene in nearly quantitative yield (Scheme 2).

The reaction produces the complexes **1** and **2** independently on the molar ratio of the reagents. The unreacted diol or ${}^t\text{Bu}_3\text{M}$ is present in the post-reaction

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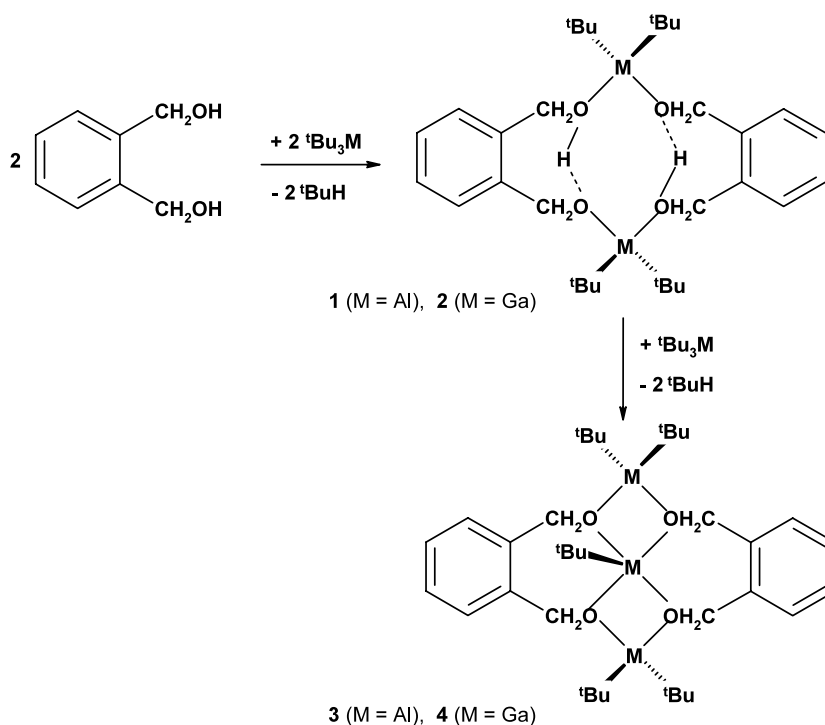
Scheme 1. Binuclear and trinuclear metal diolate complexes.

mixture when the molar ratio of the reagents is other than 1:1. In the presence of Group 13 alkyls the compounds **1** and **2** are considered as bifunctional (two OH groups), tetradentate (4O) ligands. They react with the excess of $t\text{Bu}_3\text{M}$ to give trimetallic products $[\text{tBu}_5\text{M}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2]$ [M = Al (**3**); M = Ga (**4**)] (Scheme 2). It was observed that after one month at r.t. in the presence of one equivalent of $t\text{Bu}_3\text{Al}$, 60% of **1** was transformed into **3** (on the basis of the integration of CH_2O groups signals of **1** and **3** in $^1\text{H-NMR}$ spectrum of the post-reaction mixture). The same reaction in refluxing toluene yields **3** after 4 h. Com-

pound **1** may be stored for long time at -25°C without changes. The complexes **1–4** were characterised by ^1H - and ^{13}C -NMR as well as elemental analysis and molecular weight determination. Unfortunately, we were unable to characterise the complexes crystallographically.

The $^1\text{H-NMR}$ spectra of **1** and **2** indicate the presence of alcohol protons involved in intra-molecular hydrogen bonding. Downfield shifted broadened singlets (16.35 and 14.48 ppm in the spectra of **1** and **2**, respectively) are consistent with the increased acidity of the OH protons. Similar intra-molecular hydrogen bonding was observed in *tert*-butylmetallane complexes of 2,2-dimethylpropane-1,3-diol [4], 2,2'-di(hydroxymethyl)biphenyl [5] and butane-1,4-diol [3i]. In recent years, it has been demonstrated that inter- and intra-molecular hydrogen bonds play a significant role in the structure engineering of Group 13 compounds incorporating multidentate ligands [6]. The CH_2 protons of diol moieties are equivalent and appear as singlets (at 4.61 ppm for **1** and 4.65 ppm for **2**) in the $^1\text{H-NMR}$ spectra. The $^{13}\text{C-NMR}$ spectrum of **1** reveals one signal of CH_2O carbon atoms (at 66.18 ppm) and one signal of $\text{AlC}(\text{CH}_3)_3$ carbon atoms (at 30.94 ppm) which is fully consistent with the structure **1**. The NMR spectroscopy of the *tert*-butylgallane complex **2** is also consistent with the proposed constitution (see Section 3).

The $^1\text{H-NMR}$ spectrum of the trinuclear complex **3** reveals the signals of two $(\text{CH}_3)_3\text{CAI}$ groups *syn* and two $(\text{CH}_3)_3\text{CAI}$ groups *anti* (the singlets at 1.40 and 1.16 ppm) to the *tert*-butyl group bonded to the central



Scheme 2.

aluminium atom (singlet at 0.68 ppm). The CH_2 protons of the ligands with hindered rotation (AB system) appear as the doublet of doublets ($\delta_A = 4.73$ ppm, $\delta_B = 4.58$ ppm, $J_{AB} = 12.4$ Hz). The presence of one signal (at 66.24 ppm) of CH_2O carbons in the ^{13}C -NMR spectrum indicates the equivalence of CH_2O groups. The NMR spectra of compound **4** reveal similar signals, because the trinuclear alkylalane and alkylgallane complexes **3** and **4** are isostructural (see Section 3).

A similar trimetallic methylalane complex of 1,2-di(hydroxymethyl)benzene $\text{Me}_5\text{Al}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**5**) was earlier synthesised by reaction of Me_3Al with 1,2-di(hydroxymethyl)benzene and characterised by spectroscopy [3a]. In this paper we report the crystal structure of **5**. Data collection and structure analysis are presented in Table 1. The molecular structure of **5** is shown in Fig. 1.

The centrosymmetric molecule of **5** consists of a tetracyclic structure formed from two Al_2O_2 four-membered rings and two AlO_2C_4 seven-membered rings. The geometry about the central aluminium atom is a distorted trigonal bipyramid with O(1) and O(1') occupying the axial positions [$\text{O}(1)\text{--Al}(1)\text{--O}(1')$ $156.39(15)^\circ$] and C(11), O(3) and O(3') defining the equatorial sites. The sum of the angles about the O(1)

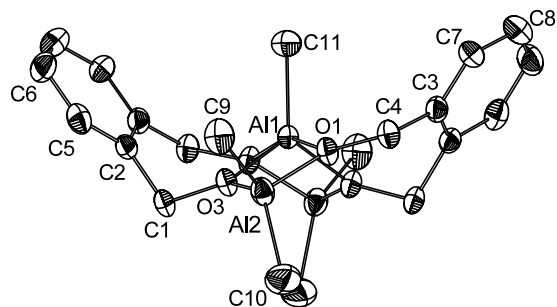


Fig. 1. Crystal structure of the trialuminium complex $\text{Me}_5\text{Al}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**5**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$): Al(1)–O(1) 1.918(2), Al(1)–O(3) 1.836(2), Al(1)–C(11) 1.938(5), Al(2)–O(1) 1.809(2), Al(2)–O(3) 1.813(2), O(3')–Al(1)–O(3) 116.8(2), O(1)–Al(1)–O(1') 156.4(2), O(3')–Al(1)–O(1) 91.1(1), O(3)–Al(1)–O(1) 76.5(1), O(3)–Al(1)–C(11) 121.6(8), O(1)–Al(1)–C(11) 101.8(1).

and O(3) atoms are equal to 359.9 and 360.0° , respectively, which indicates a lack of strain in the seven-membered cycles. The terminal aluminium centres in **5** are coordinated in a distorted tetrahedral fashion by two alkyl groups and two oxygen atoms of the diol moiety. The molecule adopts a boat-like conformation with the two aromatic rings and methyl group bonded to the central aluminium atom in *syn* position.

Table 1
Crystal data and data collection parameters for **5**–**7**

	5	6	7
Empirical formula	$\text{C}_{21}\text{H}_{31}\text{Al}_3\text{O}_4$	$\text{C}_{33}\text{H}_{55}\text{Ga}_3\text{O}_4$	$\text{C}_{27}\text{H}_{43}\text{Ga}_3\text{O}_4$
Formula weight	428.40	724.93	640.77
Temperature (K)	293(2)	293(2)	293(2)
Wavelength Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions			
a (Å)	15.938(3)	11.688(2)	11.279(2)
b (Å)	16.298(3)	15.038(3)	11.354(2)
c (Å)	9.750(2)	20.700(4)	12.411(2)
α ($^\circ$)	90	90	90.16(3)
β ($^\circ$)	96.64(3)	90.85(3)	102.62(3)
γ ($^\circ$)	90	90	90.14(3)
V (Å ³)	2515.6(8)	3637.9(12)	1551.0(5)
Z	4	4	2
D_{calc} (g cm ⁻³)	1.131	1.324	1.372
Absorption coefficient (mm ⁻¹)	0.171	2.237	2.614
$F(000)$	912	1512	660
Crystal size (mm ³)	$0.25 \times 0.20 \times 0.15$	$0.35 \times 0.25 \times 0.20$	$0.35 \times 0.25 \times 0.22$
θ Range for data collection ($^\circ$)	3.59–22.49	3.25–28.97	3.47–23.00
Index ranges	$-21 \leq h \leq 21$, $-22 \leq k \leq 22$, $-13 \leq l \leq 13$	$-15 \leq h \leq 15$, $-20 \leq k \leq 16$, $-27 \leq l \leq 28$	$-12 \leq h \leq 12$, $-12 \leq k \leq 11$, $-13 \leq l \leq 13$
Reflections collected	14928	32160	9516
Independent reflections	1650 [$R_{\text{int}} = 0.0422$]	8890 [$R_{\text{int}} = 0.1543$]	4316 [$R_{\text{int}} = 0.0634$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1649/0/146	8890/0/361	4316/0/308
Goodness-of-fit on F^2	0.907	0.917	1.012
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0691$, $wR_2 = 0.2067$	$R_1 = 0.0758$, $wR_2 = 0.1733$	$R_1 = 0.0572$, $wR_2 = 0.1485$
R indices (all data)	$R_1 = 0.0795$, $wR_2 = 0.2311$	$R_1 = 0.2214$, $wR_2 = 0.2547$	$R_1 = 0.0779$, $wR_2 = 0.1760$
Largest difference peak and hole (e Å ⁻³)	0.867 and -0.279	1.216 and -1.215	1.146 and -0.561

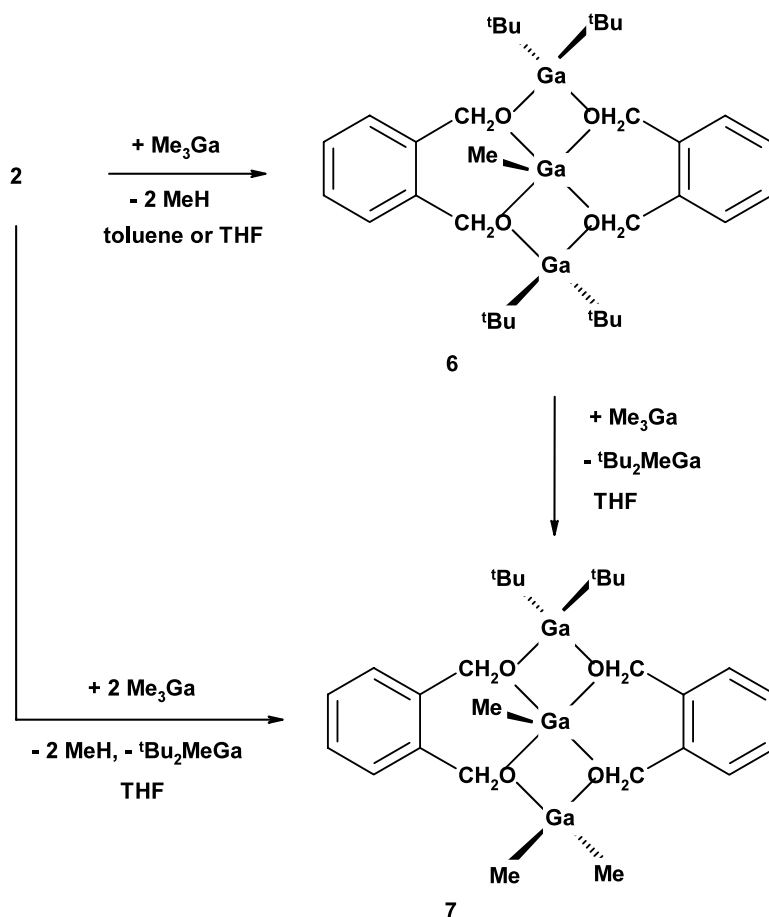
Bimetallic compound ${}^t\text{Bu}_4\text{Ga}_2(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH})_2$ (**2**) reacts with Me_3Ga at r.t. to form complexes with different substituents at the gallium atoms ${}^t\text{Bu}_4\text{MeGa}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**6**) and ${}^t\text{Bu}_2\text{Me}_3\text{Ga}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**7**) depending on the molar ratio of the reagents (Scheme 3). The product **6** is the result of the reaction of the two hydroxyl groups of **2** with one equivalent of Me_3Ga and inclusion of the third metal atom. The crystal structure of the product was determined by X-ray diffraction. A perspective view of the molecule with the atom numbering system is shown in Fig. 2.

Crystal and structure refinement data are listed in Table 1. The angles $\text{O}(3)\text{--Ga}(1)\text{--O}(1)$ $122.0(2)$ and $\text{O}(2)\text{--Ga}(1)\text{--O}(4)$ $147.3(2)^\circ$ indicate that the geometry around the central Ga(1) atom in **6** is close to a trigonal-bipyramid with O(2) and O(4) occupying the axial positions and C(17), O(3) and O(1) defining the equatorial sites. The sums of the three X–O–Y angles at all oxygen atoms are about 360° indicating the lack of strain in the seven-membered rings. It was earlier observed for similar trinuclear methylalane 1,2-catecholate ${}^t\text{Bu}_5\text{Al}_3(\text{OC}_6\text{H}_4\text{O})_2$ that the sum of X–O–Y angles in the strained molecule is about 140° [7].

The ${}^1\text{H}$ -NMR spectrum of **6** reveals two singlets of the *tert*-butyl group protons (at 1.38 and 1.31 ppm) and one singlet at -1.04 ppm of the methyl group bonded to the central gallium atom. The integration ratio of these signals indicates the presence of four *tert*-butyl groups and one methyl group, which is in agreement with the proposed structure.

The reaction of **2** with two or more equivalents of Me_3Ga in THF leads to the formation of the transmetalation product **7** possessing three methyl groups and two ${}^t\text{Bu}$ groups. It was found by means of an X-ray diffraction study and NMR spectroscopy that one methyl group is bonded to the central gallium atom, whereas two methyl groups are bonded to one of the terminal metal atoms. The molecular structure of **7** is shown in Fig. 3. Crystal and structure refinement data are listed in Table 1.

The molecular structure of **7** consists of a trimer formed by the alkoxide termini of two ligands bridging ${}^t\text{Bu}_2\text{Ga}$ and Me_2Ga units [Ga(2) and Ga(3), respectively] and a central MeGa unit [Ga(1)]. Like the five-coordinate gallium in compounds **5** and **6**, the geometry around Ga(1) in compound **7** is close to a trigonal-bipyramidal geometry [$\text{O}(4)\text{--Ga}(1)\text{--O}(2)$ $147.1(2)$,



Scheme 3.

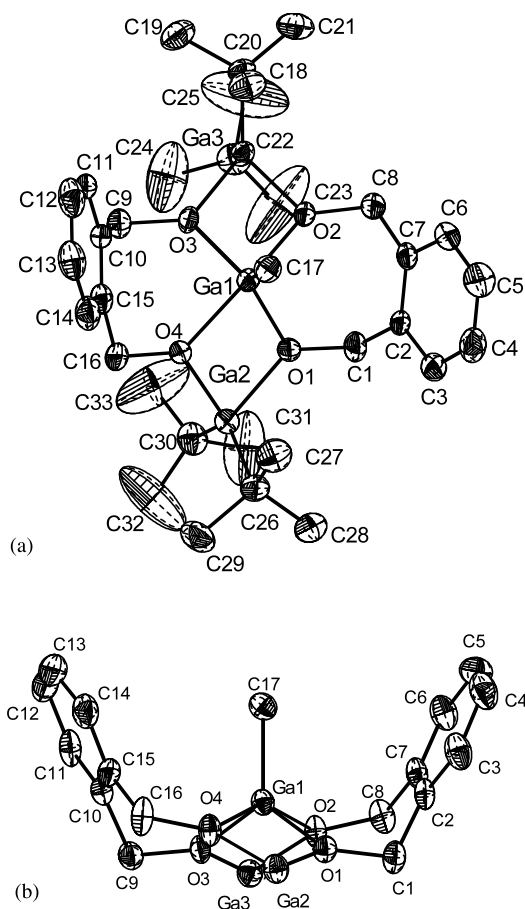


Fig. 2. (a) Crystal structure of ${}^t\text{Bu}_4\text{MeGa}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**6**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$): Ga(1)–C(17) 1.915(8), Ga(1)–O(3) 1.926(5), Ga(1)–O(1) 1.928(5), Ga(1)–O(2) 2.023(5), Ga(1)–O(4) 2.033(5), Ga(2)–O(4) 1.902(5), Ga(2)–O(1) 1.942(5), Ga(3)–O(2) 1.911(5), Ga(3)–O(3) 1.935(5), O(3)–Ga(1)–O(1) 122.0(2), O(2)–Ga(1)–O(4) 147.3(2), C(17)–Ga(1)–O(3) 118.2(3), C(17)–Ga(1)–O(1) 119.9(3), C(17)–Ga(1)–O(2) 105.4(3), C(17)–Ga(1)–O(4) 107.3(3). (b) Co-ordination sphere of Ga(1) in ${}^t\text{Bu}_4\text{MeGa}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**6**), showing the aromatic rings and Me group bonded to the central Ga atom in the *syn* position. Four alkyl groups bonded to the terminal Ga atoms are omitted for clarity. The core of the molecule **7** is the same.

O(1)–Ga(1)–O(3) 120.4(2)] with C(17), O(3) and O(1) defining the equatorial sites. The Ga(1)–C(17) bond and all the Ga–O bonds are slightly longer than the same bonds in compound **6**. The methyl group bonded to the central metal atom and aromatic rings in both compounds are in *syn* position (Fig. 2(b)).

The ${}^1\text{H}$ -NMR spectrum of compound **7** exhibits two AB patterns for the CH_2O resonances ($\delta_{\text{A}1} = 4.96$ ppm, $\delta_{\text{B}1} = 4.82$ ppm and $\delta_{\text{A}2} = 4.42$ ppm, $\delta_{\text{B}2} = 4.27$ ppm), two singlets at 1.37 and 1.32 ppm for the ${}^t\text{Bu}$ group resonances and three singlets at 0.03, 0.00 and -1.11 ppm for the methyl resonances, which is in agreement with the proposed structure. The appearance of two signals of the CH_2O carbon atoms (at 67.44 and 65.63 ppm) in the ${}^{13}\text{C}$ -NMR spectrum indicates the presence of two kinds of inequivalent CH_2O carbon atoms.

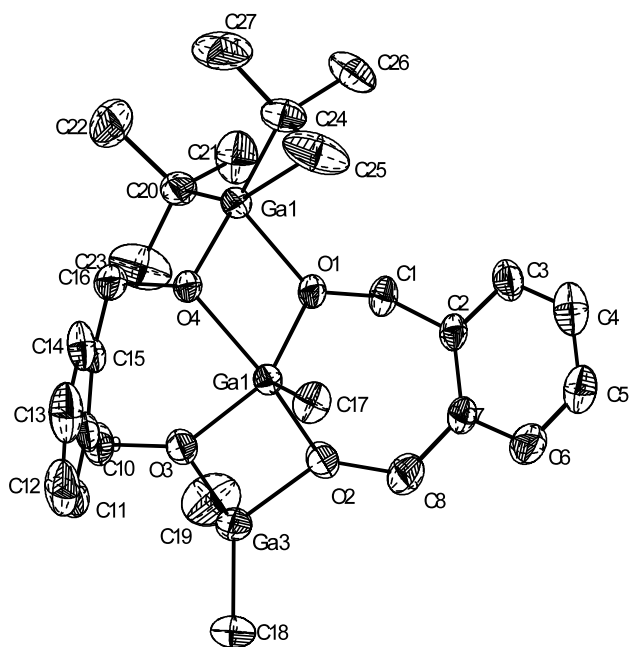


Fig. 3. Crystal structure of ${}^t\text{Bu}_2\text{Me}_3\text{Ga}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**7**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$): Ga(1)–O(1) 1.935(4), Ga(1)–O(3) 1.935(4), Ga(1)–O(4) 2.038(4), Ga(1)–O(2) 2.039(5), Ga(1)–C(17) 1.943(7), Ga(2)–O(4) 1.922(4), Ga(2)–O(1) 1.933(4), Ga(3)–O(2) 1.906(4), Ga(3)–O(3) 1.922(4), O(1)–Ga(1)–O(3) 120.4(2), O(4)–Ga(1)–O(2) 147.1(2), C(17)–Ga(1)–O(4) 107.2(3), C(17)–Ga(1)–O(2) 105.7(3), O(1)–Ga(1)–C(17) 119.6(3), O(3)–Ga(1)–C(17) 120.0(3).

We found that the compound **7** is the sole product in the reaction of **6** with one equivalent of Me_3Ga (Scheme 3). The post-reaction mixture consisted of the almost pure product **7**. The further reaction of **7** with the excess of Me_3Ga and formation of $\text{Me}_5\text{Ga}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ was not observed. It means that the first step of the interaction of **2** with Me_3Ga is the formation of the complex **6**. Subsequently **6** undergoes rather a transmetalation reaction with the next equivalent of Me_3Ga exchanging a ${}^t\text{Bu}_2\text{Ga}$ by a Me_2Ga moiety than the alkyl group exchange. The proposition of the transmetalation pathway is supported by the fact that the compound **7** possessing two methyl groups bonded to one of the terminal metal atoms is the sole product. Moreover the alkyl group exchange mechanism can result in additional products: $(\text{Me}^t\text{BuGa})({}^t\text{Bu}_2\text{Ga})(\text{MeGa})(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ and $(\text{Me}^t\text{BuGa})(\text{Me}^t\text{BuGa})(\text{MeGa})(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ which have been never observed in the post-reaction mixture [8]. It seems that the oxygen atoms of compound **6** can coordinate to the molecule of Me_3Ga . The intramolecular transition of one methyl group from Me_3Ga to gallium atom of ${}^t\text{Bu}_2\text{Ga}$ unit and elimination of $\text{Me}^t\text{Bu}_2\text{Ga}$ results in the formation of the transmetalation product **7**. The reaction depends on the kind of the solvent. The presence of a Lewis base like THF facilitates the exchange reaction, whereas in toluene the post-reaction mixture consists of

the product **7** and unreacted complex **6**. Probably the Lewis base causes the cleavage of the metal–oxygen bonds. We have previously observed similar influence of Lewis bases on alkylaluminium catecholates, which undergo decomposition in the presence of Et₂O, THF and pyridine yielding trialkylalane complexes with Lewis bases and organoaluminium oligomers [9].

The transmetalation reaction of group 13 alkyls with trinuclear complexes of the general formula [R₅M₃(diol–(2H))₂] [where R = alkyl, M = Al, Ga, In] can be considered as a useful method of synthesis of mixed-ligand and mixed-metal alkylmetallane diolates.

In conclusion, binuclear complexes [tBu₄M₂(OCH₂C₆H₄CH₂OH)₂] [M = Al (**1**); M = Ga (**2**)] possessing two hydroxyl groups react with aluminium- and gallium trialkyls to yield trinuclear products [tBu₅M₃(OCH₂C₆H₄CH₂O)₂] [M = Al (**3**); M = Ga (**4**)] and tBu₄MeGa₃(OCH₂C₆H₄CH₂O)₂ (**6**). The transmetalation of the product **6** with Me₃Ga results in the formation of the product tBu₂Me₃Ga₃(OCH₂C₆H₄CH₂O)₂ (**7**).

Further studies on the transmetalation reaction, as a method of synthesis for mixed-ligand and mixed-metal alkylmetallane diolates will be continued.

3. Experimental

All manipulations were carried out using standard Schlenk techniques in anhydrous solvents under an inert gas atmosphere. tBu₃Al, tBu₃Ga and 1,2-di(hydroxymethyl)benzene were synthesised as described in the literature [10–12]. ¹H- and ¹³C-NMR spectra were run on a Mercury-400BB spectrometer. ¹H-NMR spectra were recorded at 400.09 MHz. Chemical shifts were referenced to the residual proton signals of C₆D₆ (7.15 ppm) and ¹³C-NMR spectra were run at 100.60 MHz (standard: benzene ¹³CC₅D₆, 128 ppm). Elemental analyses were obtained on a Perkin Elmer 2400 analyser. The molecular weight of the compounds was determined by cryoscopy in benzene.

3.1. The synthesis of tBu₄Al₂(OCH₂C₆H₄CH₂OH)₂ (**1**)

A sample (1.387 g, 5.1 mmol) of tBu₃Al·OEt₂ in 20 cm³ of Et₂O was placed in 100 cm³ two-necked flask and cooled to –78 °C. The solution of 0.690 g (5.0 mmol) of 1,2-di(hydroxymethyl)benzene in 20 cm³ of Et₂O was then added drop by drop. After 24 h all volatiles were removed from the post-reaction mixture and the product **1** was crystallised from C₆H₁₂ at –25 °C as a colourless solid (yield 1.098 g, 2.0 mmol, 79%). M.p.: > 275 °C.

¹H-NMR (C₆D₆) δ 16.35 (s, 2H, OH), 6.95–6.92 (m, 8H, H_{aromat.}), 4.61 (s, 8H, CH₂O), 1.20 (s, 36H, AlC(CH₃)₃). ¹³C-NMR (C₆D₆) δ 138.55, 129.42,

128.95 (C_{aromat.}), 66.18 (CH₂O), 30.94 (AlC(CH₃)₃), 16.00 (AlC(CH₃)₃) ppm.

Molecular weight (C₆H₆): Found: 525. Calc.: 556. Anal. Found: Al, 9.37; hydrolysable *tert*-butyl groups, 40.60. Calc.: Al, 9.71; tBu, 41.01%.

3.2. The synthesis of tBu₄Ga₂(OCH₂C₆H₄CH₂OH)₂ (**2**)

The compound **2** was obtained as described in Section 3.1 using 0.690 g (5.0 mmol) of 1,2-di(hydroxymethyl)benzene and 1.229 g (5.1 mmol) of tBu₃Ga. The pure product **2** was isolated by crystallisation from C₆H₁₂ at –25 °C as a colourless solid (yield: 1.364 g, 2.1 mmol, 85%). M.p.: 166–167 °C.

¹H-NMR (C₆D₆) δ 14.48 (s, broad, 2H, OH), 6.98 (m, 8H, H_{aromat.}), 4.65 (s, 8H, CH₂O), 1.25 (s, 36H, GaC(CH₃)₃). ¹³C-NMR (C₆D₆) δ 140.34, 129.10, 128.42 (C_{aromat.}), 67.49 (CH₂O), 30.84 (GaC(CH₃)₃), 24.16 (GaC(CH₃)₃) ppm.

Molecular weight (C₆H₆): Found: 628. Calc.: 641. Anal. Found (Calc.) for C₃₂H₅₄Ga₂O₄: C, 59.36 (59.87); H, 8.55 (8.42)%.

3.3. The synthesis of tBu₅Al₃(OCH₂C₆H₄CH₂O)₂ (**3**)

3.3.1. Method 1

The solution of tBu₃Al·OEt₂ (0.272 g, 1.0 mmol) in 5 cm³ of C₆H₅CH₃ was added to the solution of **1** (0.556 g, 1.0 mmol) in 5 cm³ of C₆H₅CH₃ at room temperature (r.t.). Then the mixture was refluxed during 4 h. ¹H-NMR spectrum revealed the lack of the signals of **1** in the post-reaction mixture. The volume of the solution was concentrated by vacuum. After several days standing at –25 °C crystalline solid of **3** was obtained in 55% yield.

¹H-NMR (C₆D₆) δ 6.94 (m, 8H, H_{aromat.}), 4.73 (δ_A), 4.58 (δ_B) (dd, ²J_{H–H} = 12.4 Hz, 8H, CH₂O, AB pattern), 1.40 (s, 18H, AlC(CH₃)₃), 1.16 (s, 18H, AlC(CH₃)₃), 0.68 (s, 9H, AlC(CH₃)₃). ¹³C-NMR (C₆D₆) δ 138.27, 130.91, 129.13 (C_{aromat.}), 66.24 (CH₂O), 32.89, 32.49, 31.66 (AlC(CH₃)₃), 16.50, 15.94 (AlC(CH₃)₃) ppm.

Molecular weight (C₆H₆): Found: 625. Calc.: 638. Anal. Found: Al, 12.50; hydrolysable *tert*-butyl groups, 44.20. Calc.: Al, 12.70; tBu, 44.67%.

The reaction of **1** with an excess of tBu₃Al·OEt₂ proceeds also with the formation of **3**.

3.3.2. Method 2

The reaction mixture prepared as described in Section 3.3.1 was allowed to stand for 1 month at r.t. The post-reaction mixture consisted of the product **3** and unreacted complex **1** (on the basis of ¹H-NMR spectrum). The integration ratio of the CH₂O signals of **3** (the doublet of doublets at 4.73 and 4.58 ppm) and CH₂O signals of **1** (the singlet at 4.61 ppm) is equal 3:2.

3.4. The synthesis of ${}^t\text{Bu}_5\text{Ga}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**4**)

The compound **4** was obtained as described for **3** (Section 3.3.1) using 0.642 g (1.0 mmol) of **2** and 0.241 g (1.0 mmol) of ${}^t\text{Bu}_3\text{Ga}$. The pure product was isolated by crystallisation from $\text{C}_6\text{H}_5\text{CH}_3$ at -25°C as a white solid (yield 70%).

${}^1\text{H-NMR}$ (C_6D_6) δ 7.01 (m, 8H, $\text{H}_{\text{aromat.}}$), 5.03 (δ_{A}), 4.50 (δ_{B}) (dd, ${}^2J_{\text{H-H}} = 11.6$ Hz 8H, CH_2O , AB pattern), 1.42 (s, 18H, $\text{GaC}(\text{CH}_3)_3$), 1.39 (s, 18H, $\text{GaC}(\text{CH}_3)_3$), 0.52 (s, 9H, $\text{GaC}(\text{CH}_3)_3$). ${}^{13}\text{C-NMR}$ (C_6D_6) δ 140.68, 130.91, 128.59 ($\text{C}_{\text{aromat.}}$), 68.30 (CH_2O), 32.12, 31.82, 31.02 ($\text{GaC}(\text{CH}_3)_3$), 25.68, 25.38 ($\text{GaC}(\text{CH}_3)_3$) ppm.

Molecular weight (C_6H_6): Found: 752. Calc.: 766. Anal. Found (Calc.) for $\text{C}_{36}\text{H}_{61}\text{Ga}_3\text{O}_4$: C, 56.02 (56.39); H, 8.25 (7.96)%.

3.5. The synthesis of $\text{Me}_5\text{Al}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**5**)

Compound **5** was synthesised as described in the literature [3a]. M.p.: 174°C .

3.6. The synthesis of ${}^t\text{Bu}_4\text{MeGa}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**6**)

A solution of 0.115 g of Me_3Ga (1 mmol) in 2 cm^3 of $n\text{-C}_5\text{H}_{12}$ was added by a syringe to a solution of 0.642 g of **2** (1 mmol) in 10 cm^3 of $\text{C}_6\text{H}_5\text{CH}_3$ at r.t. After 24 h the solvent was removed under reduced pressure. The pure product **6** was obtained quantitatively.

${}^1\text{H-NMR}$ (C_6D_6) δ 6.99 (m, 8H, $\text{H}_{\text{aromat.}}$), 4.97 (δ_{A}), 4.44 (δ_{B}) (dd, ${}^2J_{\text{H-H}} = 11.6$ Hz, 8H, CH_2O , AB pattern), 1.38 (s, 18H, $\text{GaC}(\text{CH}_3)_3$), 1.31 (s, 18H, $\text{GaC}(\text{CH}_3)_3$), -1.04 (s, 3H, GaCH_3). ${}^{13}\text{C-NMR}$ (C_6D_6) δ 139.80, 130.10, 128.66 ($\text{C}_{\text{aromat.}}$), 67.58 (CH_2O), 31.27, 31.05 ($\text{GaC}(\text{CH}_3)_3$), 24.96, 24.47 ($\text{GaC}(\text{CH}_3)_3$), -5.55 (GaCH_3) ppm.

The same reaction in THF yielded the product **6** slightly polluted by unidentified products. X-ray quality crystals were obtained by crystallisation from an $n\text{-C}_6\text{H}_{14}\text{-CH}_2\text{Cl}_2$ solution. M.p. 154°C . Molecular weight (C_6H_6): Found: 708. Calc.: 724. Anal. Found (Calc.) for $\text{C}_{33}\text{H}_{55}\text{Ga}_3\text{O}_4$: C, 54.12 (54.68); H, 8.08 (7.60)%.

3.7. The synthesis of ${}^t\text{Bu}_2\text{Me}_3\text{Ga}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2$ (**7**)

3.7.1. Method 1

A solution of 0.253 g of Me_3Ga (2.2 mmol) in 4 cm^3 of $n\text{-C}_5\text{H}_{12}$ was added via syringe to the solution of 0.642 g of **2** (1 mmol) in 10 cm^3 of THF at r.t. After 24 h the volatiles were removed under vacuum. The pure product **7** was obtained quantitatively.

${}^1\text{H-NMR}$ (C_6D_6) δ 6.95 (m, 8H, $\text{H}_{\text{aromat.}}$), 4.96 (δ_{A1}), 4.82 (δ_{B1}) (dd, ${}^2J_{\text{H-H}} = 11.2$ Hz, 4H, CH_2O , AB pattern), 4.42 (δ_{A2}), 4.27 (δ_{B2}) (dd, ${}^2J_{\text{H-H}} = 11.2$ Hz,

4H, CH_2O , AB pattern), 1.37 (s, 9H, $\text{GaC}(\text{CH}_3)_3$), 1.32 (s, 9H, $\text{GaC}(\text{CH}_3)_3$), 0.03 (s, 3H, GaCH_3), 0.00 (s, 3H, GaCH_3), -1.11 (s, 3H, GaCH_3).

${}^{13}\text{C-NMR}$ (C_6D_6) δ 140.11, 139.85, 130.17, 129.70, 128.74, 128.52 ($\text{C}_{\text{aromat.}}$), 67.44, 65.63 (CH_2O), 30.86, 30.78 ($\text{GaC}(\text{CH}_3)_3$), 24.64, 24.29 ($\text{GaC}(\text{CH}_3)_3$), -6.75 , -7.10 (GaCH_3)

The same reaction in $\text{C}_6\text{H}_5\text{CH}_3$ yielded the mixture of **6** and **7**. X-ray quality crystals were obtained by crystallisation from an $n\text{-C}_6\text{H}_{14}\text{-CH}_2\text{Cl}_2$ solution. M.p.: $128\text{--}129^\circ\text{C}$. Molecular weight (C_6H_6): Found: 652. Calc.: 640. Anal. Found (Calc.) for $\text{C}_{27}\text{H}_{43}\text{Ga}_3\text{O}_4$: C, 49.70 (50.61); H, 7.20 (6.72)%.

3.7.2. Method 2

A solution of 0.115 g of Me_3Ga (1 mmol) in 2 cm^3 of $n\text{-C}_5\text{H}_{12}$ was added via syringe to the solution of 0.725 g of the pure compound **6** (1 mmol) in 10 cm^3 of THF at r.t. After 24 h the solvent and other volatile products were distilled off, collected and carefully concentrated. ${}^1\text{H-NMR}$ spectrum of the solution besides the signals of THF and $n\text{-C}_5\text{H}_{12}$ protons revealed the signals of $\text{GaC}(\text{CH}_3)_3$ protons (at 1.342 and 1.255 ppm) of ${}^t\text{Bu}_x\text{Me}_{(3-x)}\text{Ga}$. The solid residue consisted of the almost pure product **7** (on the basis of NMR spectroscopy).

3.8. X-ray crystal structure analyses.

Determination of the crystal structures of **5**, **6** and **7** were performed on a KUMA KM4CCD κ -axis diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation. The crystals were positioned at 62.25 mm from the KM4CCD camera. For compound **5** 1000 frames were measured in 1.2° intervals with a counting time of 20 s. For compound **6** 400 frames were measured in 1.5° intervals with a counting time of 15 s. For compound **7** 600 frames were measured in 1.0° intervals with a counting time of 25 s. All of the data were corrected for Lorentz and polarisation effects. No absorption correction was applied. Data reduction and analysis were carried out using the KUMA Diffraction (Wroclaw) programs. Structures of the investigated crystals were solved by Direct methods [13] and refined using the SHELXL computer program [14]. All hydrogen atoms placed in the calculated positions and their thermal parameters were refined isotropically. Scattering factors were taken from the literature (Tables 6.1.1.4 and 4.2.4.2 in Ref. [15]).

The X-ray structures were measured in the Crystallography Unit of the Physical Chemistry Laboratory at the Chemistry Department of the University of Warsaw.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 212284–212286 for compounds **5**, **6** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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