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Journal of Organometallic Chemistry 689 (2004) 2056–2065
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Sterically crowded diolates of group 13 metals

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Received 27 November 2003; accepted 22 January 2004

Abstract

The dependence of the structure of complexes of sterically crowded 2,4-dimethylpentane-2,4-diol with group 13 metals trialkyls on the kind of metal, as well as steric bulk of the substituents on the metal atoms is reported. The reaction of $^{t}Bu_3Ga$ with 2,4-dimethylpentane-2,4-diol leads to the formation of an unstable dimeric product $\{^{t}Bu_2Ga[(OC(CH_3)_2CH_2C(CH_3)_2OH]\}_2$ (**1**) possessing a four-membered Ga_2O_2 core and two unreacted hydroxyl groups. Compound **1** undergoes further intramolecular reaction to yield the unusual (monoalkyl)gallane *O*,*O*′-chelate complex $\{^{t}BuGa[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ (**2**). In contrast to $^{t}Bu_3Ga$, $^{t}Bu_3In$ reacts with 2,4-dimethylpentane-2,4-diol to give the stable dimeric complex $^{t}Bu_4In_2[OC(CH_3)_2CH_2C(CH_3)_2OH]_2$ (**4**) stabilised by two intramolecular O–H···O bonds. At higher temperature compound 4 reacts with an excess of $^{t}Bu_3In$ to form the trinuclear complex $^{t}Bu_5In_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2$ (**5**). The reactions of 2,4-dimethylpentane-2,4-diol with trialkylmetallane with small alkyl groups, i.e. Me_3Ga and Me_3In allow for the isolation of the trinuclear diolates $\{Me_5M_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ [M = Ga (**3**), M = In (**6**)]. The crystal structures of **2**, **3** and **4** have been determined by single crystal X-ray diffraction. The reactions of *tert*-butylmetallane diolates with trimethyl metallanes have been studied. The interaction of the allane complex $\{^{t}BuAl[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ with Me_3Al results in the formation of the trialuminium mixed-ligand product $\{Me_3(^{t}Bu)_2Al_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ (**7**). Compounds **2** and **4** undergo a total transmetallation reaction in the presence of Me_3M to yield $[Me_5M_3(diol\text{-}(2H))_2]$ [M = Al, Ga] products.

Keywords: Aluminium; Gallium; Indium; Diols; Steric hindrances

1. Introduction

Steric repulsion between ligands are a significant factor controlling the formation of group 13 complexes. Generally, sterically demanding ligands prevent aggregation into complexes with high coordinate metal centres [1]. Power et al. found that the unique steric bulk of $[HC(MeCDippN)_2]^-$ ligands (where Dipp = $C_6H_3{}^{i}Pr_2$-2,6) prevent dimerisation of the intermediate [HC(MeCDippN)$_2$]GaNSiMe$_3$ but allow reaction with the less crowded N_3SiMe_3 to afford the tetrazole [HC(MeCDippN)$_2$]Ga[N(SiMe$_3$)NNN]SiMe$_3$ and amide/azide [HC(MeCDippN)$_2$]Ga(N$_3$)N(SiMe$_3$)$_2$ isomers [2]. The steric bulk of $C(SiMe_3)_3$ ligand appeared advantageous for the synthesis and structural determination of the first alkylaluminium diiodide by making a rearrangement of $RAlI_2$ to the R_2AlI and AlI_3 complexes impossible [3]. The replacement of methyl and ethyl groups in trialkylalanes by sterically crowded mesityl and tris(trimethylsilyl)methyl ligands allowed to isolate and structurally characterise the intermediate products of an alumoxane formation [4]. In order for a group 13 metal compound to be useful in catalysis, it must be able to coordinate an electron donor. This implies a complex that is coordinatively unsaturated and/or electron deficient. These qualities can be achieved by employing sterically hindered substituents. The series of alkylalane complexes of sterically crowded biphenols and binols synthesised by Lin and co-workers [5] demonstrates catalytic activity in the polymerisation of cyclic esters, reduction of aldehydes and ketones and other organic

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doi:10.1016/j.jorganchem.2004.03.016

syntheses. Considering this it seems interesting to elucidate the influence of steric ligand repulsion on the structure of complexes with group 13 metal trialkyls.

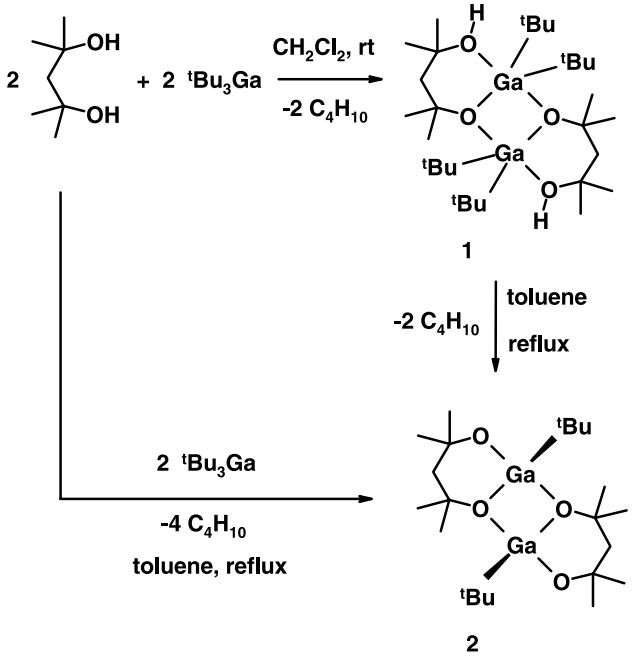
Recently, we reported the synthesis of the unusual (monoalkyl)alane *O*,*O*′–chelate complex $\{^t$BuAl[OC$(CH_3)_2CH_2C(CH_3)_2O]\}_2$ in the reaction of $^t Bu_3Al$ with the sterically crowded diol. The same reaction of $^t Bu_3Al$ with 1,3-propanediol as a diol without steric hindrance, leads to the formation of the typical trimetallic diolate $[^t Bu_5Al_3(O(CH_2)_3O)_2]$ [4]. In this paper we describe the reactions of group 13 metal trialkyls R_3M (where M = Ga, In, R = Me, ^{t}Bu) with sterically crowded 2,4-dimethylpentane-2,4-diol and the dependence of the structure of products on the bulk of metal atoms and R substituents. Moreover, the reactivity of *tert*-butylmetallane diolates toward trimethylmetallanes has been studied.

2. Results and discussion

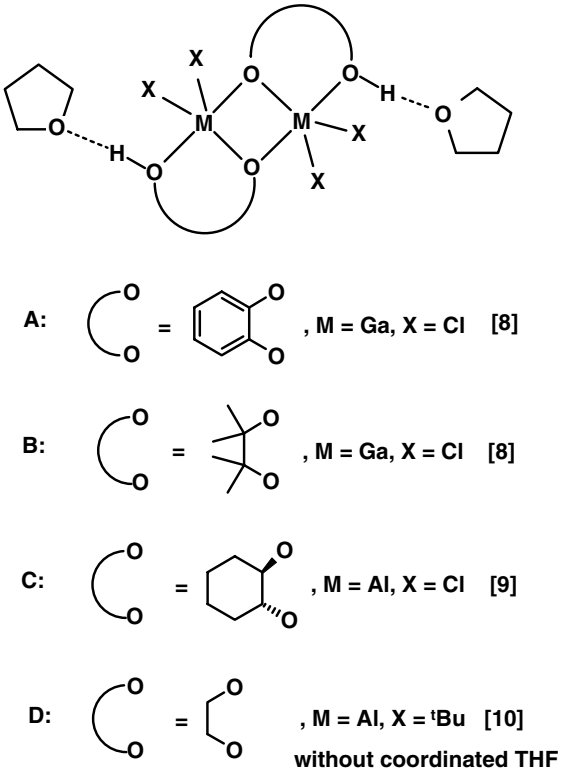
$^t Bu_3Ga$ reacts with one equivalent of 2,4-dimethylpentane-2,4-diol at room temperature to form the dimeric complex $\{^t Bu_2Ga[OC(CH_3)_2CH_2C(CH_3)_2OH]\}_2$ (**1**) (Scheme 1).

The product **1** was isolated as a residue by removing the volatiles (a solvent and small excess of $^t Bu_3Ga$) from the post-reaction mixture under reduced pressure. The structure of **1** was assigned by means of NMR spectroscopy and comparison with literature data. Attempts of crystallisation result in the decomposition of **1** to give a mixture of unknown products. The presence of a broad signal at 3.87 ppm of two alcohol protons in the ^{1}H NMR spectrum of **1** indicates the absence of inter- and intramolecular hydrogen bonds. In recent years, it has been demonstrated that the signals of highly acidic protons involved in intramolecular hydrogen bonds in binuclear alane and gallane diolates $\{R_4M_2[diol\text{-}(H)]_2\}$ are shifted downfield (14–17 ppm) [6,7]. The $(CH_3)_3$CGa protons, CH_2 and $(CH_3)_2$C protons of the diol units of 1 are equivalent and appear in the ^{1}H NMR spectrum as singlets at 1.42, 1.24 and 1.09 ppm, respectively. The integration ratio of the signals is in good agreement with the proposed structure of 1. The similar alane and gallane compounds **A**–**C** (Scheme 2) were obtained and structurally characterised by Schmidbaur [8] and Wuest [9]. The compounds are stabilised by OH···THF hydrogen bonds. Moreover, Barron [10] proposed the related *tert*-butylalane glycolate **D** as an intermediate product in formation of the trinuclear complex $[^t Bu_5Al_3(OCH_2CH_2O)_2]$. Considering the NMR spectra of **1** and the reported examples of similar compounds, we propose the structure of **1** as a dimer with Ga_2O_2 core and two unreacted OH groups.

In our opinion the compound **1** is the intermediate product in the formation of product **2**, because it undergoes an easy transformation to $\{^t$BuGa$[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ (**2**) upon refluxing in toluene. The reaction of $^t Bu_3Ga$ with 2,4-dimethylpentane-2,4-diol in refluxing toluene leads directly to product **2** (Scheme 1).



Scheme 1.



Scheme 2.

Compound **2** was spectroscopically and crystallographically characterised. Data collection and structure analysis details are presented in Table 1. The molecular structure of **2** is shown in Fig. 1. The compound **2** consists of a Ga_2O_2 dimeric core and it is isostructural to the earlier reported alane derivative [4]. The ^{t}Bu groups are *cis* oriented with respect to the Ga_2O_2 ring. The sums of angles about the O(1) and O(3) atoms are 342.4° and 342.3°, respectively, which indicates steric strain in the molecule. The same angles in the isostructural aluminium complex are slightly bigger, 345.6° and 345.8°.

The ^{1}H NMR spectrum of 2 shows four singlets (at 1.40, 1.37, 1.33 and 1.31 ppm) of the protons of eight CH_3 groups of the diol moieties. The presence of one signal at 1.09 ppm assigned to the protons of ^{t}Bu groups indicates the equivalence of the alkyl groups bonded to the gallium atoms. Two signals of the inequivalent oxygen bound carbon atoms (at 76.83 and 72.10 ppm) in the ^{13}C NMR spectrum are in agreement with the presence of two- and three-coordinate oxygen atoms.

The first step of the interaction of 2,4-dimethylpentane-2,4-diol with ^{t}Bu$_3$Ga is the formation of the complex **1**. Subsequently, **1** undergoes an intramolecular reaction of two hydroxyl groups with ^{t}Bu groups to give the product **2**. According to our knowledge compound **2** is the first structurally characterised example for a (monoalkyl)gallane diolate. It is known that ^{t}Bu$_3$Ga reacts with sterically less hindered diols to give trinuclear products $\{^t$Bu$_5$Ga[diol-(2H)]$_2\}$ [7b,7c]. Besides the isostructural alane compound $\{^t$BuAl[OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O]$\}_2$ [4], there are two aluminium compounds similar to **2**: $[(Me_3Si)_3CAlO(CH_2)_4]_2$, where one oxygen atom at each Al atom is replaced by a CH_2 group and the two Al–O–C$_4$ rings adopt a *cis* conformation [11] and a methylaluminium derivative of tetraphenol [12].

The reaction of 2,4-dimethylpentane-2,4-diol with the sterically less crowded trialkylgallane Me_3Ga results in the formation of a typical trigallium diolate $\{Me_5Ga_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ (**3**) despite the steric hindrances of the diol moieties (Scheme 3). Numerous examples of similar alane complexes have been published [13].

The solid state structure of the compound 3 was determined by X-ray crystallography and is shown in Fig. 2. Data collection and structure analysis details are presented in Table 1. Compound **3** is isostructural to the earlier reported alane derivative $\{Me_5Al_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ [14]. The molecular structure of **3** consists of a trimer formed by the alkoxide termini of two ligands bridging two Me_2Ga units [Ga(2) and Ga(3)]

Table 1
Crystal data and data collection parameters for **2**–**4**

	2	**3**	**4**
Empirical formula	$C_{22}H_{46}Ga_2O_4$	$C_{19}H_{43}Ga_3O_4$	$C_{30}H_{66}In_2O_4$
Formula weight	514.03	544.69	720.47
Temperature (K)	120(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	8.936(2)	11.114(2)	8.841(2)
b (Å)	12.119(2)	12.674(3)	18.480(4)
c (Å)	23.884(5)	18.178(4)	11.503(2)
α (°)	90	90	90
β (°)	92.63(3)	91.73(3)	105.05(3)
γ (°)	90	90	90
V (Å^3)	2583.8(9)	2559.4(9)	1814.9(6)
Z	4	4	2
D_{calc} (g cm^{-3})	1.321	1.414	1.318
Absorption coefficient (mm^{-1})	2.107	3.153	1.298
F(0 0 0)	1088	1128	752
Crystal size (mm)	0.25 × 0.20 × 0.15	0.40 × 0.30 × 0.30	0.25 × 0.25 × 0.20
Θ range for data collection (°)	3.75–24.00	3.35–22.50	3.37–25.00
Index ranges	$-10 \leqslant h \leqslant 9, -13 \leqslant k \leqslant 13, -27 \leqslant l \leqslant 27$	$-9 \leqslant h \leqslant 11, -13 \leqslant k \leqslant 13, -19 \leqslant l \leqslant 19$	$-11 \leqslant h \leqslant 8, -24 \leqslant k \leqslant 24, -15 \leqslant l \leqslant 15$
Reflections collected	16 645	14 461	13 085
Independent reflections	4040 [$R_{int} = 0.1199$]	3333 ($R_{int} = 0.1748$)	3186 ($R_{int} = 0.0910$)
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	4040/0/253	3333/0/236	3176/0/200
Goodness-of-fit on F^2	1.003	1.108	0.838
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0493$, $wR_2 = 0.1189$	$R_1 = 0.0674$, $wR_2 = 0.1746$	$R_1 = 0.0392$, $wR_2 = 0.1109$
R indices (all data)	$R_1 = 0.0661$, $wR_2 = 0.1313$	$R_1 = 0.0804$, $wR_2 = 0.2020$	$R_1 = 0.0467$, $wR_2 = 0.1229$
Max/min of residual electron density	1.262 and −0.610	0.707 and −0.906	1.341 and −0.841

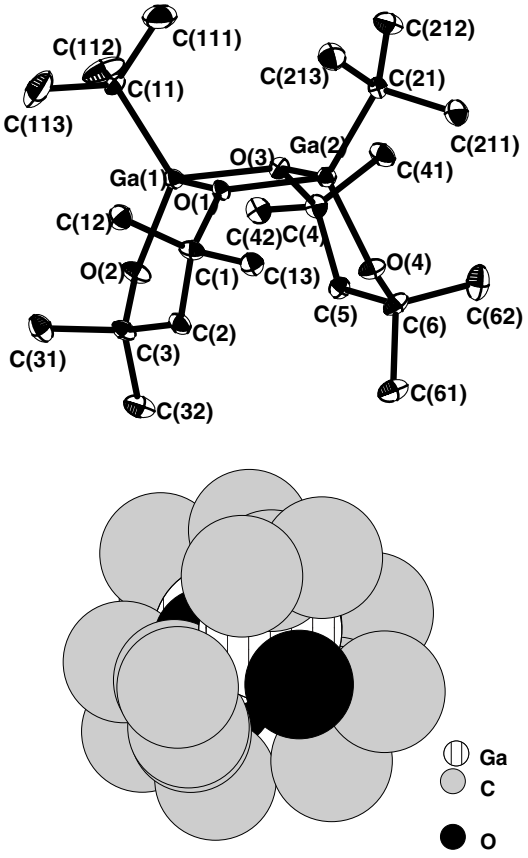
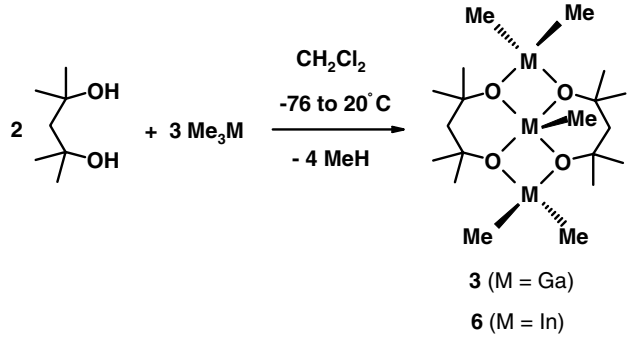


Fig. 1. (top) Molecular structure of $\{^tBuGa[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ (**2**). Thermal ellipsoids are shown at the 30% level and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ga(1)–O(2) 1.803(3), Ga(1)–O(1) 1.917(3), Ga(1)–O(3) 1.944(3), Ga(1)–C(11) 1.970(5), Ga(2)–O(4) 1.800(3), Ga(2)–O(3) 1.929(3), Ga(2)–O(1) 1.946(3), Ga(2)–C(21) 1.976(5), O(2)–Ga(1)–O(1) 104.1(1), O(2)–Ga(1)–O(3) 112.4(1), O(1)–Ga(1)–O(3) 81.9(1), O(2)–Ga(1)–C(11) 122.6(2), O(1)–Ga(1)–C(11) 116.9(2), O(3)–Ga(1)–C(11) 111.6(2), O(4)–Ga(2)–O(3) 102.8(1), O(4)–Ga(2)–O(1) 109.5(1), O(3)–Ga(2)–O(1) 81.6(1), O(4)–Ga(2)–C(21) 121.5(2), O(3)–Ga(2)–C(21) 120.2(2), O(1)–Ga(2)–C(21) 114.1(2), Ga(1)–O(1)–Ga(2) 98.4(1), Ga(2)–O(3)–Ga(1) 98.1(1). (bottom) Space filling plot of **2** showing the exposed two-coordinate oxygen atom (black ball) to be accessible for the attack of Lewis acids.



Scheme 3.

and a central MeGa unit [Ga(1)]. The angles O(3)–Ga(1)–O(1) 130.2(2) and O(2)–Ga(1)–O(4) 142.8(2)° indicate that the geometry around the central Ga(1) atom

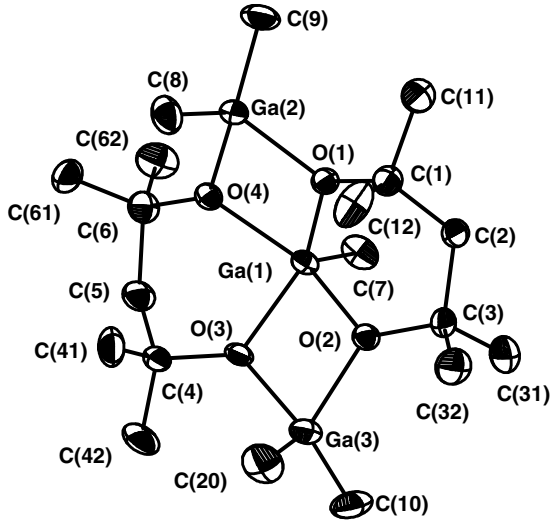


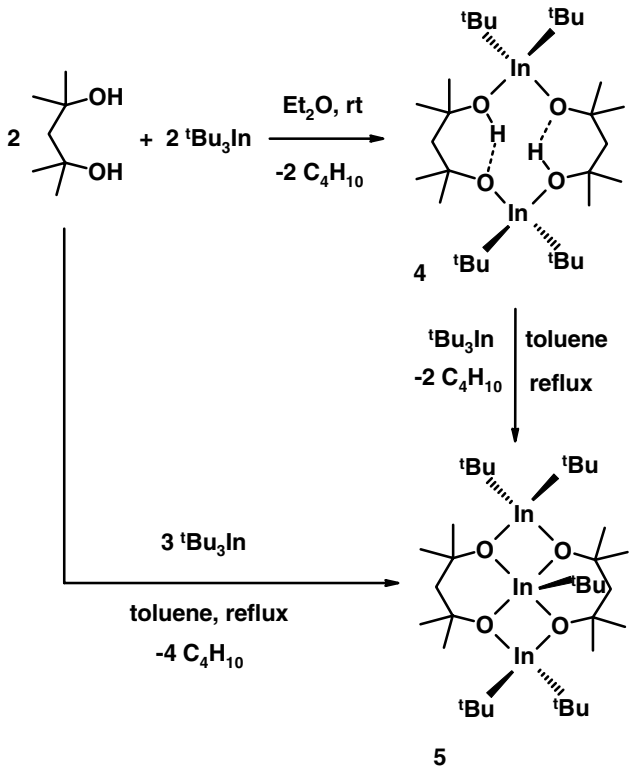
Fig. 2. Molecular structure of $\{Me_5Ga_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ (**3**). Thermal ellipsoids are shown at 20% level and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ga(1)–O(3) 1.914(4), Ga(1)–O(1) 1.922(4), Ga(1)–C(7) 1.939(7), Ga(1)–O(4) 1.975(5), Ga(1)–O(2) 1.984(5), Ga(2)–O(4) 1.901(5), Ga(2)–O(1) 1.937(4), Ga(3)–O(2) 1.895(5), Ga(3)–O(3) 1.943(5) O(3)–Ga(1)–O(1) 130.2(2), O(3)–Ga(1)–O(4) 88.7(2), O(1)–Ga(1)–O(4) 75.8(2), O(3)–Ga(1)–O(2) 75.9(2), O(1)–Ga(1)–O(2) 88.6(2), O(4)–Ga(1)–O(2) 142.8(2).

is close to a distorted square-based pyramid with four oxygen atoms occupying the basal sites. Contrary to **2**, the sums of the three X–O–Y angles at all oxygen atoms are about 360°, indicating the absence of steric strain in the six-membered GaO_2C_3 rings.

The NMR spectra of **3** are similar to those of the alane derivative $\{Me_5Al_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ [14] and are in good agreement with the proposed structure (see Section 3).

It is known that indium chemistry differs from those of gallium and aluminium due to the significantly larger indium atom radius [15]. There are the reports showing monomeric aluminium and gallium complexes whereas indium complexes with the same ligands possess a dimeric structure [16]. In contrast to the reaction of 2,4-dimethylpentane-2,4-diol with $^tBu_3Al$ [14] and $^tBu_3Ga$, the reaction with $^tBu_3In$ gives a binuclear complex $\{^tBu_4In_2[OC(CH_3)_2CH_2C(CH_3)_2OH]_2\}$ (**4**) possessing two intramolecular O–H···O bondings. The interaction of **4** with one equivalent of $^tBu_3In$ in refluxing toluene yields the trimetallic product $\{^tBu_5In_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ (**5**) (Scheme 4).

Crystals of compound 4 suitable for an X-ray structure determination were grown from a toluene solution at −25 °C. Molecular structure of **4** is shown in Fig. 3 (top). Data collection and structure analysis details are presented in Table 1. The molecules of **4** are centrosymmetric dimers with central non-planar $In_2O_4H_2$ eight-membered rings (Fig. 3 bottom). The positions of



Scheme 4.

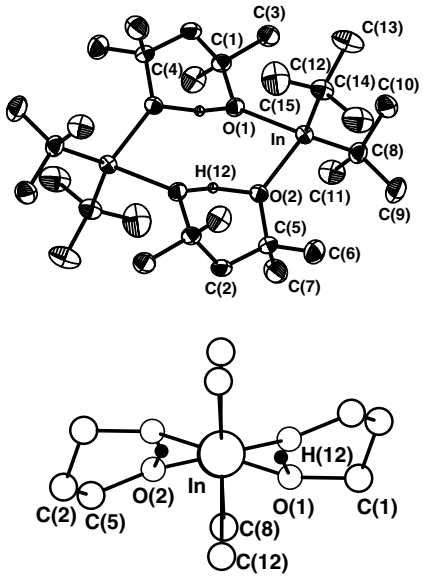


Fig. 3. (top) Molecular structure of $\{^tBu_4In_2[OC(CH_3)_2CH_2C(CH_3)_2OH]_2\}$ (**4**). Thermal ellipsoids are shown at the 30% level and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): In–O(2) 2.130(3), In–O(1) 2.195(3), In–C(12) 2.201(4), In–C(8) 2.203(4), O(2)–In–O(1) 84.0(1), O(2)–In–C(12) 105.4(1), O(1)–In–C(12) 109.1(2), O(2)–In–C(8) 116.6(2), O(1)–In–C(8) 109.7(2), C(12)–In–C(8) 124.6(2). (bottom) Partial coordination sphere of 4 viewed along the In···In vector showing the central non-planar In2O4H2 cycle.

the OH protons were located in the difference map. The downfield shifted signal of O*H* protons at 14.63 ppm in the ^{1}H NMR spectrum shows the increased acidity of the protons in benzene solution. Although the core of the molecule of **4** is similar to the butane-1,4-diol *tert*-butylalane derivative $\{^tBu_4Al_2[O(CH_2)_4OH]_2\}$ [14], the average M–C and M–O bond lengths and O–M–O angles (where M = Al, In) in both compounds are significantly different. In both structures, the metal centres have a distorted-tetrahedral geometry with O–M–O angles at 84.0(1)° and 94.0(1)° for **4** and $\{^tBu_4Al_2[O(CH_2)_4OH]_2\}$, respectively. Moreover the average In–C (2.202 Å) and In–O (2.148 Å) bonds in 4 are much longer than Al–C (1.978 Å) and Al–O (1.812 Å) bonds in $\{^tBu_4Al_2[O(CH_2)_4OH]_2\}$. Every ^{t}Bu group in structure **4** interacts with two methyl groups of diol units. The presence of long In–C and In–O bonds means that ^{t}Bu groups bonded to the indium atoms are distant from the molecule core and methyl groups of diol moieties, which causes decreasing of the steric strain. The formation of the related alane and gallane 2,4-dimethylpentane-2,4-diolates with shorter metal–carbon and metal–oxygen bonds is not feasible due to the large steric repulsion of ^{t}Bu and Me groups. Instead of the product with intramolecular hydrogen bonds compound **1** was obtained. In proposed structure **1** every ^{t}Bu group interacts only with one Me group of the diol unit which decreases the steric repulsion.

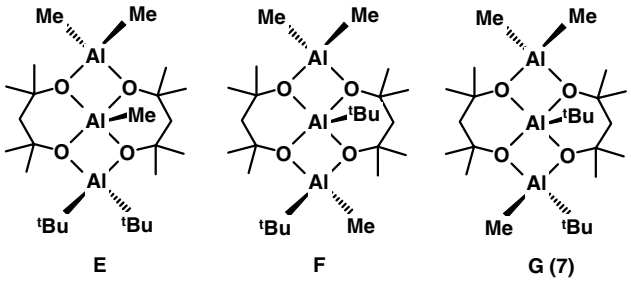
The triindium compound **5** was synthesised using two methods: in the reaction of 4 with $^tBu_3In$ and directly by the interaction of two equivalents of the diol with three equivalents of $^tBu_3In$ in refluxing toluene (Scheme 4). As the crystals of **5** were not suitable for X-ray diffraction, the structure was determined spectroscopically. The ^{1}H NMR spectrum consists of three singlets (at 1.52, 1.45 and 1.43 ppm) of $(CH_3)_3CIn$ protons with an integration ratio of 1:2:2, which is a characteristic motif of the spectra of trimetallic $\{R_5M_3[diol\text{-}(2H)]_2\}$ structures. The doublets at 1.75 and 1.38 ppm and singlets at 1.41 and 1.21 ppm correspond to the CH_2 and $(CH_3)_2C$ protons in the diol units. The ^{13}C NMR data are also consistent with the proposed structure of **5**.

Although the reactions of trialkylalane and –gallane with organic diols have been intensively studied, compounds **4** and **5** are the first indane diolates. In recent time Walawalkar [17] reported a first lithium indium silanediolate derived from disilanol $[(Ph_2SiOH)_2O]$ and $Li[InMe_4]$. In an effort to gain knowledge about the structure of indane derivatives, an investigation of the reaction of 2,4-dimethylpentane-2,4-diol with trimethylindane was undertaken. The reaction of three equivalents of Me_3In with two equivalents of the diol yields almost quantitatively the trinuclear complex $CH_3)_2CH_2C(CH_3)_2O]_2\}$ (**6**) similar to the gallane diolate (**3**) (Scheme 3). The ^{1}H and ^{13}C NMR spectra of **6** reveal the signals of the protons and carbons of five methyl

groups bonded to the metal atoms and two diol moieties similarly to the compound **3.** Crystals of **6** suitable for structural characterisation by X-ray crystallography could not be obtained.

The binuclear complexes $\{^t$BuAl[OC$(CH_3)_2CH_2$C$(CH_3)_2$O]$_2$ and **2** possess two kinds of oxygen atoms; three- and di-coordinate. The di-coordinate atoms are exposed and accessible for a Lewis acid attack (figure bottom). Compound **4** can also react with trialkyls of group 13 metals as bifunctional (two OH groups), tetradentate (four O atoms) ligand. Considering this, we have undertaken an investigations of the reactions of the binuclear *tert*-butyl metallane diolates with Me_3M (M = Al, Ga, In). In general, the reactions were carried out at room temperature in Et_2O during one month using three equivalents of Me_3M (Schemes 5, 7, 8). Then the volatiles (the solvent and volatile organometallic compounds) were removed under reduced pressure.

The reaction of the compound $\{^t$BuAl[OC$(CH_3)_2$ CH_2C$(CH_3)_2$O]$\}_2$ with Me_3Al results in the formation of the trinuclear complex $\{Me_3{}^tBu_2Al_3$[OC$(CH_3)_2CH_2$C $(CH_3)_2O]_2\}$ (**7**) (Scheme 5), whereas the reaction with Me_3Ga does not proceed at all. After **2** days the ^{1}H NMR spectrum of the reaction mixture showed the presence of two compounds only: the product **7** and the starting compound $\{^t$BuAl[OC$(CH_3)_2CH_2$C$(CH_3)_2$O]$\}$ in the molar ratio 1:1 (on the basis of an integration of CH_2 doublets at 2.10 and 2.01 ppm). After 1 month the ratio of **7** to compound $\{^t$BuAl[OC$(CH_3)_2CH_2$C $(CH_3)_2$O]$\}$ was equal 8:1. The product **7** was separated by means of fractional sublimation under reduced pressure. The structure of **7** was determined spectroscopically, because the crystals precipitated from solutions were not suitable for X-ray diffraction. Three signals of AlCH_3 protons (at −0.32, −0.33 and −0.41 ppm) and two signals of AlC(CH_3)$_3$ protons (at 1.29 and 1.27 ppm) in the ^{1}H NMR spectrum indicate the presence of three methyl groups and two *tert*-butyl groups bonded to three aluminium atoms. Moreover, ^{1}H NMR spectrum consists of one doublet of doublets of CH_2 protons (δ_A 2.10, δ_B 0.82) and four singlets of CH_3 group protons of diol moieties, which shows that compound **7** is less symmetrical than **3**, **5** and **6**. Considering the ^{1}H and ^{13}C NMR spectra three probable structures (E, F, G) can be proposed for **7** as shown in Scheme 6.

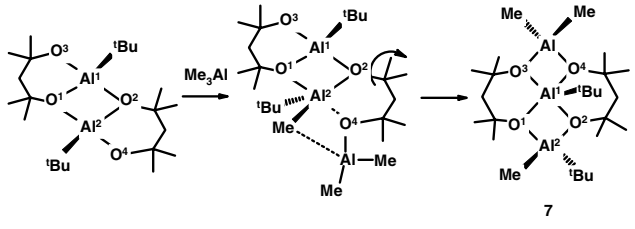


Scheme 6.

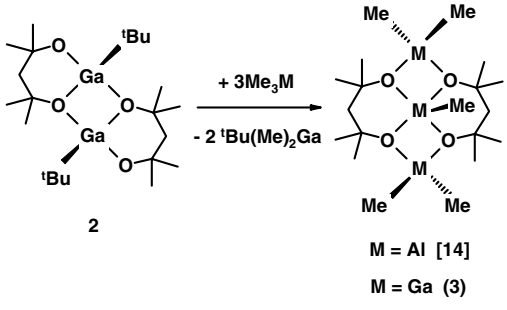
The final assignment of the structure of **7** was done by NOE measurements (NOESY). Due to the lack of cross peaks between the signal at 1.27 ppm and all signals of the CH_2 and (CH_3)$_2$CO protons, the signal at 1.27 ppm was assigned to the ^{t}Bu group bonded to the central Al atom. The structural analysis of the similar trinuclear compound **3** showed that the alkyl group bonded to the central metal atom is the most exposed and remote from diol moieties in comparison with the alkyl groups bonded to the terminal metal atoms. The analysis of NOESY spectrum indicates that ^{t}Bu group bonded to the central Al atom interacts only with one Me group bonded to the terminal Al atom (the cross peak of the signals at 1.27 and −0.41 ppm). A close proximity of two ^{t}Bu groups was not observed. Therefore structure G possessing *anti*^{t}Bu groups is proposed for compound 7 (Scheme 6).

In the proposed reaction pathway Me_3Al coordinates to the di-coordinate oxygen atom O_4. Then the methyl group is shifted to Al_2 atom and structural intramolecular reorganisation results in the formation of **7** (Scheme 5).

In contrast to the reaction of $\{^t$BuAl[OC$(CH_3)_2$ CH_2C$(CH_3)_2$O]$\}_2$ with Me_3Al the interaction of the isostructural gallium compound **2** with Me_3Al yields the earlier reported trialuminium complex [Me_5Al_3(OC $(CH_3)_2CH_2C(CH_3)_2O)_2$] [14] (Scheme 7). A similar reaction of **2** with Me_3Ga proceeds with the formation of the trigallium complex **3** (Scheme 7). The ^{1}H NMR spectrum of volatile products besides the signals of



Scheme 5.



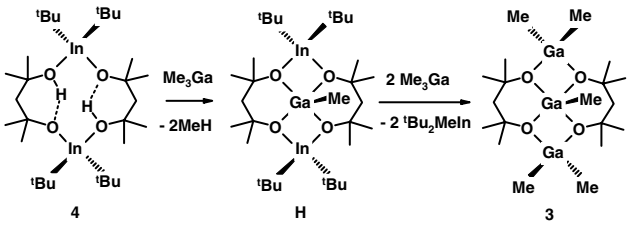
Scheme 7.

solvent protons reveals the signals of $GaC(CH_3)_3$ protons at 1.33 and 1.24 ppm of the mixture of simple gallium alkyls $^tBu_xMe_{(3-x)}Ga$.

The results of the above reactions show a less reactivity of the aluminium compound $\{^tBuAl[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ towards trimethyl metallanes in comparison with the gallium compound **2**. Compound **4** reacts with Me_3Ga to give also the complex **3** instead of an expected product $\{(MeGa)(^tBu_4In_2)[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ with a central gallium atom (Scheme 8). It was recently reported by Barron and coworkers [7b] that one equivalent of Me_3M reacts with the two acidic protons of the binuclear complexes $\{^tBu_4M'_2[diol\text{-}(H)]_2\}$, which results in the introduction of the central metal unit and formation of the stable compounds $\{(MeM)(^tBu_4M'_2)[diol\text{-}(2H)]_2\}$. However, we have found lately that those compounds can undergo a further exchange of $^tBu_2M'$ unit to yield the transmetallation product $\{(MeM)(Me_2M)(^tBu_2M')[diol\text{-}(2H)]_2\}$ [7c]. Very probably the first step of the reaction of **4** with one equivalent of Me_3Ga is the formation of the intermediate product $\{(MeGa)(^tBu_4In_2)[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ (H), which subsequently undergoes rapid exchange of two $^tBu_2In$ units (Scheme 8).

In conclusion, the length of the metal–carbon and metal–oxygen bonds determines the steric repulsion of ligands in diolate complexes and may be a decisive factor controlling the structure of compounds. The final products of the reaction of the sterically crowded diol with $^tBu_3M$ are trinuclear $\{^tBu_5M_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ and binuclear $\{^tBuM[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ depending on the M–C and M–O bond length. For longer M–C and M–O bonds present in the compounds with bulky metal atoms (for example in an indane complexes) steric repulsion of ^{t}Bu group bonded to the metal atom and two methyl groups of diol moieties decreases and the formation of compound $\{^tBu_4M_2[OC(CH_3)_2CH_2C(CH_3)_2OH]_2\}$ with the intramolecular hydrogen bonds is feasible. Therefore the reaction of 2,4-dimethyl-2,4-pentanediol with $^tBu_3In$ yields compound $\{^tBu_4In_2[OC(CH_3)_2CH_2C(CH_3)_2OH]_2\}$ (**4**) which can further react with one equivalent of $^tBu_3In$ to produce finally trinuclear complex $\{^tBu_5In_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ (**5**). Larger steric strain in alane and gallane diolates caused by shorter M–C and M–O bonds results in the formation of binuclear complexes with two OH groups (for example gallium compound **1**). Subsequently intramolecular reaction leads to bimetallic products $\{^tBuM[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$.

Binuclear complexes $\{^tBu_4M_2[OC(CH_3)_2CH_2C(CH_3)_2OH]_2\}$ and $\{^tBuM[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ react with different metal trialkyls according to the hard and soft acids and bases principle (HSAB). The harder metal (order of the hardness: Al > Ga > In) prefers the diolate ligands as the harder coordination sites whereas the softer metal leaves the aggregates as alkyl. On the other hand the reactions between *tert*-butyl metal diolates and metal trimethyls with the same metal causes the exchange of $^tBu_2M$ units into Me_2M units and reduction of steric strain.



Scheme 8.

3. Experimental

All manipulations were carried out using standard Schlenk techniques with anhydrous solvents under an inert gas atmosphere. $\{^tBuAl[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$, $^tBu_3Ga$ and $^tBu_3In$ were synthesised as described in the literature [6,18,19]. ^1H and ^{13}C 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 C_6D_6 (7.15 ppm) and CD_2Cl_2 (5.30 ppm). ^{13}C NMR spectra were run at 100.60 MHz (standards, benzene $^{13}CC_5D_6$, 128.00 ppm; dichloromethane $^{13}CD_2Cl_2$, 53.52 ppm). Elemental analyses were obtained on a Perkin–Elmer 2400 analyser. The molecular weights of the compounds were determined by cryoscopy in benzene.

3.1. Synthesis of $\{[^tBu_2Ga[OC(CH_3)_2CH_2C(CH_3)_2OH]\}_2$ (1)

To a sample (0.264 g, 2.0 mmol) of 2,4-dimethylpentane-2,4-diol in 10 cm^3 of Et_2O a solution of 0.506 g (2.1 mmol) of $^tBu_3Ga$ in 5 cm^3 of Et_2O was added via syringe. After 2 h all volatiles (the solvent and small excess of $^tBu_3Ga$) were removed from the post-reaction mixture under vacuum and the product **1** was obtained as a white solid (yield 0.620 g, 98%).

^1H NMR (C_6D_6) δ: 3.87 [s, 2H, broad, O*H*], 1.42 [s, 36H, (CH_3)$_3$CGa], 1.24 [s, 4H CH_2], 1.09 [s, 24H, (CH_3)$_2$C] ppm. ^{13}C NMR (C_6D_6) δ: 73.48 [*C*O], 51.68 [*C*H$_2$], 32.70 [(*C*H$_3$)$_3$CGa], 31.51 [(*C*H$_3$)$_2$C], 25.77 [(CH$_3$)$_3$*C*Ga] ppm. Molecular weight (C_6H_6): Found 590; Calcd 630 g mol^{-1}. Anal. Found (calcd) for $C_{30}H_{66}Ga_2O_4$: C, 56.36 (57.14); H, 11.35 (10.48)%.

During the subsequent crystallisation the product **1** undergoes decomposition yielding a mixture of solid compounds insoluble in C_6H_6.

3.2. Synthesis of [^{t}BuGa(OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O)]$_2$ (**2**)

3.2.1. Method 1

To a solution of (0.396 g, 3.0 mmol) of 2,4-dimethylpentane-2,4-diol in 10 cm^3 of $C_6H_5CH_3$ a solution of 0.795 g (3.3 mmol) of ^{t}Bu$_3$Ga in 10 cm^3 of $C_6H_5CH_3$ was added by a syringe. The mixture was refluxed during 1 h. Then the solvent and a small excess of ^{t}Bu$_3$Ga were distilled off under reduced pressure and the product **2** was sublimed yielding a white solid (100 °C, 10^{-3} Torr) (yield 0.648 g, 84%). The resulting solid was recrystallised from *n*-C_6H_{14}– CH_2Cl_2 solution at −25 °C to form X-ray quality crystals. m.p.: 122 °C.

^{1}H NMR (CD_2Cl_2): δ 2.34 (δ_A), 1.55 (δ_B) [4H, dd, ^2J (HH) 15.2 Hz, CH_2], 1.40 [6H, s, CH_3], 1.37 [6H, s, CH_3], 1.33 [6H, s, CH_3], 1.31 [6H, s, CH_3], 1.09 [18H, s, GaC(CH_3)$_3$]. ^{13}C NMR (CD_2Cl_2): δ 76.83, 72.10 [*C*O], 35.29, 33.91, 31.94, 31.59 [*C*H$_3$], 29.75 [GaC(*C*H$_3$)$_3$], 22.20 [Ga*C*(CH$_3$)$_3$] ppm. Anal. Found (calcd) for $C_{22}H_{46}Ga_2O_4$: C, 50.96 (51.36); H, 9.50 (8.95)%.

3.2.2. Method 2

A solution of **1** (0.630 g, 1.0 mmol) in 10 cm^3 of $C_6H_5CH_3$ was refluxed during 2 h. The product **2** was isolated as described in 3.2.1 (yield 0.410 g, 80%).

3.3. Synthesis of {Me$_5$Ga$_3$[OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O]$_2$} (**3**)

To a solution of 2,4-dimethylpentane-2,4-diol (0.528 g, 4.0 mmol) in 20 cm^3 of Et_2O held at −78 °C a solution of Me_3Ga (0.690 g 6.0 mmol) in 10 cm^3 of Et_2O was added by a syringe. The reaction mixture was allowed to warm to room temperature within 2 h. Then the volatiles were removed under reduced pressure. The ^{1}H NMR spectrum of the residue showed that the product **3** was formed almost quantitatively. X-ray quality crystals were obtained from *n*-C_6H_{14} solution at −25 °C. m.p.: 146–148 °C.

^{1}H NMR (C_6D_6): δ 1.69 (δ_A), 1.17 (δ_B) [4H, dd, ^2J (HH) 14.8 Hz, CH_2], 1.29 [12H, s, CH_3], 1.11 [12H, s, CH_3], 0.10 [3H, s, GaCH_3], 0.05 [6H, s, GaCH_3], −0.01 [6H, s, GaCH_3]. ^{13}C NMR (C_6D_6): δ 74.86 [*C*O], 53.06 [*C*H$_2$], 34.89, 31.39 [*C*H$_3$], −1.18, −2.25 [Ga*C*H$_3$] ppm. Anal. Found (calcd) for $C_{19}H_{43}Ga_3O_4$: C, 40.96 (41.83); H, 8.52 (7.89)%.

3.4. Synthesis of {[^{t}Bu$_4$In$_2$[OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$OH]$_2$} (**4**)

A solution of 2,4-dimethylpentane-2,4-diol (0.528 g, 4 mmol) in 10 cm^3 of Et_2O was added dropwise to a Et_2O solution of ^{t}Bu$_3$In (1.144 g, 4 mmol), at −76 °C. The solution was allowed to warm to room temperature and stirred for 2 h. Then the solvent was removed under vacuum. The product **4** was isolated by crystallisation from *n*-C_6H_{14} solution (0.605 g, yield 42%). A small amount of X-ray quality crystals was obtained by recrystallisation from $C_6H_5CH_3$ solution. m.p.: 159–161 °C.

^{1}H NMR (C_6D_6): δ 14.63 [2H, s, O*H*], 1.43 [36H, s, InC(CH_3)$_3$], 1.39 [4H, s, CH_2], 1.32 [24H, s, CH_3]. ^{13}C NMR (C_6D_6); δ 73.58 [*C*O], 51.86 [*C*H$_2$], 33.71 [*C*H$_3$], 33.10 [In*C*(CH$_3$)$_3$], 32.90 [InC(*C*H$_3$)$_3$] ppm. Anal. Found (calcd) for $C_{30}H_{66}In_2O_4$: C, 49.06 (49.97); H, 9.52 (9.16)%.

3.5. Synthesis of {^{t}Bu$_5$In$_3$[OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O]$_2$} (**5**)

3.5.1. Method 1

Product **5** was obtained as described in Section 3.2 (Method 1) using ^{t}Bu$_3$In (0.572 g, 2 mmol) and 2,4-dimethylpentane-2,4-diol (0.396 g, 3 mmol). The solvent was removed under vacuum and 0.650 g of **5** as a white solid was obtained after crystallisation at −25 °C from *n*-C_6H_{14} solution (yield 49%). m.p.: 204–205 °C.

^{1}H NMR (C_6D_6): δ 1.75 (δ_A), 1.38 (δ_B) [4H, dd, ^2J (HH) 15.4 Hz, CH_2], 1.52 [9H, s, (CH_3)$_3$CIn)], 1.45 [18H, s, (CH_3)$_3$CIn)], 1.43 [18H, s, (CH_3)$_3$CIn], 1.41 [12H, s, (CH_3)$_2$CO], 1.21 [12H, s, (CH_3)$_2$CO]. ^{13}C NMR (C_6D_6): δ 73.32 [*C*O], 55.64 [*C*H$_2$], 37.65, 34.07 [(*C*H$_3$)$_2$CO, broad], 35.00, 32.12, 30.19 [(CH$_3$)$_3$*C*In], 33.50, 33.37, 33.03 [(*C*H$_3$)$_3$CIn] ppm. Anal. Found (calcd) for $C_{34}H_{73}In_3O_4$: C, 46.56 (45.87); H, 8.62 (8.21)%.

3.5.2. Method 2

Product **5** was obtained as described in Section 3.2 (Method 2) using 0.360 g (0.5 mmol) of **4** and isolated after crystallisation from *n*-C_6H_{14} solution (yield 0,133 g, 30%).

3.6. Synthesis of {Me$_5$In$_3$[OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O]$_2$} (**6**)

Product **6** was obtained as described in Section 3.3 using 0.528 g (4.0 mmol) of 2,4-dimethylpentane-2,4-diol and 0.960 g (6.0 mmol) of Me_3In. The ^{1}H NMR analysis showed that the residue (after removing the solvent) consists of almost pure product **6** (yield 1.310 g, 98%). The attempts of crystallisation of **6** from solutions failed.

^{1}H NMR (C_6D_6): δ 1.55 (δ_A), 1.41 (δ_B) [4H, dd, ^2J (HH) 15.2 Hz, CH_2], 1.26 [12H, s, CH_3], 1.12 [12H, s, CH_3], 0.16 [6H, s, InCH_3], 0.15 [3H, s, InCH_3], 0.05 [6H, s, InCH_3]. ^{13}C NMR (C_6D_6): δ 74.53 [*C*O], 55.76 [*C*H$_2$], 36.37, 33.39 [*C*H$_3$], −1.52, −2.97, −4.99 [In*C*H$_3$] ppm. Anal. Found (calcd) for $C_{19}H_{29}In_3O_4$: C, 32.46 (33.56); H, 4.50 (4.27)%. Molecular weight (C_6H_6): Found 641; Calcd 679.4 g mol^{-1}.

3.7. Reaction of $\{^tBuAl[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ with Me_3Al

About 0.432 g (6 mmol) of Me_3Al was added to a solution of 0.856 g (2 mmol) of $\{^tBuAl[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ in 10 cm^3 of Et_2O at room temperature. After 1 month the solvent and the excess of Me_3Al were removed under vacuum. The ^1H NMR spectrum of the residue mixture reveals the signals of protons of two compounds only: **7** and $\{^tBuAl[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ in a molar ratio equal 8:1. Product **7** was isolated by fractional sublimation as a second fraction (160 °C, 10^{-3} Torr). The first fraction (120 °C, 10^{-3} Torr) contained mainly compound $\{^tBuAl[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$. Yield 0.550 g, 1.1 mmol, 55%.

^1H NMR (C_6D_6): δ 2.10 (δ_A), 0.82 (δ_B) (4H, dd, ^2J (HH) = 15.2 Hz, CH_2), 1.36 (6H, s, $OC(CH_3)_2$), 1.34 (6H, s, $OC(CH_3)_2$), 1.29 (9H, s, $AlC(CH_3)_3$) 1.27 (9H, s, $AlC(CH_3)_3$), 1.27 (6H, s, $OC(CH_3)_2$), 1.13 (6H, s, $OC(CH_3)_2$),−0.32 (3H, s, $AlCH_3$), −0.33 (3H, s, $AlCH_3$), −0.41 (3H, s, $AlCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 75.61, 74.39 ($OC(CH_3)_2$), 51.24 (CH_2), 34.79, 33.83, 31.18, 30.67 ($OC(CH_3)_2$), 33.54, 31.49 ($AlC(CH_3)_3$) ppm. Molecular weight (C_6H_6): Found 472; Calcd 500 g mol^{-1}. Anal. Found (calcd) for $C_{25}H_{55}Al_3O_4$: C, 59.06 (60.00); H, 11.55 (11.00)%.

3.8. Reactions of $\{^tBuGa[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ (2) with Me_3M (M = Al, Ga)

The reactions were carried out as described in Section 3.7 using 0.513 g (1 mmol) of **2** and 0.216 g (3 mmol) of Me_3Al (or 0.345 g (3 mmol) of Me_3Ga). The solvent and volatile organogallium and aluminium compounds were removed under reduced pressure. The compound $\{Me_5Al_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ (or $Me_5Ga_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2$ (**3**) was obtained as a sole non-volatile product of the reaction (according to NMR spectra).

3.9. Reaction of $\{^tBu_4In_2[OC(CH_3)_2CH_2C(CH_3)_2OH]_2\}$ 4 with Me_3Ga

The reaction was carried out as described in Section 3.7 using 0.628 g (1 mmol) of **4** and 0.345 g (3 mmol) of Me_3Ga. The compound $\{Me_5Ga_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ (**3**) was obtained as a sole non-volatile product of the reaction (according to NMR spectra).

3.10. X-ray crystal structure analyses

Determination of the crystal structures of **2**, **3** and **4** were performed on a KUMA KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. The crystals were positioned at 62.25 mm from the KM4CCD camera. For compound **2** 600 frames were measured in 1.2° intervals with a counting time of 15 s. For compound **3** 400 frames were measured in 1.0° intervals with a counting time of 25 s. For compound **4** 5000 frames were measured in 1.2 intervals with a counting time of 20 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 (Wrocław) programs. Structures of the investigated crystals were solved by Direct methods [20] and refined using the SHELXS/SHELXL computer programs [21]. All hydrogen atoms placed in the calculated positions and their thermal parameters were refined isotropically. The H atom bonded to the O atom was located in a difference Fourier map and refined isotropically. Scattering factors were taken from the literature (Tables 6.1.1.4 and 4.2.4.2. of [22]).

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. CCDC 225032, 225034 and 225033 for the compounds **2**, **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank Prof. K.B. Starowieyski (University of Technology, Warsaw) for trimethylgallium and indium.

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