

## Reactions of 1,2-catechol with $t\text{Bu}_3\text{M}$ (M = Ga, In). Structures of intermediate products

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### Abstract

Reactions of 1,2-catechol with  $t\text{Bu}_3\text{M}$  (M = Ga, In) have been studied. Trinuclear compounds [ $t\text{Bu}_5\text{M}_3(\text{OC}_6\text{H}_4\text{O})_2$ ] [M = Ga (**1**), M = In (**2**)] were synthesised in the reaction of 2 equiv. of  $\text{C}_6\text{H}_4(\text{OH})_2$  with 3 equiv. of  $t\text{Bu}_3\text{M}$  in refluxing solvents. At room temperature the reaction of 1,2-catechol with  $t\text{Bu}_3\text{In}$  in  $\text{Et}_2\text{O}$  leads to the formation of a binuclear complex [ $t\text{Bu}_4\text{In}_2(\text{OC}_6\text{H}_4\text{O}-\text{H})_2 \cdot 2\text{Et}_2\text{O}$ ] (**3**) possessing a four-membered  $\text{In}_2\text{O}_2$  core and two unreacted hydroxyl groups. The same reaction carried out in a non-coordinating solvent ( $\text{CH}_2\text{Cl}_2$ ) results in formation a compound [ $t\text{Bu}_3\text{In}_2(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{OH})$ ] (**4**), which undergoes a reaction with  $t\text{Bu}_3\text{In}$  to yield the product **2**. Moreover two intermediate isomeric products **5** and **6** of formula [ $t\text{Bu}_3\text{Ga}_2(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{OH})$ ] were isolated from the post-reaction mixture of 1,2-catechol with  $t\text{Bu}_3\text{Ga}$ . The compound **6** possessing a different coordination of gallium atoms than **5** is a result of the intramolecular rearrangement of the compound **5** to decrease the steric repulsion between ligands. Compounds **3** and **6** were structurally characterised. According to the structure of intermediate products **3–6** a reaction pathway of 1,2-catechols with group 13 metal trialkyls was proposed.

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**Keywords:** Gallium; Indium; 1,2-Catechol; Aromatic diols

### 1. Introduction

Biphenolate and BINOLate (where BINOL = 2,2'-dihydroxy-1,1'-binaphthyl) complexes of the group 13 of metals are very effective reagents for organic synthesis, especially for enantioselective synthesis involving Hetero-Diels–Alder reactions of various aldehydes with activated Danishefsky-type dienes [1], asymmetric hydrophosphinations of aldehydes [2] and Michael reactions [3–5]. Recently, it has been reported by Lin and co-workers [6] that the alkylalane 2,2'-methylenebiphenolates and their derivatives are highly efficient catalysts for the polymerisation of cyclic esters and they show

excellent catalytic activities toward hydrogen transfer reactions between aldehydes and 2-propanol. In comparison with the BINOLs and 2,2'-methylenebiphenols complexes, metallane catecholates are highly unexplored. Post-reaction mixtures of the unseparated products of reactions of catechols with diethylzinc were reported to be catalysts for epoxide polymerisation [7]. Reactions of hydroquinone and resorcinols with trimethylaluminium lead to a polymer containing (dioxybenzene)bis(dimethylaluminium) units [8]. Recently Barron and co-workers [9] have published the crystal structure of 1,4-dioxobenzene di-*tert*-butylaluminium analogues. We found, that the reaction of 1,2-catechol with  $\text{R}_3\text{Al}$  (where R = Me, Et,  $t\text{Bu}$ ,  $i\text{Bu}$ ) results in the formation of trinuclear complexes [ $\text{R}_5\text{Al}_3(\text{OC}_6\text{H}_4\text{O})_2$ ] [10]. There are numerous examples of similar trinuclear compounds obtained in the reactions of diols with group

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13 metal trialkyls [11]. Although the binuclear complexes **A** are reported as the intermediate products in the formation of trinuclear alkylmetallane aliphatic diolates **B** (Scheme 1), the reaction pathway of aromatic diols involving in 1,2-catechols and biphenols with group 13 metal trialkyls is unknown. The aim of our work was an isolation of intermediate products and proposition of the reaction course of 1,2-catechol with metal trialkyls.

## 2. Results and discussion

The reaction of 3 equiv. of  $t\text{Bu}_3\text{M}$  (where  $\text{M} = \text{Ga}$ ,  $\text{In}$ ) with 2 equiv. of 1,2-catechol in refluxing solvents (toluene for  $t\text{Bu}_3\text{Ga}$  and the a mixture of hexane and methylene dichloride for  $t\text{Bu}_3\text{In}$ ) yields trimetallic products [ $t\text{Bu}_5\text{M}_3(\text{OC}_6\text{H}_4\text{O})_2$ ] [ $\text{M} = \text{Ga}$  (**1**),  $\text{M} = \text{In}$  (**2**)] (Scheme 2).

Complexes **1** and **2** were characterised by  $^1\text{H}$  and  $^{13}\text{C}$  NMR as well as elemental analysis and molecular weight determination. Unfortunately, we were unable to characterise the complexes crystallographically. The NMR spectra of **1** and **2** are similar to those of structurally characterised *tert*-butylalane 1,2-catecholate [ $t\text{Bu}_5\text{Al}_3(\text{OC}_6\text{H}_4\text{O})_2$ ] [10]. This indicates that compounds **1** and **2** and the alane derivative are isostructural.  $^1\text{H}$  NMR spectra reveal three singlets of the protons of  $t\text{Bu}$  groups (at 1.44, 1.22, 0.98 and 1.54, 1.27, 1.09

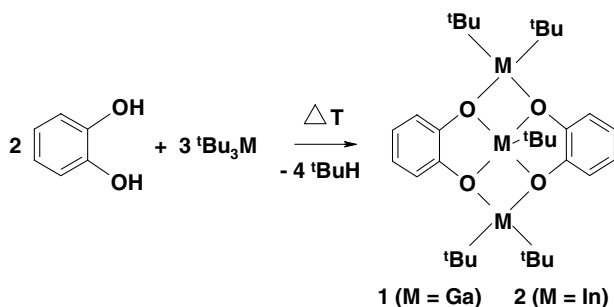
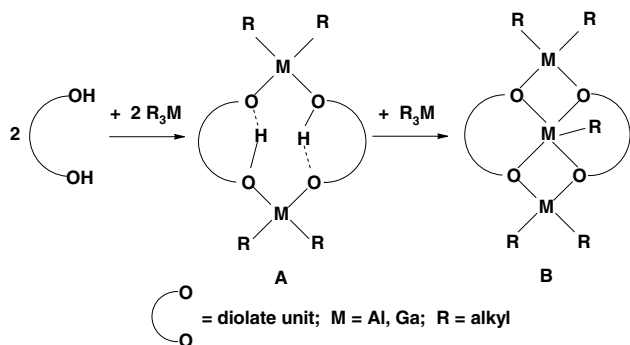
ppm of **1** and **2**, respectively) with an integration ratio of 2:1:2. Moreover the integration ratio of the signals of aromatic protons and *tert*-butyl protons indicates the presence of two aromatic diol units and five  $t\text{Bu}$  groups, which is fully consistent with the proposed structures of **1** and **2**.

The use of a lower temperature and different solvents allowed us to obtain intermediate products of the reaction of tri-*tert*-butylgallane and -indane with 1,2-catechol and to propose a reaction pathway (Scheme 3). The reaction of  $t\text{Bu}_3\text{In}$  with one equivalent of 1,2-catechol in a mixture of  $n\text{-C}_6\text{H}_{14}\text{-Et}_2\text{O}$  at room temperature yields the product [ $t\text{Bu}_4\text{In}_2(\text{OC}_6\text{H}_4\text{OH})_2 \cdot 2\text{Et}_2\text{O}$ ] **3** (Scheme 3), which precipitates from the post-reaction mixture as a colourless solid.

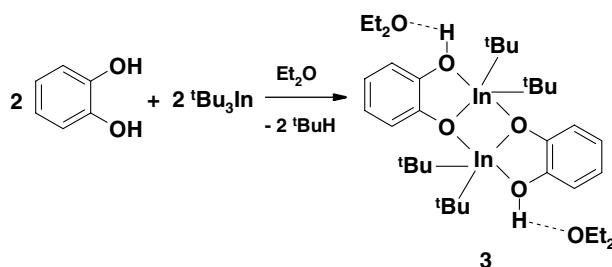
The  $^1\text{H}$  NMR spectrum of **3** reveals the signals of aromatic protons, singlets at 1.48 and 6.03 ppm of the protons of  $t\text{Bu}$  and  $\text{OH}$  groups, and the signals of the protons of  $\text{Et}_2\text{O}$ .

Crystals of the compound **3** suitable for an X-ray structure determination were grown from a  $\text{CH}_2\text{Cl}_2$  solution at  $-25^\circ\text{C}$ . The molecular structure of **3** is shown in Fig. 1 (top). Data collection and structure analysis details are presented in Table 1.

Crystals of compound **3** contain two kinds of molecules in the cell slightly differing in bond lengths and angles. Molecule of **3** exists as a centrosymmetric dimer with a central  $\text{In}_2\text{O}_2$  cycle. As shown in Fig. 1 (bottom), two  $\text{InO}_2\text{C}_2$  cycles, two aromatic rings and the central  $\text{In}_2\text{O}_2$  cycle are coplanar. The hydroxyl groups form hydrogen bonds with diethyl ether. The presence of a  $^1\text{H}$  NMR signal of  $\text{OH}$  protons at 6.03 ppm indicates dissociation of the  $\text{OH} \cdots \text{OEt}_2$  hydrogen bonds in solution. The signals of hydrogen bond protons in complexes of group 13 metals are reported to be these shifted downfield (at 14–17 ppm) [11c, 11f, 11g, 12]. The indium atoms are five-coordinate with a geometry close to that of a trigonal bipyramid. The O(1) and O(2) atoms [O(3) and O(4) in the second molecule] occupy the axial positions [O(1)–In(1)–O(2)  $140.5(1)^\circ$ , O(4)–In(2)–O(3)  $140.3(1)^\circ$ ]. The equatorial sites are defined by O(1)#1 [O(4)#2 in the second molecule] and two carbon atoms of  $t\text{Bu}$  groups. Similar aluminium chloride alkoxides and gallane complexes with 1,2-diols were



Scheme 2.



Scheme 3.

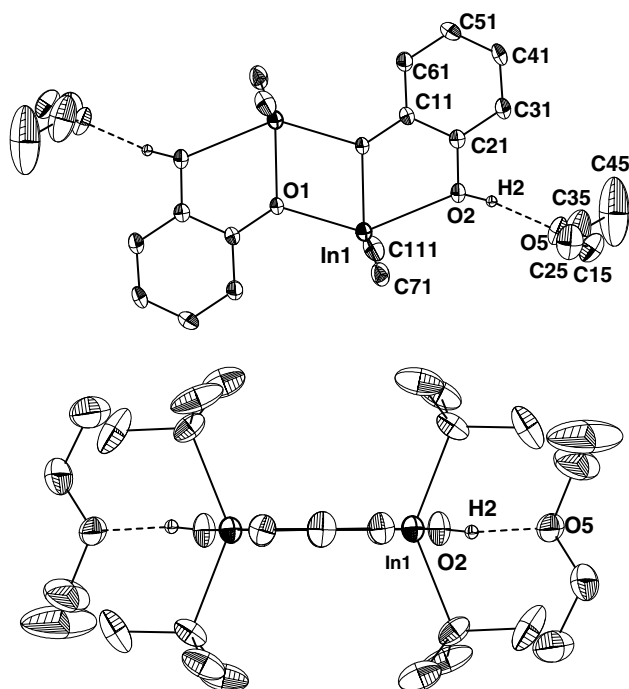


Fig. 1. (top) Molecular structure of  ${}^t\text{Bu}_4\text{In}_2[\text{OC}_6\text{H}_4\text{OH}]_2 \cdot 2(\text{OEt}_2)$ . Thermal ellipsoids are shown at the 20% level. Hydrogen atoms attached to carbon and methyl groups of  ${}^t\text{Bu}$  groups bonded to indium atoms are omitted for clarity. Selected bond distances (Å) and angles ( $^\circ$ ): structure (1) In(1)–O(1) 2.282(3), In(1)–O(2) 2.551(3), In(1)–O(1)#1 2.185(3), O(2)–H(2) 0.87(5), In(1)–C(111) 2.183(6), In(1)–C(71) 2.185(5), C(111)–In(1)–C(71) 136.1(3), C(111)–In(1)–O(1)#1 110.2(2), C(71)–In(1)–O(1)#1 110.2(2), C(111)–In(1)–O(1) 104.2(2), C(71)–In(1)–O(1) 104.1(2), O(1)#1–In(1)–O(1) 71.9(1), C(111)–In(1)–O(2) 90.0(2), C(71)–In(1)–O(2) 89.1(2), O(1)#1–In(1)–O(2) 68.6(1), O(1)–In(1)–O(2) 140.5(1); structure (2) In(2)–C(72) 2.187(6), In(2)–C(112) 2.191(6), In(2)–O(4)#2 2.194(3), In(2)–O(4) 2.269(3), In(2)–O(3) 2.549(4), O(3)–H(3) 0.70(4), C(72)–In(2)–C(112) 136.5(3), C(72)–In(2)–O(4)#2 109.8(2), C(112)–In(2)–O(4)#2 109.9(2), C(72)–In(2)–O(4) 103.8(2), C(112)–In(2)–O(4) 104.3(2), O(4)#2–In(2)–O(4) 72.7(1), C(72)–In(2)–O(3) 89.8(2), C(112)–In(2)–O(3) 89.4(2), O(4)#2–In(2)–O(3) 67.6(1), O(4)–In(2)–O(3) 140.3(1). (bottom) View of the molecule showing that the central  $\text{In}_2\text{O}_2$  cycle, two  $\text{InO}_2\text{C}_2$  cycles and the two aromatic rings are coplanar.

obtained and structurally characterised by Wuest [13] and Schmidbauer [14].

In a presence of a non-coordinating solvent ( $\text{CH}_2\text{Cl}_2$ ), the reaction of  ${}^t\text{Bu}_3\text{In}$  with 1 equiv. of 1,2-catechol yields the compound [ ${}^t\text{Bu}_3\text{In}_2(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{OH})$ ] (**4**), which was isolated by precipitation from an *n*-hexane solution of the post-reaction mixture (Scheme 4).

Presumably, in the absence of a Lewis base, a compound **3** is unstable and undergoes further alkane elimination reaction to yield the product **4**. Upon refluxing in methylene dichloride compound **4** reacts with 1 equiv. of  ${}^t\text{Bu}_3\text{In}$  to yield compound **2**. The structure of **4** was assigned by means of NMR spectroscopy. The  ${}^1\text{H}$  NMR spectrum comprises the signals of aromatic pro-

tons and three singlets (1.57, 1.33 and 0.92 ppm) of  $(\text{CH}_3)_3\text{CIn}$  protons with an integration ratio of 8:3:3:3, which is consistent with the proposed constitution of **4**. The signal of the OH protons is broad and positioned in the region of 5–6 ppm. The chemical shift of the OH protons indicates the absence of intra- and intermolecular hydrogen bonds.

As described above, the reaction of  ${}^t\text{Bu}_3\text{Ga}$  with 1,2-catechol proceeds with formation of compound **1**, which was isolated by crystallisation from a toluene–hexane solution (Scheme 2). However, a careful analysis of the  ${}^1\text{H}$  NMR spectrum of the post-reaction mixture showed, that besides the major product **1**, minor amounts of the isomeric compounds **5** and **6** [ ${}^t\text{Bu}_3\text{Ga}_2(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{OH})$ ] are present (Scheme 5).

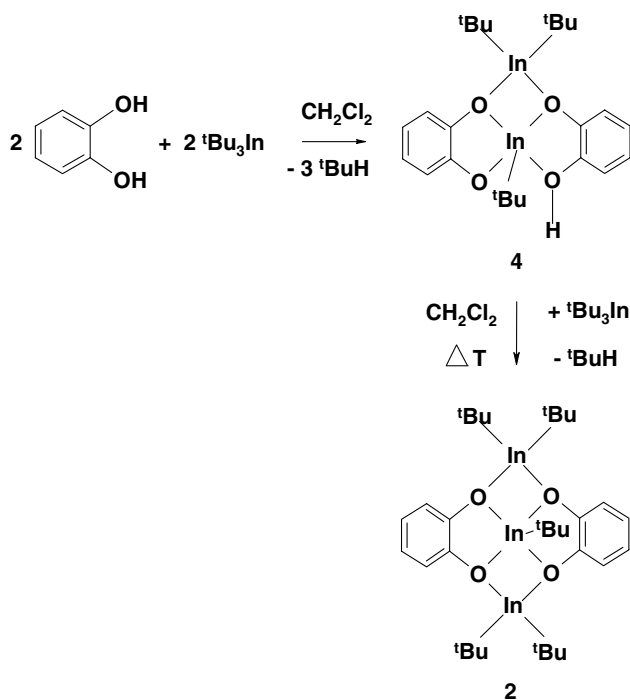
A crystallisation from  $\text{CH}_2\text{Cl}_2$ –hexane solution of the post-reaction mixture yielded a crystalline material containing the compound **6**, which was determined by X-ray measurements of a single crystal. However,  ${}^1\text{H}$  NMR spectrum of the crystalline material revealed proton signals of the mixture of compounds **6** and **5** in a molar ratio equals 4:1 (according to the integration ratio of  ${}^t\text{Bu}$  proton signals). This indicates that the crystalline material can be a mixture of **5** and **6**. It is also possible that the pure compound **6** precipitates from the post-reaction mixture and upon dissolution dynamic behaviour results in formation of the compound **5**. To elucidate this point we recorded temperature dependent  ${}^1\text{H}$  NMR spectra of a  $\text{CDCl}_3$  solution of a crystalline solid precipitated from a solution of the post-reaction mixture (see Section 3). We found that the molar ratios of **5** and **6** (according to the integration ratio of OH proton signals) are the same, independently on the temperature. It means that **5** and **6** crystallise together from the solution of the post-reaction mixture.

The solid-state structure of the compound **6** was determined by X-ray crystallography and is shown in Fig. 2 (top).

Data collection and structure analysis details are presented in Table 1. The structure determination reveals that crystals of compound **6** contain two kinds of crystallographically independent molecules slightly differing in bond lengths and angles. The molecular structure consists of a dimer formed by the alkoxide termini of two ligands bridging  ${}^t\text{Bu}_2\text{Ga}$  and  ${}^t\text{BuGa}$  units [Ga(1) and Ga(2), respectively]. The five-coordinate Ga(1) gallium atom resides in a distorted square pyramidal geometry with the basal plane consisting of four oxygen atoms of the diol units and the  ${}^t\text{Bu}$  group residing in an apical position. The coordination geometry of this atom is more close to a square pyramidal structure [i.e., O(3)–Ga(2)–O(4) 128.0(2), O(2)–Ga(2)–O(1) 138.6(2)] than to a trigonal-bipyramidal geometry. The OH group is involved in an intermolecular hydrogen bond with an  $\text{H}\cdots\text{O}(7)$  distance of 1.46(6) Å (Fig. 2, bottom). The presence of the down-

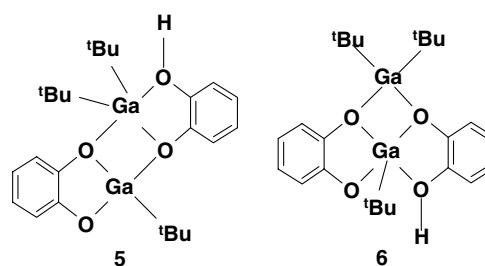
Table 1  
Crystal data and collection parameters for **3** and **6**

|  | <b>3</b>  | <b>6</b>   |
|--|---|--|
| Empirical formula  | C <sub>36</sub> H <sub>66</sub> In <sub>2</sub> O <sub>6</sub>  | C <sub>24</sub> H <sub>36</sub> Ga <sub>2</sub> O <sub>4</sub> ·0.5CH <sub>2</sub> Cl <sub>2</sub> |
| Formula weight   | 824.53  | 1140.86  |
| Temperature (K)  | 293(2)  | 293(2)   |
| Wavelength (Å)   | 0.71073   | 0.71073  |
| Crystal system   | Monoclinic  | Triclinic  |
| Space group  | <i>P</i> 2 <sub>1</sub> / <i>c</i>                              | <i>P</i> $\bar{1}$   |
| <i>a</i> (Å)   | 21.321(4)   | 11.598(2)  |
| <i>b</i> (Å)   | 13.737(3)   | 14.648(3)  |
| <i>c</i> (Å)   | 14.414(3)   | 16.633(3)  |
| $\alpha$ (°)   | 90  | 97.60(3)   |
| $\beta$ (°)  | 90.52(3)  | 93.54(3)   |
| $\gamma$ (°)   | 90  | 91.82(3)   |
| <i>V</i> (Å <sup>3</sup> )                                   | 4221.5(15)  | 2793.3(9)  |
| <i>Z</i>   | 4   | 4  |
| <i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )               | 1.297   | 2.713  |
| Absorption coefficient (mm <sup>-1</sup> )                   | 1.129   | 4.099  |
| <i>F</i> (000)   | 1712  | 2360   |
| Crystal size (mm)  | 0.20 × 0.20 × 0.10  | 0.38 × 0.25 × 0.22   |
| $\theta$ range for data collection (°)                       | 3.19–28.80  | 3.37–28.80   |
| Index ranges   | –28 ≤ <i>h</i> ≤ 28, –18 ≤ <i>k</i> ≤ 18, –19 ≤ <i>l</i> ≤ 14   | –15 ≤ <i>h</i> ≤ 15, –19 ≤ <i>k</i> ≤ 19, –22 ≤ <i>l</i> ≤ 22                                      |
| Reflections collected  | 37445   | 50657  |
| Independent reflections ( <i>R</i> <sub>int</sub> )          | 10303 (0.093)   | 13539 (0.100)  |
| Refinement method  | Full-matrix least-squares on <i>F</i> <sup>2</sup>              | Full-matrix least-squares on <i>F</i> <sup>2</sup>   |
| Data/parameters  | 10297/405   | 13539/569  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                     | 1.069   | 0.956  |
| Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]          | <i>R</i> <sub>1</sub> = 0.0490, <i>wR</i> <sub>2</sub> = 0.0883 | <i>R</i> <sub>1</sub> = 0.0621, <i>wR</i> <sub>2</sub> = 0.1534                                    |
| <i>R</i> indices (all data)                                  | <i>R</i> <sub>1</sub> = 0.1316, <i>wR</i> <sub>2</sub> = 0.1086 | <i>R</i> <sub>1</sub> = 0.1385, <i>wR</i> <sub>2</sub> = 0.1898                                    |
| Residual electron density peak and hole (e Å <sup>-3</sup> ) | 0.494 and –0.652  | 1.119 and –0.996   |



Scheme 4.

field shifted signal of the OH protons (at 17.79 ppm) in the <sup>1</sup>H NMR spectrum indicates that intermolecular hydrogen bonds exist also in solutions of **6**. In our



Scheme 5.

opinion the gallium compound **6** and the indium compound **4** are isostructural, which was concluded on the basis of similarities of NMR spectra. The <sup>1</sup>H NMR spectrum of **6** as that of the compound **4** reveals three singlets (1.48, 1.30 and 0.81 ppm) of protons of three inequivalent <sup>t</sup>BuGa groups.

The composition of compound **5** is proposed only on the basis of an <sup>1</sup>H NMR spectrum of the mixture of **5** and **6**, because we could not isolate it. The <sup>1</sup>H NMR spectrum, besides the signals of **6**, contains three singlets (1.47, 1.34 and 0.91 ppm) of the protons of three <sup>t</sup>BuGa groups and one signal at 16.77 ppm of the OH group with an integration ratio of 9:9:9:1. It suggests the same composition of both products, **5** and **6**. It seems that compound **5** is an intermediate product between the compounds **C** and **E** (Scheme 6).

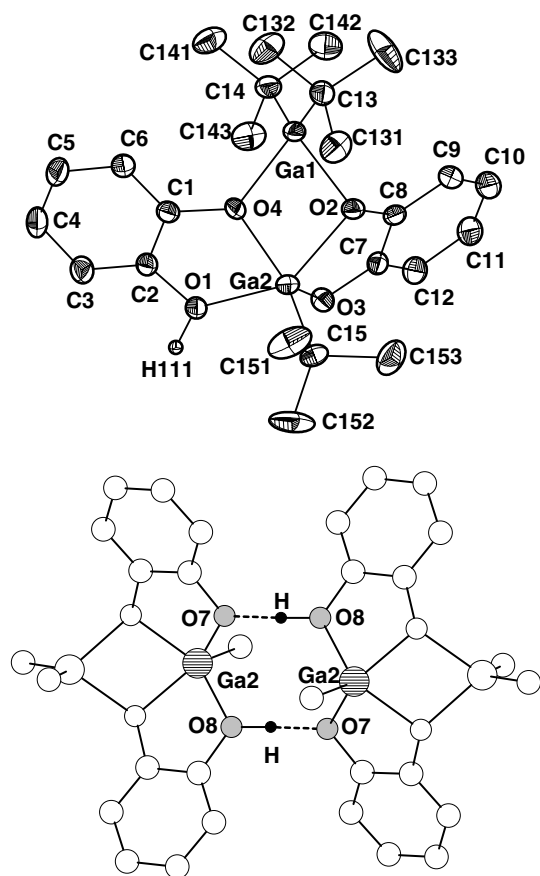


Fig. 2. (top) Molecular structure of  $[\text{tBu}_3\text{Ga}_2(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{OH})]$  (**6**). Thermal ellipsoids are shown at the 20% level and hydrogen atoms attached to carbon and the molecule of the solvent are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): structure (**1**) Ga(1)–C(13) 1.973(5), Ga(1)–C(14) 1.978(6), Ga(1)–O(2) 1.992(3), Ga(1)–O(4) 1.994(3), Ga(2)–O(3) 1.957(3), Ga(2)–O(4) 1.962(3), Ga(2)–C(15) 1.965(5), Ga(2)–O(2) 2.015(3), Ga(2)–O(1) 2.042(4), O(1)–H(111) 0.97(6), O(3)–Ga(2)–O(4) 128.0(2), O(3)–Ga(2)–C(15) 111.6(2), O(4)–Ga(2)–C(15) 120.4(2), O(3)–Ga(2)–O(2) 81.1(1), O(4)–Ga(2)–O(2) 77.2(1), C(15)–Ga(2)–O(2) 113.2(2), O(3)–Ga(2)–O(1) 87.5(1), O(4)–Ga(2)–O(1) 79.2(1), C(15)–Ga(2)–O(1) 108.0(2), O(2)–Ga(2)–O(1) 138.6(2); structure (**2**) Ga(3)–C(30) 1.966(6), Ga(3)–O(6) 1.978(4), Ga(3)–O(7) 1.990(4), Ga(3)–O(5) 1.999(4), Ga(3)–O(8) 2.005(4), Ga(4)–C(28) 1.967(7), Ga(4)–O(5) 1.988(4), Ga(4)–O(6) 1.999(4), Ga(4)–C(29) 1.999(7), C(30)–Ga(3)–O(6) 119.7(2), C(30)–Ga(3)–O(7) 109.4(2), O(6)–Ga(3)–O(7) 130.8(2), C(30)–Ga(3)–O(5) 113.4(2), O(6)–Ga(3)–O(5) 76.6(2), O(7)–Ga(3)–O(5) 81.2(2), C(30)–Ga(3)–O(8) 110.1(2), O(6)–Ga(3)–O(8) 80.2(2), O(7)–Ga(3)–O(8) 86.8(2), O(5)–Ga(3)–O(8) 136.4(2). (bottom) View of two molecules of  $[\text{tBu}_3\text{Ga}_2(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{OH})]$  (**6**) showing the intermolecular hydrogen O–H $\cdots$ O bonds. The H $\cdots$ O(7) distance is 1.46(6) Å. Aromatic hydrogen atoms and methyl groups were omitted for clarity.

According to the structure of compounds **1–6** we propose the reaction pathway of 1,2-catechols with trialkyls of group 13 metals (Scheme 6). The intermediate products of the reaction of  $\text{R}_3\text{Al}$  with 1,2-catechol were not obtained [10], however in our opinion the reaction course is the same for indium, gallium and aluminium trialkyls.

The first step of the reaction affords the binuclear complex **C** with penta-coordinate metal atoms chelated and bridged by mono-deprotonated catechol ligands. The subsequent intramolecular reaction of one  $\text{tBu}$  group with an OH group results in the formation of the intermediate product **D**, which undergoes the intramolecular rearrangement to yield the compound **E**. This compound reacts further with  $\text{R}_3\text{M}$  whereby the final trinuclear product **F** is formed. Recently Barron reported two products,  $[\text{tBu}_3\text{Al}_2(\text{OCH}_2\text{CH}_2\text{O})(\text{OCH}_2\text{CH}_2\text{OH})]$  (**E** type) and  $[\text{tBu}_3\text{Al}_3(\text{OCH}_2\text{CH}_2\text{O})_2]$  (**F** type), of the reaction of ethane-1,2-diol with  $\text{tBu}_3\text{Al}$ . He proposed the similar reaction course to the one presented in Scheme 6 [15].

Taking into account the structure of the reaction products of 1,2-catechol and ethane-1,2-diol with  $\text{tBu}_3\text{M}$  we conclude that all 1,2-diols react with metal trialkyls according to the same pathway independently on the aromatic or aliphatic nature of 1,2-diols. Reactions of 1,2-diols and diols possessing longer carbon backbones with metal group 13 trialkyls result in formation of the same final products  $[\text{R}_5\text{M}_3(\text{diol}-(2\text{H}))]$ , however the reaction courses are different. Presumably the formation of the intermediate product **A** (Scheme 1) typical for 1,3- and longer diols is not feasible in the case of 1,2-diols due to the strain in five-membered rings  $\text{C}_2\text{O}_2\text{H}$ . Therefore, instead of **A**, the intermediate product **C** with, typical for alkoxy compounds, central four-membered ring  $\text{M}_2\text{O}_2$  is produced.

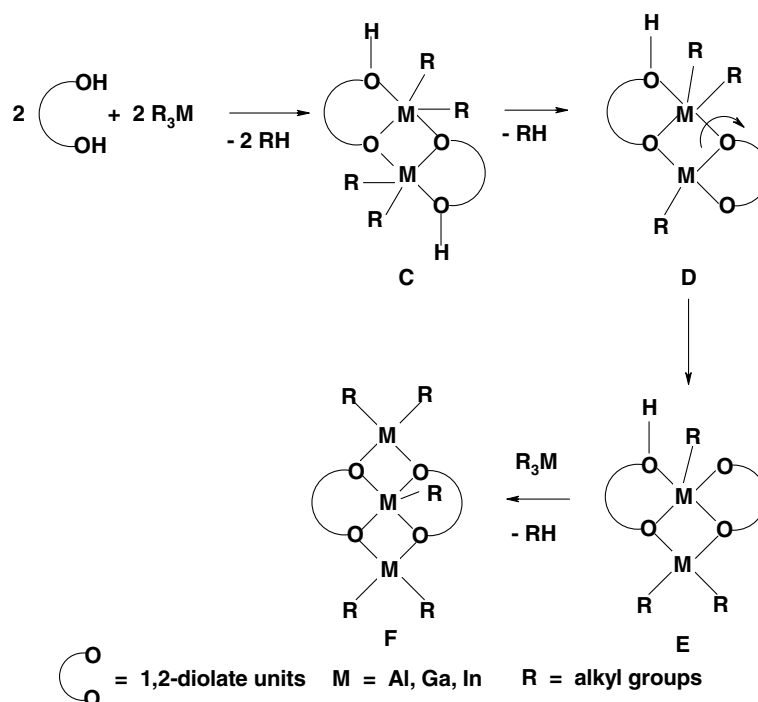
### 3. Experimental

All manipulations were carried out using standard Schlenk techniques with anhydrous solvents under an inert gas atmosphere.  $\text{tBu}_3\text{Ga}$  and  $\text{tBu}_3\text{In}$  were synthesised as described in the literature [16,17].  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were run on a Mercury-400BB spectrometer.  $^1\text{H}$  NMR spectra were recorded at 400.09 MHz. Chemical shifts were referenced to the residual proton signals of  $\text{C}_6\text{D}_6$  (7.15 ppm) and  $\text{CDCl}_3$  (7.26 ppm).  $^{13}\text{C}$  NMR spectra were run at 100.60 MHz (standard, benzene  $^{13}\text{CC}_5\text{D}_6$ , 128.00 ppm). FT-IR spectra were recorded on a Perkin-Elmer System 2000 instrument. 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 $[\text{tBu}_3\text{Ga}_3(\text{OC}_6\text{H}_4\text{O})_2]$ (**1**)

To a solution of 1,2-catechol (0.220 g, 2.0 mmol) in  $10\text{ cm}^3$  of  $\text{C}_6\text{H}_5\text{CH}_3$  held at  $-78\text{ }^\circ\text{C}$  a solution of  $\text{tBu}_3\text{Ga}$  (0.723 g 3.0 mmol) in  $10\text{ cm}^3$  of  $\text{C}_6\text{H}_5\text{CH}_3$  was added by a syringe. The reaction mixture was allowed to warm to room temperature within 1 h. Then the mixture was refluxed during 3 h. The volatiles were removed under





Scheme 6.

reduced pressure and 0.380 g of **1** as a white solid was obtained after crystallisation at  $-25\text{ }^{\circ}\text{C}$  from  $n\text{-C}_6\text{H}_{14}\text{-C}_6\text{H}_5\text{CH}_3$  solution (yield 53%). M.p.:  $210\text{--}215\text{ }^{\circ}\text{C}$ .

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.68 (8H, m, H arom.), 1.44 (18H, s,  $\text{GaC}(\text{CH}_3)_3$ ), 1.22 (9H, s,  $\text{GaC}(\text{CH}_3)_3$ ), 0.98 (18H, s,  $\text{GaC}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  149.47, 121.77, 116.95 (C arom.), 31.05, 30.82, 30.52 ( $\text{GaC}(\text{CH}_3)_3$ ), 29.01, 26.37 ( $\text{GaC}(\text{CH}_3)_3$ ) ppm. Anal. Found (calcd) for  $\text{C}_{32}\text{H}_{53}\text{Ga}_3\text{O}_4$ : C, 53.08 (54.01); H, 8.02 (7.45)%. Molecular weight ( $\text{C}_6\text{H}_6$ ): Found 670; Calcd  $711\text{ gmol}^{-1}$ .

### 3.2. Synthesis of [ $^t\text{Bu}_3\text{In}_3(\text{OC}_6\text{H}_4\text{O})_2$ ] (**2**)

Product **2** was obtained as described in Section 3.1 using a solution of 0.220 g (2.0 mmol) of 1,2-catechol in  $10\text{ cm}^3$  of  $\text{CH}_2\text{Cl}_2$  and a solution of 0.858 g (3.0 mmol) of  $^t\text{Bu}_3\text{In}$  in  $10\text{ cm}^3$  of  $n\text{-C}_6\text{H}_{14}$ . Volatiles were removed under reduced pressure and product **2** was obtained as a colourless solid almost quantitatively. 0.338 g of **2** as a colourless solid was obtained after crystallisation at  $-25\text{ }^{\circ}\text{C}$  from an  $n\text{-C}_6\text{H}_{14}$  solution (yield 40%). The crystals are very soft, extremely sensitive to traces of moisture and darken upon exposure to light.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.73 (8H, m, H arom.), 1.54 (18H, s,  $\text{InC}(\text{CH}_3)_3$ ), 1.27 (9H, s,  $\text{InC}(\text{CH}_3)_3$ ), 1.09 (18H, s,  $\text{InC}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  151.36, 120.41, 117.89 (C arom.), 41.28, 37.67 ( $\text{InC}(\text{CH}_3)_3$ ), 32.68, 32.42, 32.25 ( $\text{InC}(\text{CH}_3)_3$ ) ppm. Anal. Found

(calcd) for  $\text{C}_{32}\text{H}_{53}\text{In}_3\text{O}_4$ : C, 44.16 (45.39); H, 7.36 (6.26)%.

### 3.3. Synthesis of [ $^t\text{Bu}_4\text{In}_2(\text{OC}_6\text{H}_4\text{OH})_2 \cdot 2\text{Et}_2\text{O}$ ] (**3**)

A solution of 1,2-catechol (0.220 g, 2.0 mmol) in  $10\text{ cm}^3$  of  $\text{Et}_2\text{O}$  was added dropwise to an  $n\text{-C}_6\text{H}_{14}$  solution of  $^t\text{Bu}_3\text{In}$  (0.557 g, 2.0 mmol), at  $-76\text{ }^{\circ}\text{C}$ . The mixture was allowed to warm to room temperature and was stirred for 2 h. Compound **3** precipitated from the reaction mixture as a colourless solid (0.741 g, yield 90%).

$^1\text{H}$  NMR (immediately after the isolation from the reaction mixture) ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.00 (2H, dd,  $^3J_{\text{H-H}} = 7.9\text{ Hz}$ ,  $^4J_{\text{H-H}} = 1.4\text{ Hz}$ , *o-CH*), 6.88 (2H, td,  $^3J_{\text{H-H}} = 7.8\text{ Hz}$ ,  $^4J_{\text{H-H}} = 1.4\text{ Hz}$ , *m-CH*), 6.61 (2H, td,  $^3J_{\text{H-H}} = 7.8\text{ Hz}$ ,  $^4J_{\text{H-H}} = 1.7\text{ Hz}$ , *m-CH*), 6.43 (2H, dd,  $^3J_{\text{H-H}} = 7.9\text{ Hz}$ ,  $^4J_{\text{H-H}} = 1.4\text{ Hz}$ , *o-CH*), 6.03 (2H, s, OH) 3.22 (8H, q,  $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 1.48 (36H, s,  $\text{InC}(\text{CH}_3)_3$ ), 1.06 (12H, t,  $\text{O}(\text{CH}_2\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  150.90, 143.66, 122.34, 119.90, 117.57, 114.71 (C arom.), 65.90 ( $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 36.34 ( $\text{InC}(\text{CH}_3)_3$ ), 33.18 ( $\text{InC}(\text{CH}_3)_3$ ), 15.26 ( $\text{O}(\text{CH}_2\text{CH}_3)_2$ ) ppm.

IR (Nujol) ( $\text{cm}^{-1}$ ): 3491 (s) (OH), 3038 (m), 2833 (s), 2764 (w), 2704 (w), 1596 (m), 1583 (w), 1522 (w), 1502 (s), 1456 (s), 1363 (m), 1336 (m), 1289 (s), 1266 (s), 1236 (m), 1202 (w), 1183 (w), 1166 (m), 1155 (m), 1102 (m), 1069 (w), 1037 (m), 1016 (w), 918 (w), 858 (m), 832 (w), 812 (m), 775 (m), 749 (s), 743 (s), 603 (m), 585 (m).

The compound **3** undergoes slow transformation to the complex **4**. After 3 days, besides the signals of **3**, additional signals of the compound **4** appear in the NMR spectra.

X-ray quality crystals of **3** were obtained from a CH<sub>2</sub>Cl<sub>2</sub> solution at –25 °C. M.p. >300 °C. The crystals are insoluble in C<sub>6</sub>D<sub>6</sub>. In a CD<sub>2</sub>Cl<sub>2</sub> solution a fast decomposition of **3** occurs. Anal. Found (calcd) for C<sub>36</sub>H<sub>66</sub>In<sub>2</sub>O<sub>6</sub>: C, 51.42 (52.40); H, 8.69 (8.00)%. In the IR spectrum of the crystals of **3** the absorption at 3491 cm<sup>-1</sup> (OH) is significantly weaker in comparison with the same absorption of the precipitated solid of **3**.

### 3.4. Synthesis of [<sup>t</sup>Bu<sub>3</sub>In<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>O)(OC<sub>6</sub>H<sub>4</sub>OH)] (**4**)

A solution of 1,2-catechol (0.220 g, 2.0 mmol) in 10 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to a CH<sub>2</sub>Cl<sub>2</sub> solution (10 cm<sup>3</sup>) of <sup>t</sup>Bu<sub>3</sub>In (0.585 g, 2.1 mmol), at –76 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. Immediately after the reaction a colourless solid precipitated and was washed with *n*-C<sub>6</sub>H<sub>14</sub> and dried under reduced pressure to yield the pure compound **4** (0.470 g, yield 75%).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 6.87 (2H, dd, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.8 Hz, *o*-CH), 6.68 (6H, m, *H* arom), 1.57 (9H, s, InC(CH<sub>3</sub>)<sub>3</sub>), 1.33 (9H, s, InC(CH<sub>3</sub>)<sub>3</sub>), 0.92 (9H, s, InC(CH<sub>3</sub>)<sub>3</sub>). A broad signal of the OH protons was observed in the region of 5–6 ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 149.50, 147.06, 120.94, 120.62, 117.67, 115.85 (*C* arom.), 32.39, 32.23 (InC(CH<sub>3</sub>)<sub>3</sub>), 31.79, 31.64, 31.43 (InC(CH<sub>3</sub>)<sub>3</sub>) ppm. Anal. Found (calcd) for C<sub>24</sub>H<sub>36</sub>In<sub>2</sub>O<sub>4</sub>: C, 46.01.42 (46.60); H, 6.18 (5.83)%.

### 3.5. Reaction of [<sup>t</sup>Bu<sub>3</sub>In<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>O)(OC<sub>6</sub>H<sub>4</sub>OH)] (**4**) with <sup>t</sup>Bu<sub>3</sub>In

To a solution of (0.124 g, 0.2 mmol) of **4** in 3 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> a solution of 0.057 g (0.2 mmol) of <sup>t</sup>Bu<sub>3</sub>In in 1 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was added by a syringe. The mixture was

refluxed during 1 h. Then the solvent was removed under reduced pressure. The <sup>1</sup>H NMR spectrum of a solution of the solid residue in C<sub>6</sub>D<sub>6</sub> proves it to be pure **2**.

### 3.6. Synthesis of the mixture of [<sup>t</sup>Bu<sub>3</sub>Ga<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>O)(OC<sub>6</sub>H<sub>4</sub>OH)] (**5**) and [<sup>t</sup>Bu<sub>3</sub>Ga<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>O)(OC<sub>6</sub>H<sub>4</sub>OH)] (**6**)

The reaction was carried out as described in Section 3.1 using the same amount of reagents. The mixture was refluxed during 1 h. Then the solvent was removed under reduced pressure and the residue was redissolved in the mixture of 2 cm<sup>3</sup> of *n*-C<sub>6</sub>H<sub>14</sub> and 1 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub>. This solution cooled to –25 °C afforded crystalline mixture of **6** and **5** (0.060 g, yield 10%). M.p. (solid mixture): 228–239 °C. X-ray quality crystals of **6** were chosen from the solid mixture.

NMR spectra were done for the mixture of **5** and **6**.

Compound **6**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 17.79 (1H, s, OH), 7.07 (2H, d, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, *CH* arom.), 6.95 (2H, d, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, *CH* arom.), 6.65 (4H, m, *CH* arom.), 1.48 (9H, s, GaC(CH<sub>3</sub>)<sub>3</sub>), 1.30 (9H, s, GaC(CH<sub>3</sub>)<sub>3</sub>), 0.81 (9H, s, GaC(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 146.88, 146.02, 122.11, 121.16, 117.14, 115.18 (*C* arom.), 30.47, 29.82, 29.29 (GaC(CH<sub>3</sub>)<sub>3</sub>), 27.71, 25.50 (GaC(CH<sub>3</sub>)<sub>3</sub>) ppm.

Compound **5**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 16.77 (1H, s, OH), 1.47 (9H, s, GaC(CH<sub>3</sub>)<sub>3</sub>), 1.34 (9H, s, GaC(CH<sub>3</sub>)<sub>3</sub>), 0.91 (9H, s, GaC(CH<sub>3</sub>)<sub>3</sub>).

The molar ratio of the compound **6** to the compound **5** calculated on the basis of an integration ratio <sup>t</sup>Bu protons of both compounds is equal of 4:1.

### 3.7. Temperature dependent <sup>1</sup>H NMR spectra of the mixture of **5** and **6**

The reaction of <sup>t</sup>Bu<sub>3</sub>Ga with 1,2-catechol was carried out as described in Section 3.1. The mixture was refluxed during 0.25 h. The crystalline mixture of **5** and **6** was

Table 2

The composition of a CDCl<sub>3</sub> solution of the mixture of compounds **6** and **5** at various temperatures<sup>a</sup>

| Entry | Temperature <sup>b</sup> (°C) | Time <sup>c</sup> (h) | OH( <b>6</b> ) <sup>d</sup> (ppm) | OH( <b>5</b> ) <sup>d</sup> (ppm) | OH( <b>6</b> ):OH( <b>5</b> ) <sup>e</sup> | Molar ratio <b>6</b> : <b>5</b> |
|-------|-------------------------------|-----------------------|-----------------------------------|-----------------------------------|--|---------------------------------|
| 1     | 21                            | 0                     | 17.45                             | 16.34                             | 1.0:0.8                                    | 1.0:0.8                         |
| 2     | 9                             | 2                     | 17.52                             | 16.34                             | 1.0:0.8                                    | 1.0:0.8                         |
| 3     | 0                             | 3                     | 17.56                             | 16.35                             | 1.0:0.8                                    | 1.0:0.8                         |
| 4     | 21                            | 4                     | 17.45                             | 16.34                             | 1.0:0.8                                    | 1.0:0.8                         |
| 5     | 30                            | 4.5                   | 17.40 <sup>f</sup>                | 16.30 <sup>f</sup>                | 1.0:0.8                                    | 1.0:0.8                         |
| 6     | 40                            | 5                     | 17.33 <sup>g</sup>                | 16.27 <sup>g</sup>                | <sup>h</sup>                               | <sup>h</sup>                    |
| 7     | 21                            | 6                     | 17.45                             | 16.34                             | 1.0:0.8                                    | 1.0:0.8                         |

<sup>a</sup> On the bases of an integration ratio of OH proton signals in temperature dependent <sup>1</sup>H NMR spectra.

<sup>b</sup> Temperature of <sup>1</sup>H NMR measurements.

<sup>c</sup> Since beginning of measurements.

<sup>d</sup> Chemical shifts of OH proton signals of compounds **6** and **5**.

<sup>e</sup> Integration ratio of OH proton signals of compounds **6** and **5**.

<sup>f</sup> Broadened.

<sup>g</sup> Broad.

<sup>h</sup> The OH and <sup>t</sup>Bu proton signals are too broad for precise calculation of the integration ratio.

precipitated after 1 month from an  $n\text{-C}_6\text{H}_{14}\text{-CH}_2\text{Cl}_2$  solution at  $-25\text{ }^\circ\text{C}$ . The solid was dissolved in  $\text{CDCl}_3$  and the first  $^1\text{H}$  NMR spectrum was recorded at  $21\text{ }^\circ\text{C}$  immediately after dissolution. Next spectra were recorded at  $0\text{--}40\text{ }^\circ\text{C}$ . Molar ratios of **6:5** were calculated according to the integration of *OH* proton signals of both compounds and placed in Table 2.

### 3.8. X-ray crystal structure analyses

Determination of the crystal structures of **3** and **6** were performed on a KUMA KM4CCD  $\kappa$ -axis diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  radiation. The crystals were positioned at 62.25 mm from the KM4CCD camera. For compound **3** 600 frames were measured in  $1.0^\circ$  intervals with a counting time of 30 s. For compound **6** 1200 frames were measured in  $1.5^\circ$  intervals with a counting time of 15 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 [18] and refined using the SHELXS/SHELXL programs [19]. All hydrogen atoms were placed in 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. [20]).

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, Nos. CCDC 242177 (**3**) and 242178 (**6**). 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 www: <http://www.ccdc.cam.ac.uk>).

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