Available online at www.sciencedirect.com

SCIENCE DIRECT

Coordination Chemistry Reviews 249 (2005) 2176–2194

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Group 13 alkyl compounds incorporating aliphatic and aromatic diolate ligands[☆]

Wanda Ziemkowska*

Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, PL-00662 Warsaw, Poland

Received 26 October 2004; accepted 25 February 2005
Available online 31 May 2005

Contents

Abstract

This contribution deals with the synthesis, properties, and possible applications of complexes of aliphatic and aromatic diols with trialkylaluminum, -gallium, and -indium. The influence of steric hindrances of diolate units, the bulkiness of alkyl groups bonded to metal atoms, and the electron-withdrawing effects of ligands on the reaction courses and the structure of the products are shown and discussed. Reactions of binuclear metallane diolates, {^{t}Bu$_4$M$_2$[diol-(H)]$_2$} (M = Al, Ga), with group 13 metallanes and transition metal chlorides are presented as a route to mixed-ligand and mixed-metal complexes. Replacement of ^{t}Bu$_2$M with Me$_2$M units (transmetallation reaction) is presented as another method of mixed-complex synthesis.

Keywords: Aluminum; Gallium; Indium; Diols; Steric effects; Electronic effects

1. Introduction

Organometallic complexes of group 13 metals with (X, Y) bifunctional ligands (where X, Y = O, N, S, P) have been of great interest due to their possible uses as catalysts for polymerization [1], reagents in organic synthesis [2], precursors

---

Abbreviations: [diol-(H)], mono-deprotonated diolate ligand (HOC$_n$H$_m$O)$^-$; [diol-(2H)], di-deprotonated diolate ligand (OC$_n$H$_m$O)$^{2-}$

[☆] Dedicated to Prof. J. Ziolkowski on the occasion of his 70th birthday in recognition of his outstanding contribution to coordination chemistry.

* Tel.: +48 22 660 7316; fax: +48 22 660 5462.
E-mail address: ziemk@ch.pw.edu.pl.

0010-8545/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2005.02.022

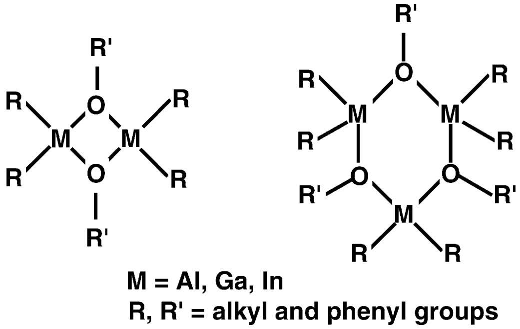
for metal organic chemical vapour deposition (MOCVD) [3], and precursors for sol–gel processes for materials and new materials [4]. Numerous examples of alane, -gallane, and -indane complexes with diacids, diamines, amino alcohols, and amino acids have been synthesized and characterized [5]. Aliphatic and aromatic diolates of group 13 alkyl metals are (O, O) chelate complexes usually synthesized in reactions of metallanes with diols and in reactions of group 13 metal halides with alkali metal diolates. Group 13 metal diolates have been investigated as potential precursors to metal oxides via sol–gel and MOCVD processes and potential catalysts in polymerization and organic synthesis. In particular, biphenolate and BINOLate (where BINOL = 2,2′-dihydroxy-1,1′-binaphthyl) complexes of group 13 metals are very effective reagents for organic synthesis, especially enantioselective syntheses [6]. This review is concerned with the synthesis, structures, and possible applications of diolates of group 13 metals, especially as potential precursors to nanosized metal oxides. BINOLates and metal polyolates will not be covered, because, unlike alkyl metal diolates, they have been reviewed several times in recent years [7].

2. Complexes of group 13 alkyl metals with aliphatic diols

Reactions of R_3M (M = Al, Ga, In; R = alkyl or aromatic group) with one equivalent of aliphatic or aromatic alcohol afford mainly dimeric complexes $[(R_2MOR^1)_2]$ containing an M_2O_2 four-membered ring core. Dialkyl alkoxides of group 13 possessing small groups (Me, OMe) are trimeric due to the sterically non-demanding ligands (Scheme 1) [8]. In contrast, bifunctional alcohols (diols) react with R_3M forming mainly trinuclear complexes $[R_5M_3(\text{diol-(2H)})_2]$ with one central 5-coordinate and two 4-coordinate metal atoms and two diolate units.

2.1. Alkylaluminum aliphatic diolates

The first alkylaluminum diolate, $[Me_5Al_3(OCH_2C_6H_4CH_2O)_2]$ **1**, was synthesized by Pasynkiewicz and Ziemkowska [9] in a reaction of Me_3Al with 1,2-di(hydroxymethyl)benzene (Scheme 2). The X-ray crystal structure revealed that the molecule of **1** adopts a boat-like conformation with the two aromatic rings and the methyl group bonded to the central aluminum atom in *syn* position (Fig. 1) [10].



Scheme 1.

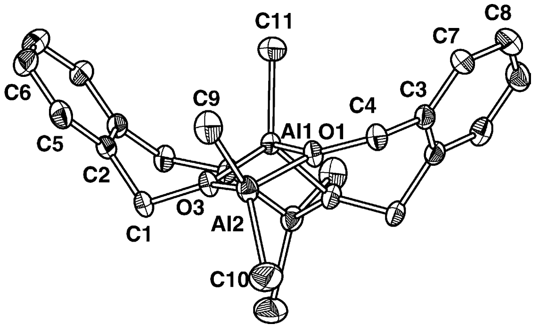
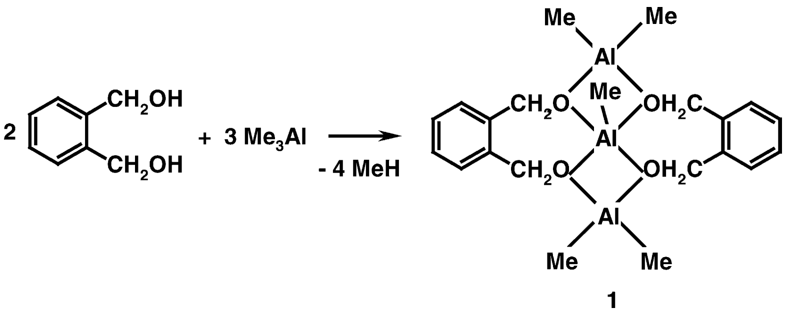


Fig. 1. Crystal structure of the trialuminum complex $[Me_5Al_3(OCH_2C_6H_4CH_2O)_2]$ (**1**). All hydrogen atoms are omitted for clarity [10].

Compound **1** is one of the first trinuclear complexes of group 13 metals. Earlier Köster synthesized complexes of triorganoboroxins $(RBO)_3$ with aluminum trichloride and -bromide possessing a similar trinuclear structure [11].

During the last decade numerous trialuminum compounds, $[R_5Al_3(\text{diol-(2H)})_2]$, have been obtained as a result of reactions of R_3Al (R = Me, Et, ^{i}Bu) with aliphatic diols



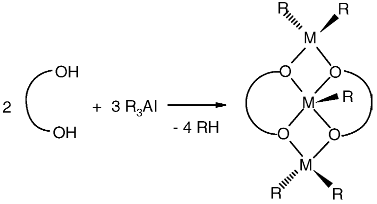
1

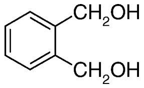
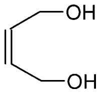
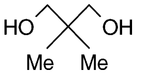
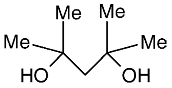
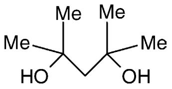
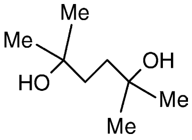
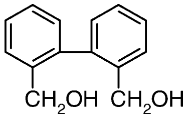
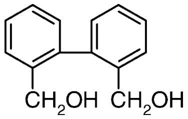
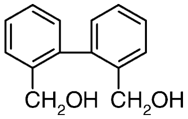
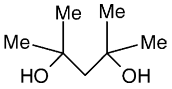
Scheme 2.

(Table 1). Most diolates are liquid. Only compounds **6**, **9**, and **11** have been characterized crystallographically (Fig. 2). The crystal structure of alane diolate was first determined by Uhl [17] for $\{[(Me_3Si)_2HC]_5Al_3(OCH_2CH_2O)_2\}$ (**14**), which was a by-product of the reaction of $[(Me_3Si)_2HC]_2AlCl$ with dipotassium glicolate $KOCH_2CH_2OK$.

Apart from cyclic diolates, organoaluminum oligomeric products are formed as amorphous solids insoluble in

Table 1
Reactions of aliphatic diols with R_3Al (R = Me, Et, ^{i}Bu) and the yield of the cyclic products



Entry	Products	Names of diols	Structure of diols	R	Yield (%)[a]	Ref.
1	**1**	1,2-Di(hydroxy methyl)benzene		Me	[b]	[9,10]
2	**2**	*cis*-2-Butene-1,4-diol		Me	40.2	[12]
3	**3**	Propane-1,3-diol		Me	8.5	[13]
4	**4**	Butane-1,4-diol		Me	47.0	[13]
5	**5**	2,2-Dimethyl-pentane-1,3-diol		Me	7.2	[13]
6	**6**	2,4-Dimethyl-pentane-2,4-diol		Me	82.5	[14]
7	**7**	2,4-Dimethyl-pentane-2,4-diol		Et	83.0	[14]
8	**8**	2,5-Dimethyl-hexane-2,5-diol		Me	0	[14]
9	**9**	2,2′-Di(hydroxy methyl)biphenyl		Me	95	[15]
10	**10**	2,2′-Di(hydroxy methyl)biphenyl		Et	71	[15]
11	**11**	2,2′-Di(hydroxy methyl)biphenyl		^{i}Bu	48	[15]
12	**12**	Butane-1,4-diol		^{i}Bu	79	[16]
13	**13**	2,4-Dimethyl-pentane-2,4-diol		^{i}Bu	76	[16]

[a] Isolated yield of cyclic products.
[b] No data.

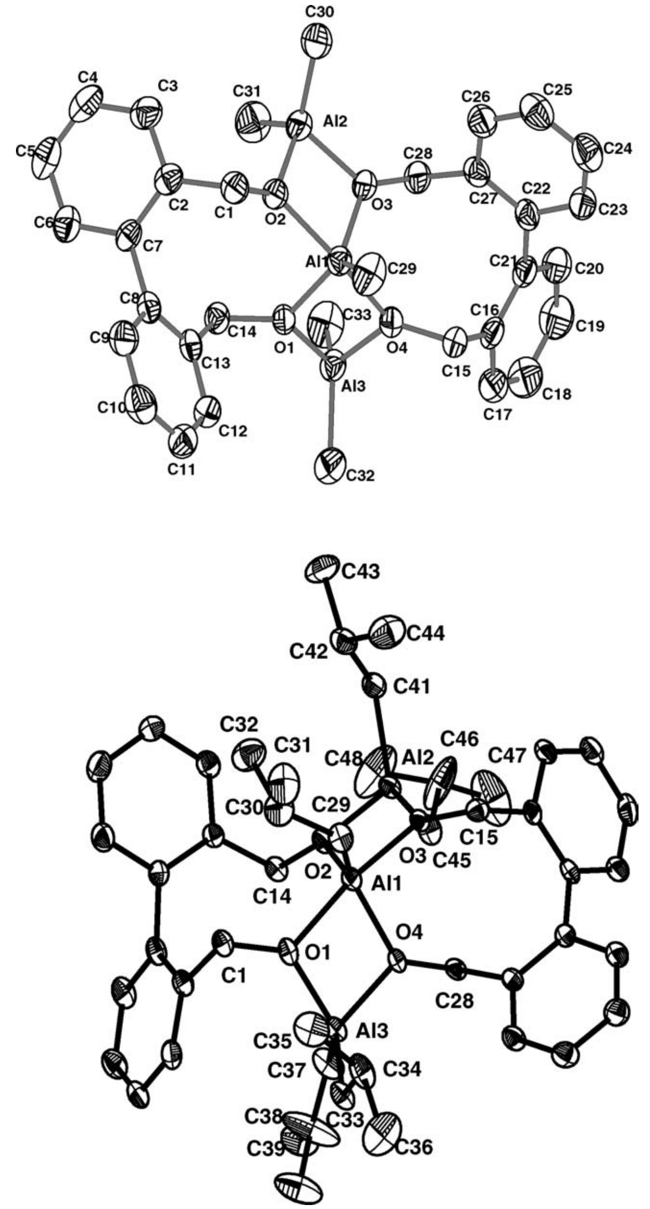


Fig. 2. Crystal structure of $[R_5Al_3(OCH_2C_{12}H_8CH_2O)_2]$; (top) R = Me (**9**), (bottom) R = ^{i}Bu (**11**). All hydrogen atoms are omitted for clarity [15].

common organic solvents. As shown in Table 1, the yield of some diolates is low (items 3 and 5) or even cyclic diolates are not formed at all (item 8). According to Pasynkiewicz and co-workers [14], the distance between the reacting hydroxyl groups of the diol is the factor determining the yield of cyclic complexes. Cyclic diolates can be formed only if the hydroxyl groups are situated close to each other, as in 2,4-dimethyl-pentane-2,4-diol (items 6, 7, and 13). This sterically overcrowded diol exists in a sterically convenient conformation with remote methyl groups and OH groups located close to each other. Therefore cyclic alane 2,4-dimethyl-pentane-2,4-diolates are formed in high yield.

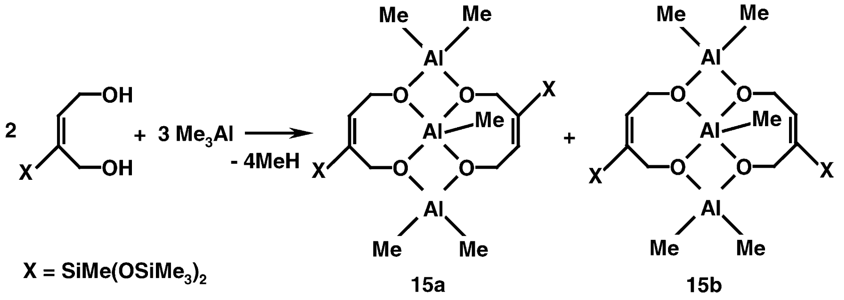
Reactions of asymmetric aliphatic diols with alanes result in the formation of mixtures of isomers of the formula $[R_5Al_3(\text{diol-(2H)})_2]$ (R = Me, Et, ^{i}Bu). 2-Methyl-bis(trimethylsiloxy)silyl]but-2-en-1,4-diol reacts with Me_3Al to yield two isomers, **15a** and **15b**, which demonstrate *trans* and *cis* ligand geometries (Scheme 3) [18]. Similar complexes, $[R_5Al_3(OC_6H_4CH_2O)_2]$ [**16a**,**b** (R = Me)], [**17a**,**b** (R = Et)] and $[Me_5Al_3(OC_6H_4CH_2CH_2O)_2]$ [**18a**,**b**], have been obtained in reactions of 2-hydroxybenzyl and 2-hydroxyphenethyl alcohols with R_3Al [19].

Aliphatic saturated unsymmetrical diols, 1-methyl-1,3-propanol and 1,1,3-trimethyl-1,3-propanol, in reactions with Me_3Al give mixtures of six isomers (**19a**–**f** and **20a**–**f**) (Scheme 4) [13,14].

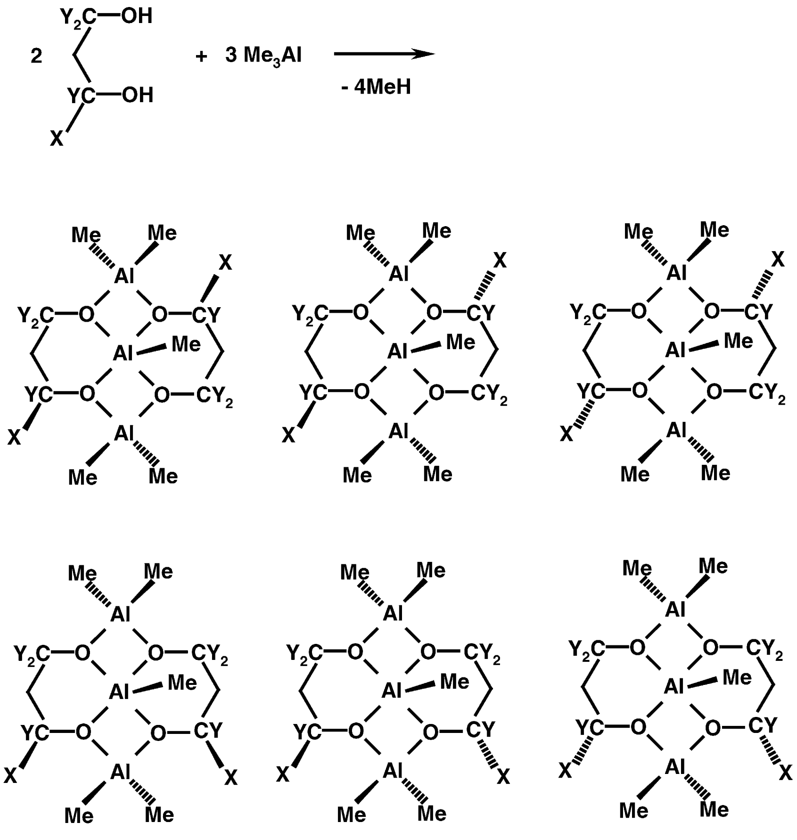
The above reactions demonstrate that unsymmetrical diols react with R_3Al forming mixtures of all possible isomeric products.

In contrast to reactions of trimethyl-, triethyl-, and tri-*iso*-butylaluminum with diols, the use of R_3Al with bulky *tert*-butyl groups makes it possible to synthesise binuclear complexes $[^tBu_4Al_2(\text{diol-(H)})_2]$, possessing two unreacted hydroxyl groups of diolate moieties and stabilized by two intra-molecular hydrogen bonds (Scheme 5). The reaction of butane-1,4-diol with one equivalent of $^tBu_3Al$ results in the formation of the dimeric product $[^tBu_4Al_2(O(CH_2)_4OH)_2]$ (**21**). The crystal structure of **21** reveals the located position of the alcohol's protons in the difference map (Fig. 3 top). As may be seen from Fig. 3 bottom, the central $Al_2O_4H_2$ eight-membered cycle is not planar.

As presented above, 2,2′-di(hydroxymethyl)biphenyl reacts with R_3Al (R = Me, Et, ^{i}Bu) to yield trimetallic



Scheme 3.



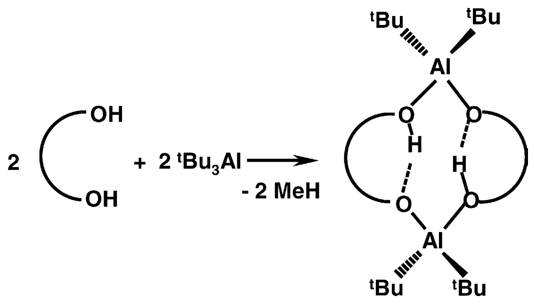
X = Me, Y = H (19a-f)

X = H, Y = Me (20a-f)

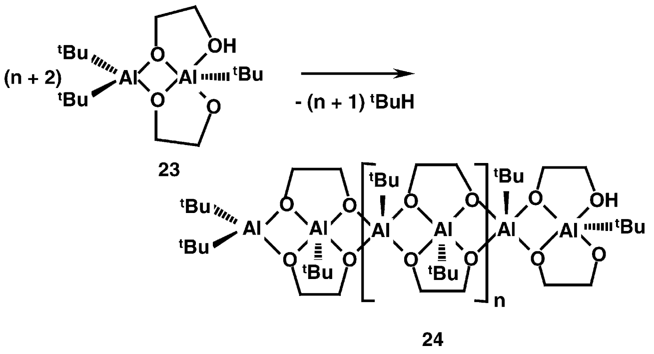
Scheme 4.

complexes **9**–**11** [15]. A similar reaction of 2,2′-di(hydroxymethyl)biphenyl with ^{t}Bu$_3$Al leads to the formation of the binuclear product [^{t}Bu$_4$Al$_2$(OCH$_2$C$_{12}$H$_8$CH$_2$O)$_2$] (**22**) (Fig. 4) [20]. The presence of alcohol protons in [^{t}Bu$_4$Al$_2$(diol-(H))$_2$] complexes has been confirmed by means of ^{1}H NMR spectroscopy. Signals of OH protons are shifted downfield (16–17 ppm), which is consistent with the increased acidity of hydroxyl protons. Intra-molecular hydrogen bonds play a significant role in stabilizing the compounds. In recent years it has been demonstrated that inter- and intra-molecular hydrogen bonds are very important in the structure engineering of group 13 compounds incorporating multidentate ligands [5d,e,o,21].

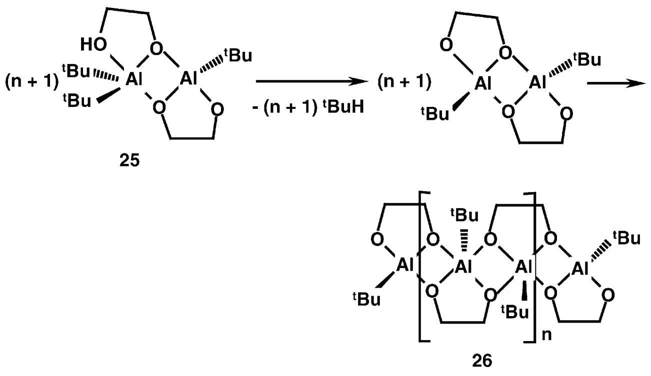
Reactions of trialkylaluminums with diols, in addition to forming soluble cyclic products, often yield organoaluminum oligomers (alucones) in the form of a white amorphous pre-



Scheme 5.



Scheme 6.



Scheme 7.

cipitate. Although the structure of alucones is not easily determined due to their insolubility in organic solvents, several methods have been reported in literature. Barron [22] has obtained alucones as the main products in the reaction of ethane-1,2-diol with $^{t}Bu_3Al$ in *n*-hexane solution. According to Barron's proposition, alucone **24** can be formed as a result of the condensation reaction of an intermediate product, $\{^{t}Bu_3Al_2[O(CH_2)_2O][O(CH_2)_2OH]\}$ (**23**) (Scheme 6). An alucone (**26**) with a decreased number of alkyl groups can also be formed from another intermediate product, **25** (isomer of **23**) (Scheme 7).

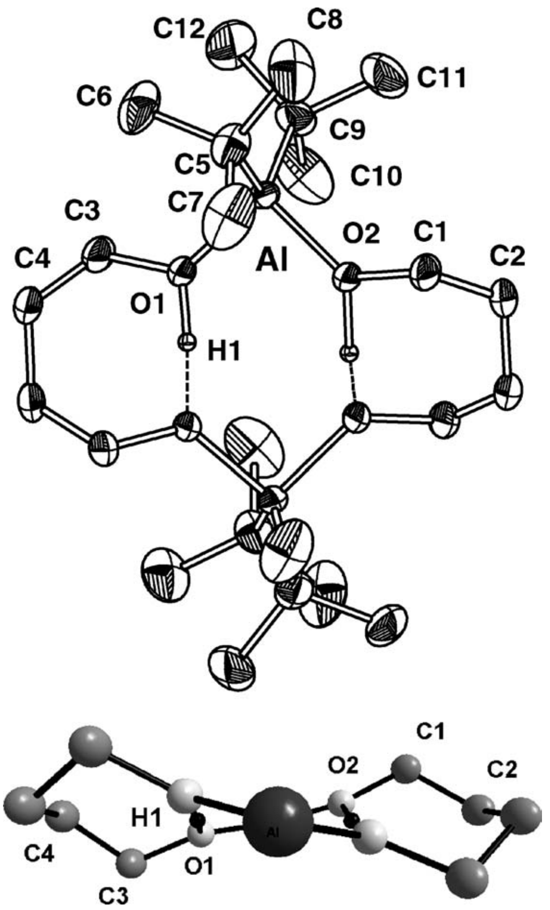


Fig. 3. (Top) Crystal structure of $[^{t}Bu_4Al_2(O(CH_2)_4OH)_2]$ (**21**). All hydrogen atoms (besides of OH) are omitted for clarity. (Bottom) Partial coordination sphere of $[^{t}Bu_4Al_2(O(CH_2)_4OH)_2]$ (**21**) viewed along the Al···Al vector showing the central non-planar $Al_2O_4H_2$ cycle [16].

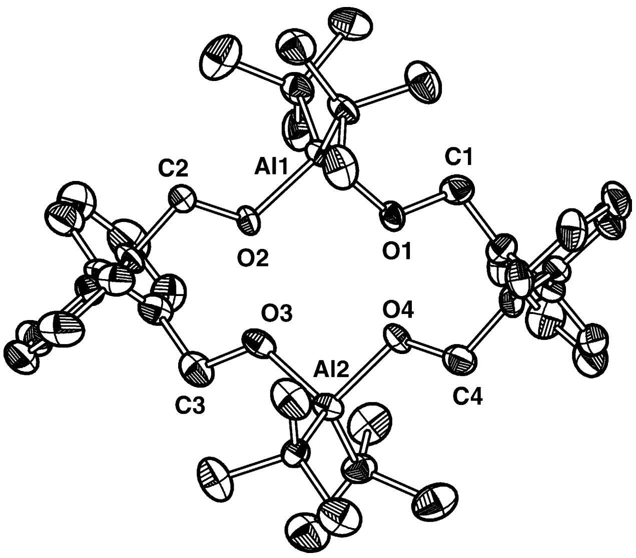
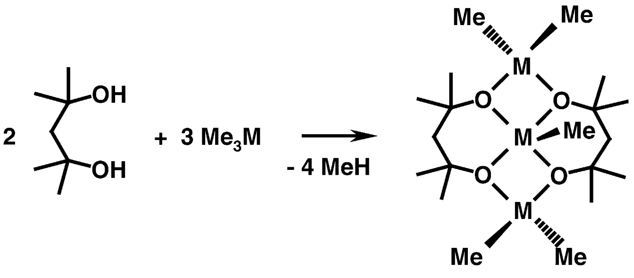


Fig. 4. Crystal structure of $[^{t}Bu_4Al_2(OCH_2C_{12}H_8CH_2O)_2]$ (**22**). All hydrogen atoms are omitted for clarity [20].

Earlier, Pasynkiewicz, and Ziemkowska [18] proposed a structure similar to that of alucone **26** for the aluminum oligomeric product of reactions of *cis*-but-2-ene-1,4-diols with trialkylaluminum.

2.2. *Alkylgallium and -indium aliphatic diolates*

Although reactions of alanes with diols have been intensively studied, gallane and indane diolates are rather rare. With R_3M (R = small alkyl groups, M = Ga, In) diols form similar trinuclear cyclic products as with R_3Al. Reactions of 2,4-dimethylpentane-2,4-diol with trimethylgallane and -indane result in the formation of typical trimetallic diolates, $\{Me_5M_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ [M = Ga (**27**), M = In (**28**)] (Scheme 8) [23]. Compound **27** has been structurally characterized in the solid state.



27 (M = Ga)

28 (M = In)

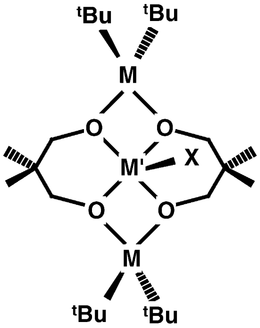
Scheme 8.

2.3. Binuclear metallane diolates ${}^{t}Bu_4M_2[diol\text{-}(H)]_2$ (M = Al, Ga) as bifunctional tetradentate ligands

Metallane diolates ${}^{t}Bu_4M_2[diol\text{-}(H)]_2$ (M = Al, Ga) have only been produced from reactions of 1,3- and longer diols with ${}^{t}Bu_3M$. The chemistry of these complexes shows that they may be regarded as bifunctional tetradentate ligands in reactions of group 13 halides and alkyls due to the presence of two OH groups and four O atoms. Barron [24] reported the preparation of numerous trimetallic 2,2-dimethylpropane-1,3-diolates (**31**–**37**) in reactions of $\{{}^{t}Bu_4M_2[OCH_2C(Me)_2CH_2OH]_2\}$ [M = Al (**29**), Ga (**30**)] dimers with aluminum and gallium hydrides and alkyls (Scheme 9). The trimetallic products are formed as a result of the reaction of the hydride and alkyl groups with two acidic protons of the hydroxyl groups of the dimer and an evolution of two equivalents of alkane.

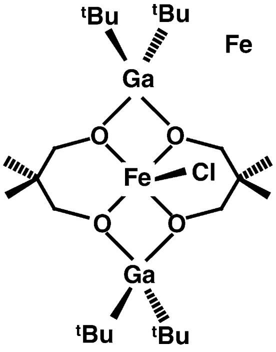
The synthesis of bimetallic compounds ${}^{t}Bu_4M_2[diol\text{-}(H)]_2$ with two OH groups provides a route to trimetallic species with different central metals as well as different substituents on the central metal atom. The mixed gallium transition metal (Fe, Co, Ni, Cu) complexes **38**–**41** were obtained in modest yields by the reaction of $\{{}^{t}Bu_4Ga_2[OCH_2C(Me)_2CH_2OH]_2\}$ (**30**) with the appropriate metal halide and Proton Sponge (Scheme 10) [25].

Some ${}^{t}Bu_4M_2[diol\text{-}(H)]_2$ binuclear diolates are inactive towards group 13 alkyls. Unlike compound **29** reported by Barron [24], the *tert*-butylaluminum complex of 2,2′-di(hydroxymethyl)biphenyl (**22**) does not form trialuminum compounds $[{}^{t}Bu_4RAl_3(OCH_2C_{12}H_8CH_2O)_2]$ with trialkylaluminums [20]. Even prolonged heating of **22** with an excess of Me_3Al only causes the diolate to decompose to organoaluminum oligomeric products. Steric repulsion is unlikely to be the reason for the inactivity. Probably the basicity of the aluminum alkyl groups is smaller or similar compared with the oxygen atoms of **22**. Therefore acidic OH protons are more likely to form hydrogen bonds (O–H · · · O) than to react with alkyl groups. On the other hand, the reaction of propane-1,3-diol with ${}^{t}Bu_3Al$ produces only traces of the binuclear product $\{{}^{t}Bu_4Al_2[O(CH_2)_3OH]_2\}$ (**42**) and the main trimetallic product $\{{}^{t}Bu_5Al_3[O(CH_2)_3O]_2\}$ (**43**) [16]. Presumably the shorter length of the diol backbone restricts the formation of intra-molecular hydrogen bonds. Due to good accessibility of OH groups, **42** reacts with the excess of ${}^{t}Bu_3Al$ to finally yield the trimetallic product **43**.

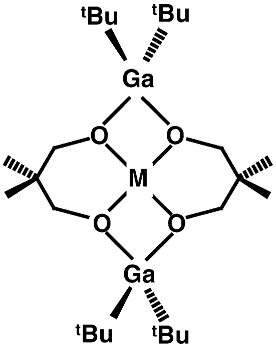


M = M' = Al, X = H (31)
M = M' = Al, X = Me (32)
M = M' = Al, X = Cl (33)
M = M' = Ga, X = ^{t}Bu (34)
M = Ga, M' = Al, X = ^{t}Bu (35)
M = Ga, M' = Al, X = H (36)
M = Ga, M' = Al, X = Me (37)

Scheme 9.



38



M = Co (39), Ni (40), Cu (41)

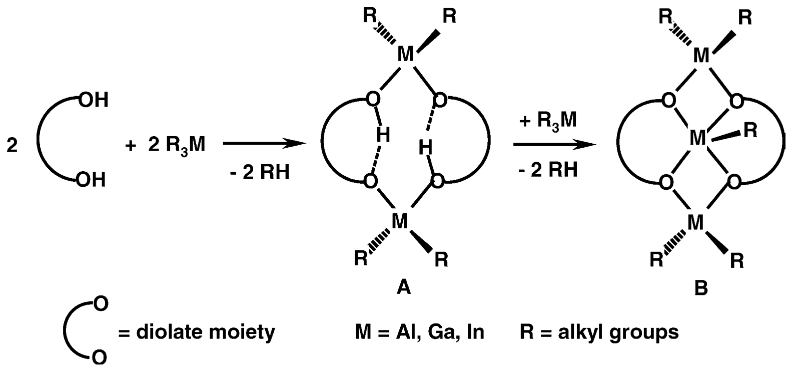
Scheme 10.

2.4. The course of the reaction of 1,3- and longer diols with group 13 trialkyl metals

As shown earlier, reactions of R_3M (M = Al, Ga, In; R = Me, Et, ^{i}Bu) with diols lead directly to trimetallic products of the form $[R_5M_3(diol\text{-}(2H))_2]$. Although not isolated, it is very probable that binuclear methyl-, ethyl-, and *iso*-butylmetallane diolates (analogues of *tert*-butyl derivatives) are formed as intermediates. Based on the structure of the reaction products of tri-*tert*-butyl metallanes with diols, the pathway of the reaction of 1,3- and longer backbone diols with R_3M is proposed in Scheme 11. The first step in the reaction is the formation of dimer **A** with two unreacted hydroxyl groups. Subsequently one equivalent of trialkylmetal reacts with the two acidic protons of dimer **A**, which results in the introduction of the central metal. 1,2-Diols react with trialkylmetals in another way, which is described in Section 4.

2.5. The transmetallation reaction

Besides the reaction of binuclear *tert*-butyl metallane diolates, $[{}^{t}Bu_4M_2(diol\text{-}(H))_2]$, with alkyl metals and halides, the transmetallation reaction is a method of preparation of some mixed-ligand and mixed-metal complexes of group 13 alkyls with multidentate ligands. The binuclear complex $[{}^{t}Bu_4Ga_2(OCH_2C_6H_4CH_2OH)_2]$ (**44**) formed by the reaction of ${}^{t}Bu_3Ga$ with 1,2-di(hydroxymethyl)benzene interacts with Me_3Ga to yield complexes with different substituents at the gallium atoms $[(Me){}^{t}Bu_4Ga_3(OCH_2C_6H_4CH_2O)_2]$

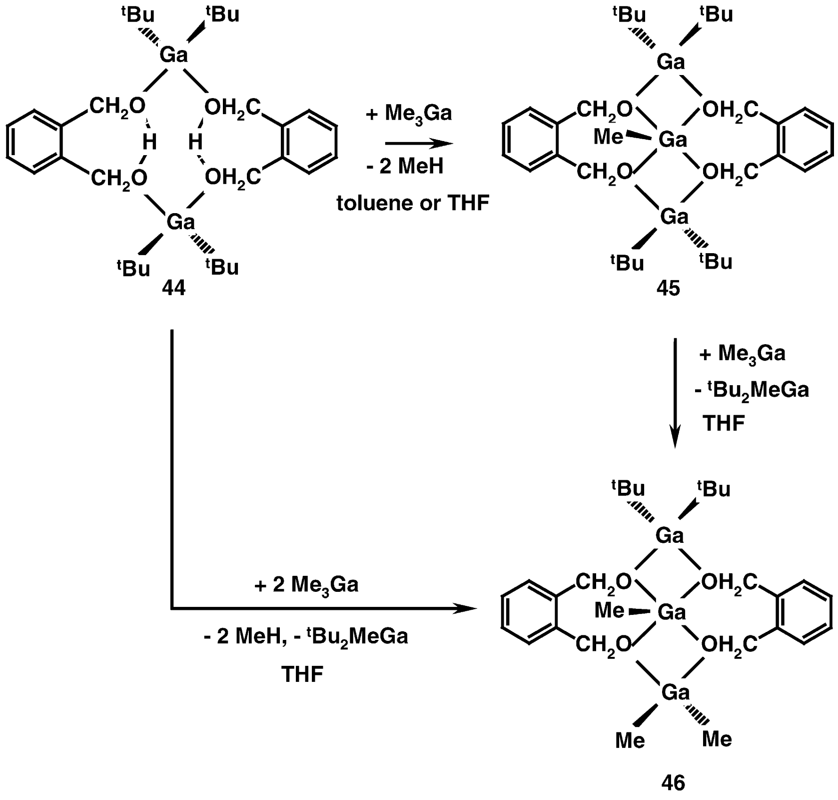


Scheme 11.

(**45**) and $[Me_3{}^tBu_2Ga_3(OCH_2C_6H_4CH_2O)_2]$ (**46**), depending on the molar ratio of the reagents (Scheme 12) [10]. The mixed-ligand product **45** is the result of the reaction of the two hydroxyl groups of **44** with one equivalent of Me_3Ga and the inclusion of the third metal atom. The reaction of **44** with two or more equivalents of Me_3Ga leads to the formation of the other mixed-ligand compound **46**, which has three methyl groups and two *tert*-butyl groups. The product **46** is formed as a result of the transmetallation reaction of **45** with the next equivalent of Me_3Ga replacing $^tBu_2Ga$ with a Me_2Ga unit. Compounds **45** and **46** have been structurally characterized in the solid state (Figs. 5 and 6).

2.6. Steric effects in metallane diolates

Steric repulsion between ligands is a significant factor controlling the formation of group 13 complexes. Recently it has been reported that the structure of sterically crowded diolates of group 13 metals depends on the steric bulk of the substituents of the metal atoms as well as the kind of metal. The results of an investigation of reactions of a sterically crowded 2,4-dimethylpentane-2,4-diol with various metallanes indicate that trimethyl-, triethyl-, and tri-*iso*-butylalanes with diols yield trinuclear complexes of the general formula $\{R_5Al_3[diol\text{-}(2H)]_2\}$ irrespective of the diol unit steric hindrances (see com-



Scheme 12.

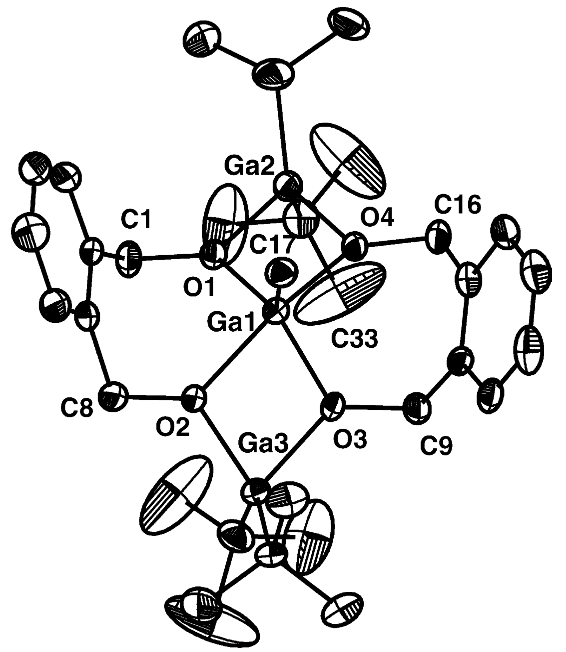


Fig. 5. Crystal structure of $[(Me)^tBu_4Ga_3(OCH_2C_6H_4CH_2O)_2]$ (**45**). All hydrogen atoms are omitted for clarity [10].

pounds **6**, **7**, and **13**, Table 1). Like the alane diolates, methylgallane- and methylindane-2,4-dimethylpentane-2,4-diolates, $\{Me_5M_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ [M = Ga (**27**), M = In (**28**)] (see Section 2.1), are trinuclear.

In contrast, reactions of $^tBu_3M$ with 2,4-dimethylpentane-2,4-diol lead to unique (monoalkyl)metallane complexes $\{^tBuM[OC(Me)_2CH_2C(Me)_2O]\}_2$ [M = Al (**47**), Ga (**48**)] (Scheme 13) [16,23]. According to the molecular structures (Fig. 7) the isostructural compounds consist of M_2O_2 dimeric cores. The ^{t}Bu groups are oriented *cis* to the M_2O_2 rings. The sums of angles about the oxygen atoms of M_2O_2 cycles are less than 360° (345.6° and 345.8° for **47**, 342.4° and 342.3° for **48**), which indicates a steric strain in the molecules.

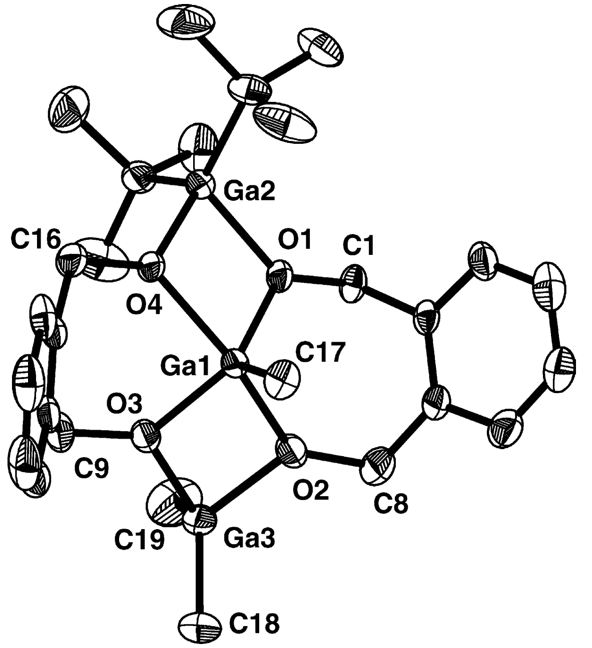
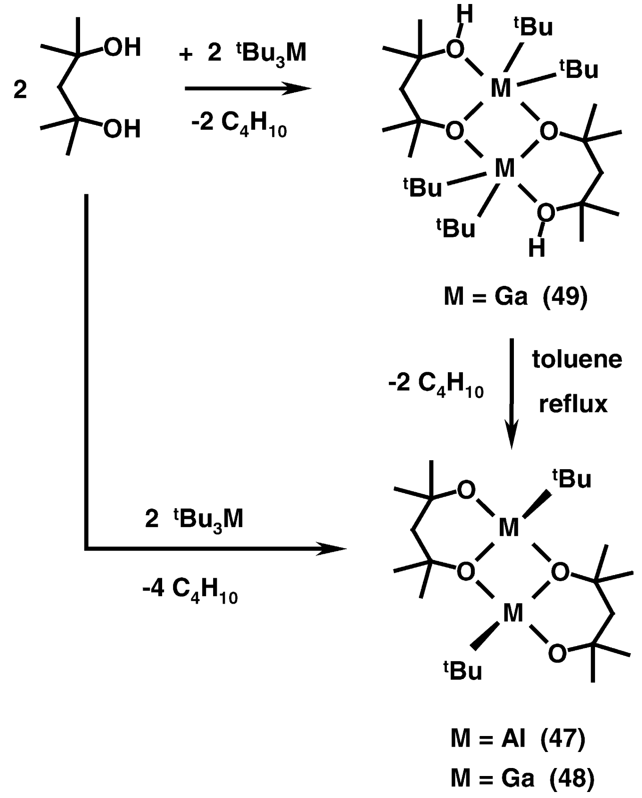


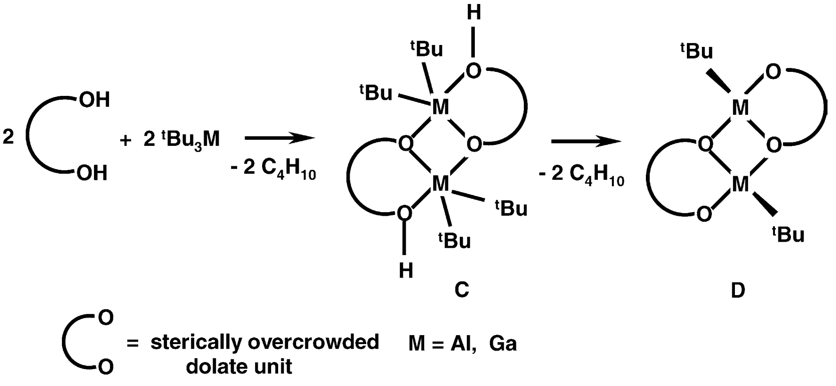
Fig. 6. Crystal structure $[Me_3{}^tBu_2Ga_3(OCH_2C_6H_4CH_2O)_2]$ (**46**). All hydrogen atoms are omitted for clarity [10].



Scheme 13.

The reaction of $^tBu_3Al$ with 2,4-dimethylpentane-2,4-diol leads directly to the final product **47**. An intermediate product was only isolated from the reaction mixture of $^tBu_3Ga$ with the diol at room temperature (Scheme 13). It is the unstable gallium product $\{^tBu_2Ga[OC(Me)_2CH_2C(Me)_2OH]\}_2$**49** with two hydroxyl groups. The ^{1}H NMR spectrum of **49** reveals a broad signal at 3.87 ppm corresponding to the two alcohol protons, which indicates the absence of inter- and intra-molecular hydrogen bonds. Compound **49** easily undergoes transformation to **48** upon refluxing in toluene.

Reactions of $^tBu_3Al$ and $^tBu_3Ga$ with 2,4-dimethylpentane-2,4-diol illustrate how steric properties of the ligands may affect the course of the reaction and the products obtained. As shown in Scheme 11, complexes of type **A**, stabilized by two intra-molecular hydrogen bonds, are the intermediate products in the reactions of diols with group 13 alkylmetals. However, in the case of overcrowded diols and bulky alkyl groups the formation of type **A** complexes is unfeasible due to the steric repulsion of ligands. Therefore, complex **C** with reduced steric strain, an analogue of compound **49**, is produced as an intermediate product in these reactions. The next step is the intra-molecular reaction of hydroxyl groups with ^{t}Bu substituents and the formation



Scheme 14.

of the final product $\{{}^t BuM[diol\text{-}(2H)]\}_2$ (M = Al, Ga) (**D**) (Scheme 14).

In contrast to the reaction of 2,4-dimethylpentane-2,4-diol with ${}^tBu_3Al$ and ${}^tBu_3Ga$, the reaction with ${}^tBu_3In$ gives the binuclear complex $\{{}^tBu_4In_2[OC(Me)_2CH_2C(Me)_2OH]_2\}$ (**50**) with two intra-molecular hydrogen O–H · · · O bonding [23]. The interaction of **50** with one equivalent of ${}^tBu_3In$ yields the trimetallic product $\{{}^tBu_5In_3[OC(Me)_2CH_2C(Me)_2O]_2\}$ (**51**) (Scheme 15). The molecular structure of **50** demonstrates a typical intermediate product of type **A** shown in Scheme 11 (Fig. 8). Besides lithium indium silanediolate reported by Walawalkar [26], **50**, **51**, and $\{Me_5In_3[OC(Me)_2CH_2C(Me)_2O]_2\}$ (**28**) are, as far as we are aware, the only indane diolates.

A comparison of reactions of sterically crowded diols with ${}^tBu_3Al$, ${}^tBu_3Ga$, and ${}^tBu_3In$ shows that the length of the metal–carbon and metal–oxygen bonds can determine the steric repulsion of ligands and may be a decisive factor controlling the structure of compounds. The core of a molecule of **50** is similar to that of the butane-1,4-diol *tert*-butylalane derivative $[{}^tBu_4Al_2(O(CH_2)_4OH)_2]$ (**21**); however, the av-

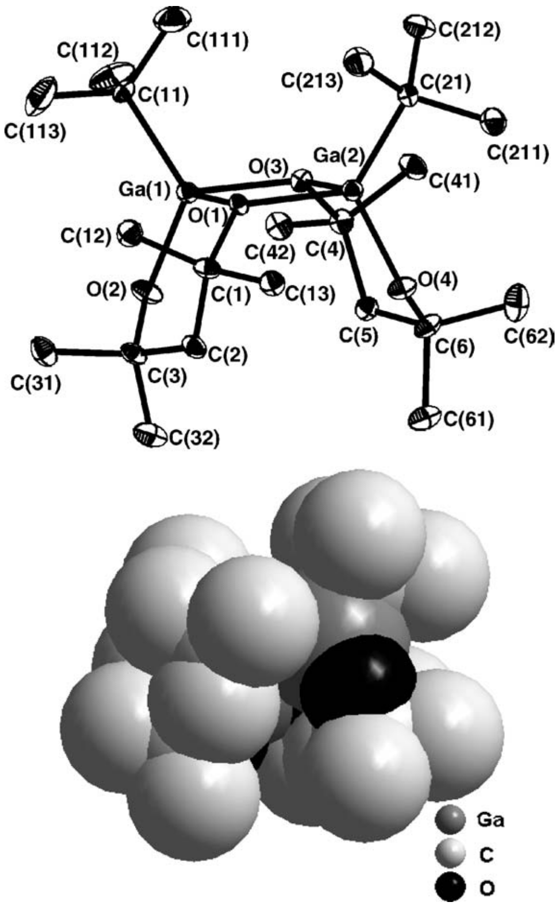
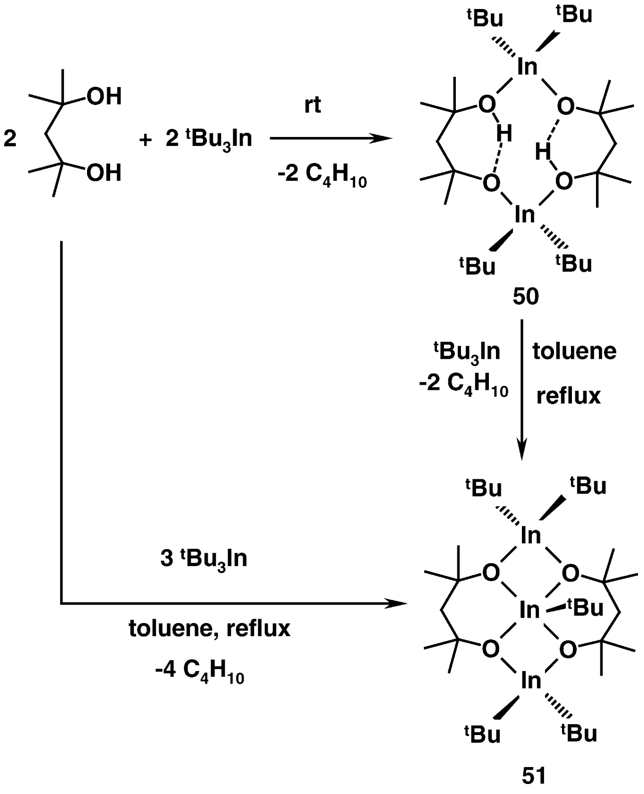


Fig. 7. (Top) Crystal structure of $\{{}^tBuGa[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ (**48**). All hydrogen atoms are omitted for clarity [23]. (Bottom) Space filling plot of **48** showing the exposed two-coordinate oxygen atom (black ball) to be accessible for the attack of Lewis acids.



Scheme 15.

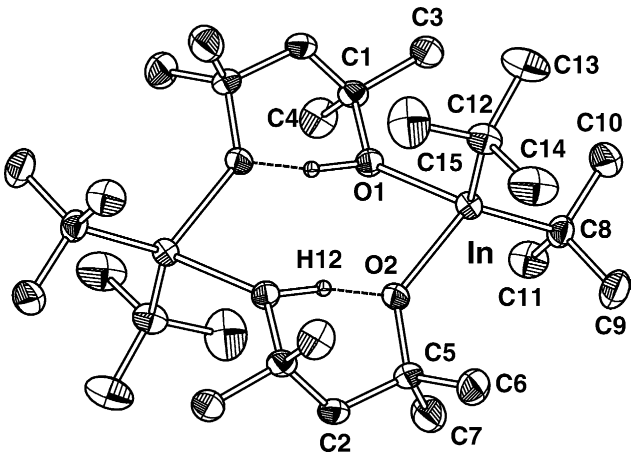
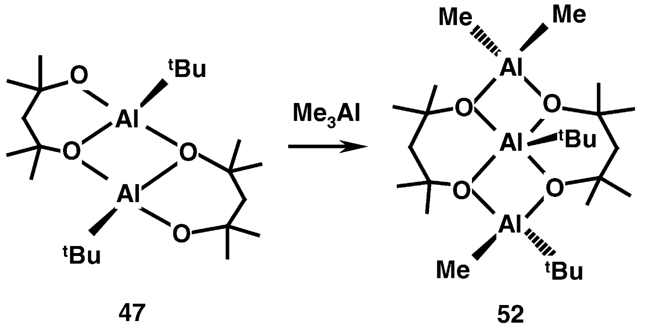


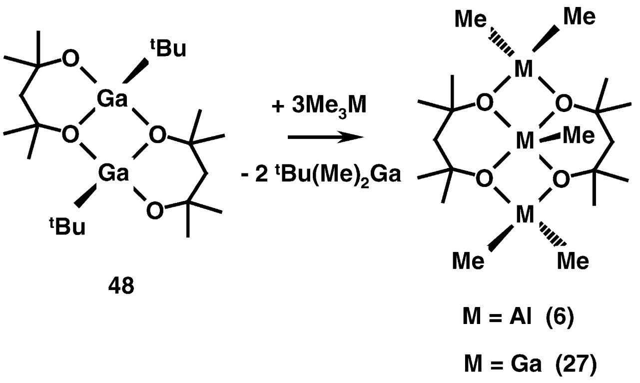
Fig. 8. Crystal structure of $\{^t\mathrm{Bu}_4\mathrm{In}_2[\mathrm{OC(CH_3)_2CH_2C(CH_3)_2OH}]_2\}$ (**50**). All hydrogen atoms (besides of OH) are omitted for clarity [23].

erage In–C (2.202 Å) and In–O (2.148 Å) bonds in **50** are much longer than the Al–C (1.978 Å) and Al–O (1.812 Å) bonds in **21** [16]. Every ^{t}Bu group in the structure of **50** interacts with two methyl groups of diolate 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 the methyl groups of diol moieties, which causes a decrease in 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 the ^{t}Bu and Me groups. Instead of products with intra-molecular hydrogen bonds, complexes of type **C** (Scheme 14) are obtained. In the proposed structure **C**, every ^{t}Bu group interacts only with one Me group of the diol unit, which reduces steric repulsion.

The binuclear complexes **47** and **48** besides the three-coordinate oxygen atoms, also possess di-coordinate ones, exposed and accessible to a Lewis acid attack (Fig. 7 bottom) [10]. Compound **47** reacts with $\mathrm{Me_3Al}$ to yield the trinuclear mixed-ligand complex $\{\mathrm{Me_3}{}^t\mathrm{Bu_2Al_3}[\mathrm{OC(Me)_2CH_2C(Me)_2O}]_2\}$ (**52**) (Scheme 16), whereas the reaction with $\mathrm{Me_3Ga}$ does not proceed at all. The structure of **52** with *anti*-^{t}Bu groups and one ^{t}Bu group bonded to the central metal atom has been proposed on the basis of NOESY measurements.



Scheme 16.



Scheme 17.

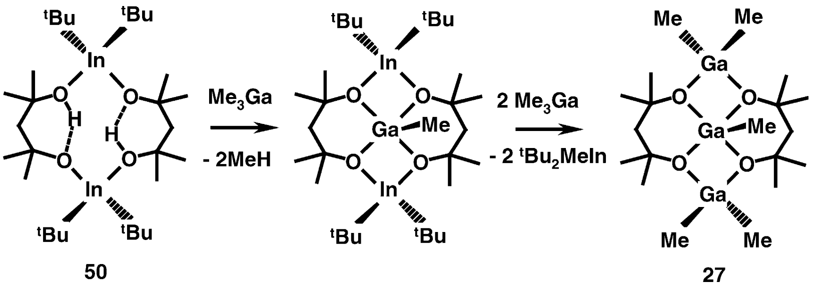
In contrast to the above reaction, the isostructural gallium compound **48** in the reaction with $\mathrm{Me_3Al}$ yields the trialuminum complex $\{\mathrm{Me_5Al_3}[\mathrm{OC(CH_3)_2CH_2C(CH_3)_2O}]_2\}$ (**6**). A similar reaction of **48** with $\mathrm{Me_3Ga}$ proceeds with the formation of a trigallium product, $\{\mathrm{Me_5Ga_3}[\mathrm{OC(CH_3)_2CH_2C(CH_3)_2O}]_2\}$ (**27**) (Scheme 17).

tert-Butylindane diolate **50** can also react with group 13 metallanes as a bifunctional (two OH groups) tetradentate (four O atoms) ligand. However, the reaction of **50** with $\mathrm{Me_3Ga}$ results in the formation of the trigallium complex **27** instead of the expected product, $\{(\mathrm{MeGa})({}^t\mathrm{Bu_4In_2})[\mathrm{OC(Me)_2CH_2C(Me)_2O}]_2\}$, with a central gallium atom. In our opinion this compound is formed as an intermediate product and subsequently undergoes rapid exchange of two $^t\mathrm{Bu_2In}$ units in a transmetallation reaction (Scheme 18).

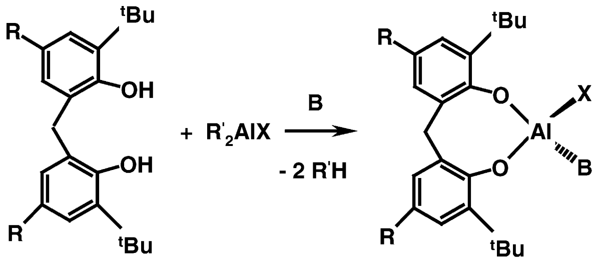
The reactions presented above show that the binuclear complexes **47**, **48**, and **50** react with different trialkylmetals according to the hard and soft acids and bases principle (HSAB). Harder metals (hardness order: Al > Ga > In) prefer diolate ligands as harder coordination sites, whereas softer metals leave the aggregates as alkyls. On the other hand reactions between *tert*-butyl metal diolates and metal trimethyls with the same metal cause the replacement of $^t\mathrm{Bu_2M}$ units with $\mathrm{Me_2M}$ units and reduction of steric strain.

3. Aromatic diolates of group 13 metals

Several alane 2,2′-methylenebisphenolates were prepared by Lin and co-workers and used as catalysts in various reactions. In contrast to sterically crowded aliphatic diols, reactions of sterically crowded 2,2′-methylenebisphenols with $\mathrm{R_2AlX}$ in the presence of a Lewis base lead to monomeric diolates (**53**–**58**) with a four-coordinate aluminum atom bonded to the methyl group, two oxygen atoms of the diol unit, and one molecule of the Lewis base (THF or $\mathrm{Et_2O}$). The crystal structures of the compounds demonstrate that the conformation of the eight-membered heterocycles containing aluminum is controlled by the intra-molecular C–H · · · O hydrogen bond between the methylene proton and the oxygen atom of the coordinate molecule of the Lewis base (Scheme 19).



Scheme 18.



X = Br, R = ᵗBu (53) X = Et, R = ᵗBu (54)

X = ⁱBu, R = Me (55) X = Cl, R = ᵗBu (56)

X = Et, R = Me (57) X = Cl, R = Me (58)

R' = alkyl group

B = Et₂O or THF

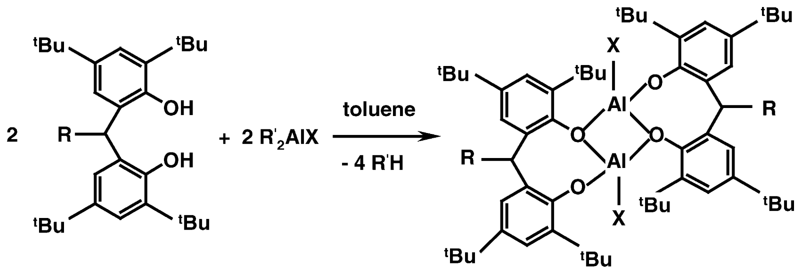
Scheme 19.

Similar reactions of Et_2AlCl or $^iBu_3Al$ with bisphenols in a toluene solution, instead of a Lewis base, result in the formation of dimeric products **59** and **60** with a central four-membered Al_2O_2 cycle (Scheme 20) [27]. The crystal structure of **59** has been determined crystallographically. The core of the molecule is similar to those of alane and gallane 2,4-dimethylpentane-2,4-diolates (**47** and **48**) (see Section 2.6). However, unlike compounds **47** and **48**, which have *cis* conformations, the isolated product **59** adopts a *trans* conformation. Some of the compounds **53**–**60** show catalytic activities towards the reaction of cyclopentadiene with methacrolein.

Monomeric aromatic diolates are usually transformed into dimeric aluminum alkoxides in reactions with alcohols (Scheme 21). The complexes demonstrate catalytic activity in polymerization and organic reactions. Compounds **61** and **63** are highly efficient catalysts for the polymerization of ε-caprolactone and ι-lactide [28,29]. Compounds **61** and **62** show catalytic activity towards Meerwein–Ponndorf–Verley (MPV) hydrogen transfer reactions of aldehydes and ketones [30].

The reaction of substituted biphenyl-2,2′-diol with two equivalents of Me_3Al in the presence of one equivalent of 2,4-dimethyl-3-pentanol produces alane biphenolate (**64**) (Scheme 22), which demonstrates moderate activity as the initiator of ring-opening polymerization (ROP) of *rac*-lactide [31].

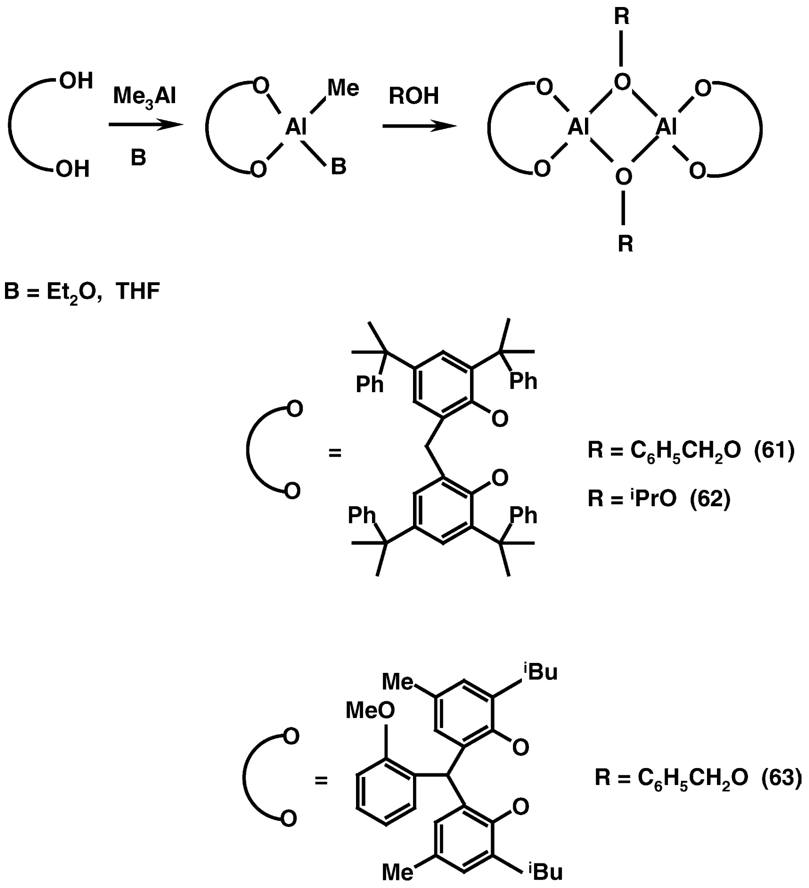
1,4- and 1,3-Dioxobenzene compounds of group 13 have been synthesized as bifunctional Lewis acids and potential chemically triggered switches or chemical sensors. First Gabbai noticed that hydroquinone and resorcinol interact with Me_3Al in a THF solution to produce the dimeric compounds $\{[1,4\text{-}(Me_2AlO)_2C_6H_4]\cdot THF\}_2$ (**65**) and $\{[1,3\text{-}(Me_2AlO)_2C_6H_4]\cdot THF\}_2$ (**66**), respectively [32]. In pyridine, compounds **65** and **66** are easily converted into monomeric pyridine adducts (**67** and **68**) (alane hydroquinone derivatives are presented in Scheme 23). 1,4- and 1,3-Dioxobenzene compounds of aluminum are considered bifunctional Lewis acids due to the presence of two coordinatively unsaturated metal atoms per diolate unit. The Lewis acid centres are neutralized through the coordination of solvent molecules.



R = Me, X = Cl, R' = Et (59)

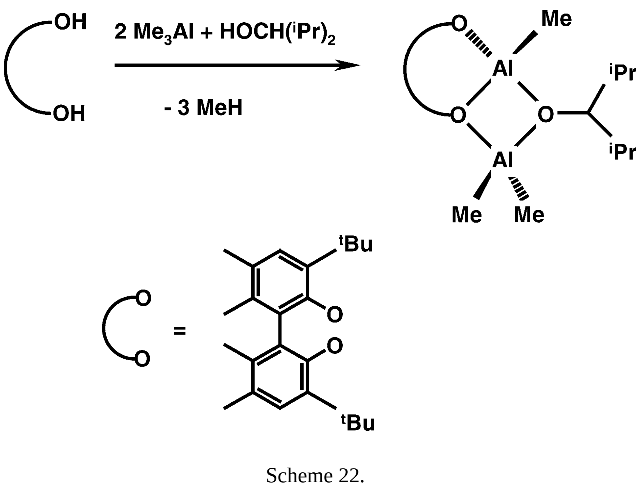
R = H, X = R' = ⁱBu (60)

Scheme 20.



Scheme 21.

The reaction of ^{t}Bu$_3$Ga with hydroquinone leads to the formation of the polymeric product $\{[(^t\mathrm{Bu})_2\mathrm{Ga}]_2(\mu\text{-}\mathrm{OC_6H_4O})\}_n$ (**69**), which reacts with pyridines to yield the yellow compound $\{[(^t\mathrm{Bu})_2\mathrm{Ga(L)}]_2(\mu\text{-}\mathrm{OC_6H_4O})\}$ [L = py (**70**), 4-Me$_2$py (**71**), 3,5-Me$_2$py (**72**)] via cleavage of the Ga$_2$O$_2$ dimeric core. It has been found that pyridines form reversible binding to **69** in the solid state (Scheme 24) [33]. Solid state thermolysis of compounds **70–72** results in the loss of the Lewis base and the formation of **69**. On the other hand, addition of the vapour of the appropriate ligand results in the solid state reformation of **70–72**. It means that the gallium aryloxide polymer **69** exhibits the characteristics of a molecular sensor and/or switch, where the polymer is the host and pyridine acts as a guest.



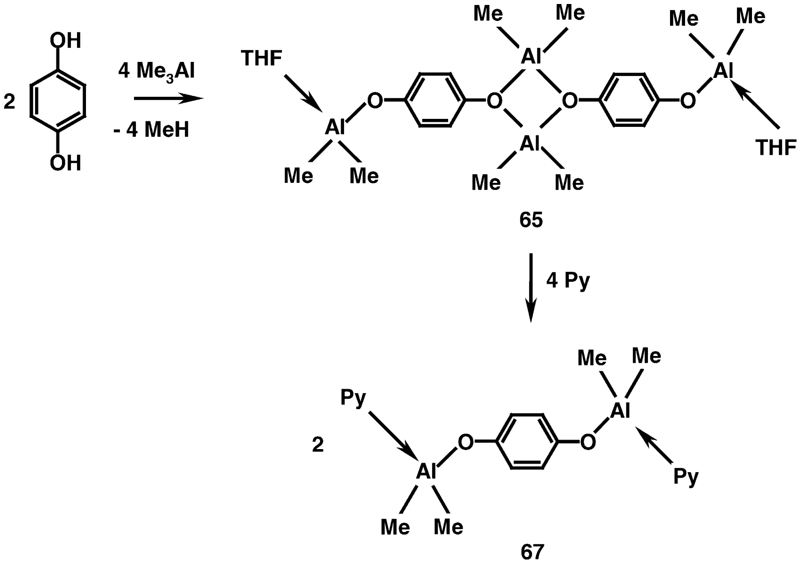
Scheme 22.

^{t}Bu$_3$Al reacts with hydroquinone to produce a similar polymeric product, isostructural to **69**: $\{[(^t\mathrm{Bu})_2\mathrm{Al}]_2(\mu\text{-}\mathrm{OC_6H_4O})\}_n$ (**73**), which forms the complexes $\{[(^t\mathrm{Bu})_2\mathrm{Al(L)}]_2(\mu\text{-}\mathrm{OC_6H_4O})\}$ [L = py (**74**), 3,5-Me$_2$py (**75**), THF (**76**)] with Lewis bases via both a solution and a solid–vapour reaction. Unlike the gallium compounds **70–72**, thermolysis of the alane complexes **74–76** results in decomposition without the formation of the polymeric compound **73**. It means that the binding of Lewis acids to polymer **73** is not reversible in the solid state [34].

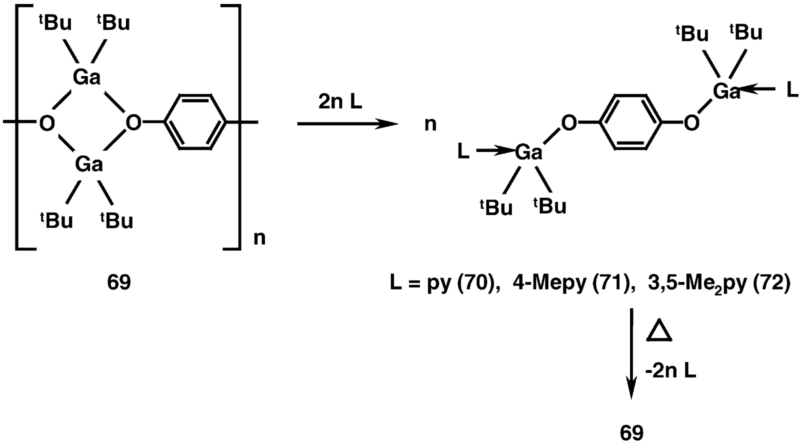
4. 1,2-Diolates of group 13 alkyls

4.1. Reactions of aromatic 1,2-diols with group 13 alkyls

Aromatic alane 1,2-diolates (1,2-catecholates) [R$_5$Al$_3$(OC$_6$H$_4$O)$_2$] [R = Me (**77**), Et (**78**), ^{i}Bu (**79**), ^{t}Bu (**80**)] have been easily synthesized via reactions of 1,2-catechol with



Scheme 23.

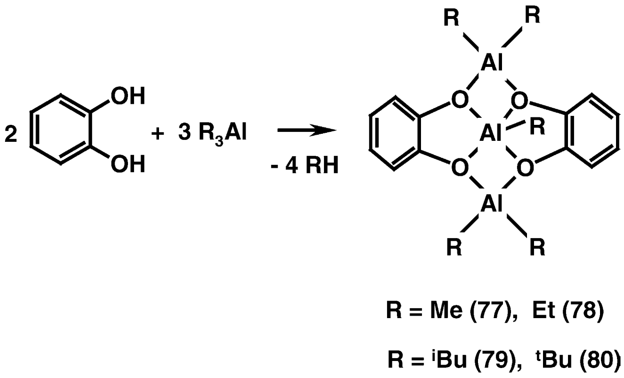


Scheme 24.

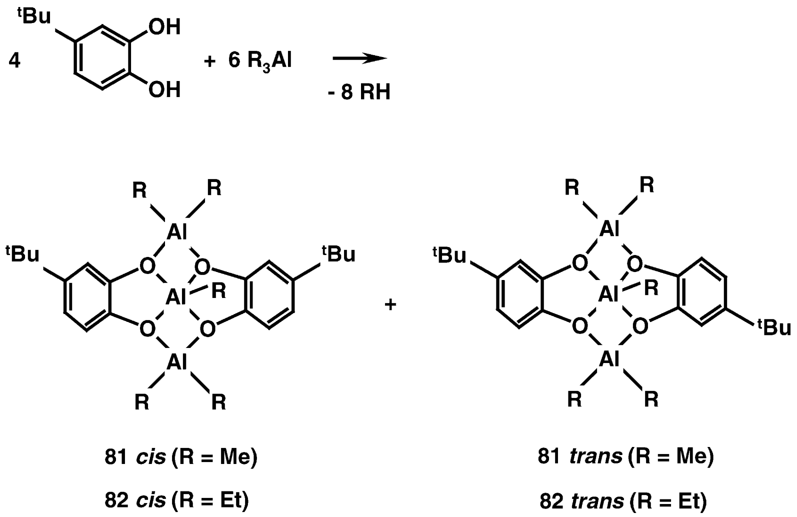
R_3Al (Scheme 25) [35]. The complexes demonstrate a trinuclear structure typical of group 13 metal diolates. In contrast to the reactions of longer diols, the interaction of 1,2-catechol with ^{t}Bu$_3$Al leads directly to the trimetallic complex **80**. The X-ray structure analysis of **80** indicates steric strain in the molecule. The sums of the angles about the two oxygen atoms of diolate units are less than 360°: 339.2° and 342.5°.

Similarly to the unsymmetrical diols described in Section 2.1, reactions of unsymmetrical aromatic 1,2-diols with alanes lead to the formation of mixtures of isomeric products. 4-*tert*-Butyl-1,2-catechol reacts with trimethyl- and triethylaluminum to yield complexes **81** and **82** which demonstrate *trans* and *cis* ligand geometries (Scheme 26).

Aliphatic alkylaluminum diolates are stable in the presence of popular Lewis bases. In contrast, alkylaluminum 1,2-catecholates show lower stability. Dissolved in diethyl ether, THF, and pyridine, complexes **77**–**79** undergo decomposition reaction with precipitation of amorphic organoaluminum oligomers insoluble in organic solvents. Moreover, complexes of trialkylaluminum with Lewis bases, $[R_3Al{\cdot}B]$ [where B = Et_2O, THF, py], have been isolated from the post-reaction mixture [36]. The reactivity of alkylaluminum 1,2-catecholates towards Lewis bases is caused by low basic-



Scheme 25.



Scheme 26.

ity of the oxygen atoms in comparison with aliphatic alane diolates. Additionally, the strain in the two five-membered AlOCCO rings facilitates the cleavage of the Al–O bonds.

Similarly to the *tert*-butylalane catecholate **80**, isostructural gallane and indane complexes, [^{t}Bu$_5$M$_3$(OC$_6$H$_4$O)$_2$] [where M = Ga (**81**), In (**82**)], can be produced via reactions of 1,2-catechol with an appropriate ^{t}Bu$_3$M. However, the syntheses require a higher temperature (refluxing toluene for ^{t}Bu$_3$Ga and refluxing a mixture of hexane and methylene dichloride for ^{t}Bu$_3$In) [37]. The use of a lower temperature and various solvents makes it possible to obtain intermediate products of ^{t}Bu$_3$Ga and ^{t}Bu$_3$In with 1,2-catechol and to propose a reaction pathway. At room temperature the reaction of 1,2-catechol with ^{t}Bu$_3$In in Et$_2$O leads to the formation of the binuclear complex [^{t}Bu$_4$In$_2$(OC$_6$H$_4$OH)$_2$·2Et$_2$O] (**83**) possessing a four-membered In$_2$O$_2$ core and two unreacted hydroxyl groups (Fig. 9). The structure is stabilized by hydrogen bonds with two molecules of Et$_2$O. The same reaction carried out in a non-coordinating solvent (CH$_2$Cl$_2$) results in the formation of the compound [^{t}Bu$_3$In$_2$(OC$_6$H$_4$O)(OC$_6$H$_4$OH)] (**84**), which undergoes a reaction with ^{t}Bu$_3$In to yield the product **82** (Scheme 27).

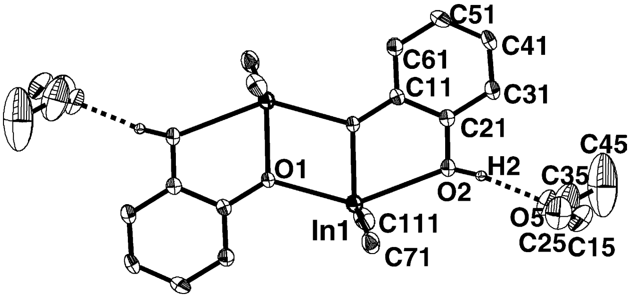
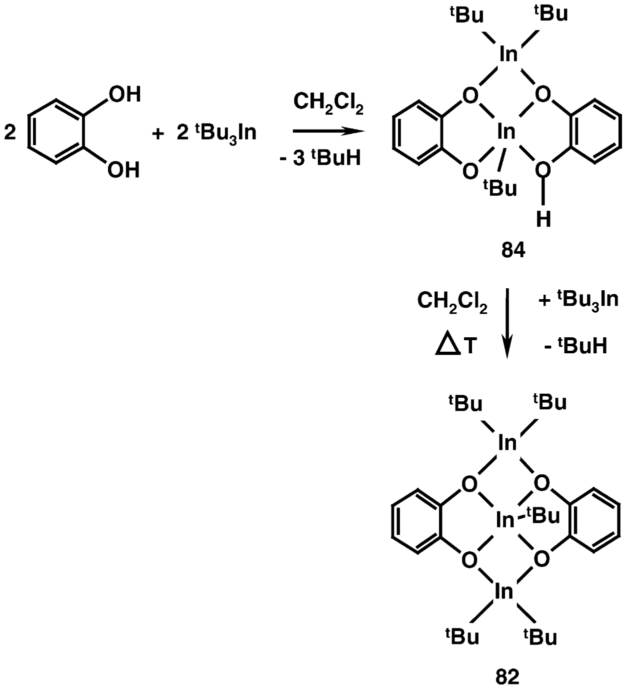


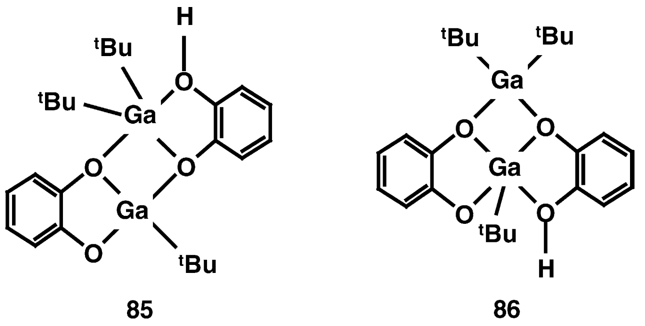
Fig. 9. Crystal structure of [^{t}Bu$_4$In$_2$(OC$_6$H$_4$OH)$_2$·2Et$_2$O] (**83**). All hydrogen atoms (besides of OH) are omitted for clarity [37].

Moreover, it was found that the post-reaction mixture of 1,2-catechol with ^{t}Bu$_3$Ga, besides the main product **81**, contained two isomeric products, **85** and **86**, of the formula [^{t}Bu$_3$Ga$_2$(OC$_6$H$_4$O)(OC$_6$H$_4$OH)] (Scheme 28). Compound **86**, which has a different coordination of gallium atoms than **85**, is a result of the intra-molecular rearrangement of compound **85** to decrease steric repulsion between ligands. According to NMR spectra, the indane compound **86** and the gallane derivative **84** are isostructural. The crystal structure of **86** demonstrates inter-molecular hydrogen bonds within the unit cell (Fig. 10).

Previously Barron [22] reported reactions of aliphatic 1,2-diol (ethane-1,2-diol) with ^{t}Bu$_3$Al. Besides organoa-



Scheme 27.



Scheme 28.

luminum polymers (alucones), he isolated two products: the trinuclear complex $[{}^t\mathrm{Bu}_5\mathrm{Al}_3(\mathrm{OCH}_2\mathrm{CH}_2\mathrm{O})_2]$ (**87**), similar to compounds **80–82**, and the binuclear complex $[{}^t\mathrm{Bu}_3\mathrm{Al}_2(\mathrm{OCH}_2\mathrm{CH}_2\mathrm{O})(\mathrm{OCH}_2\mathrm{CH}_2\mathrm{OH})]$ (**88**), which is similar to **86** and considered an intermediate product of the reaction. It can be seen from the above results that all 1,2-diols react with trialkylmetals according to the same pathway regardless of the aromatic or aliphatic nature of the 1,2-diols.

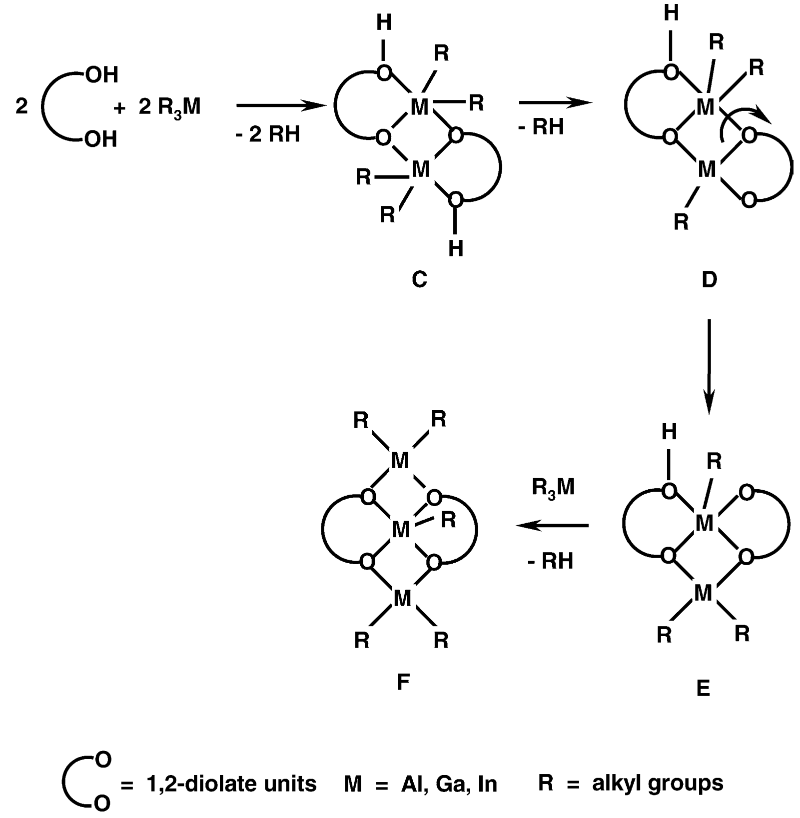
Based on the structure of intermediate products, the first step of the reaction is the formation of a binuclear complex **C**, which subsequently undergoes intra-molecular reaction of one ^{t}Bu group with an OH group (**D**) and rearrangement to yield the compound **E**. This compound reacts further with $\mathrm{R_3M}$, whereby the final trinuclear product **F** is formed (Scheme 29) [37].

4.2. Alkylaluminum benzopinacolates

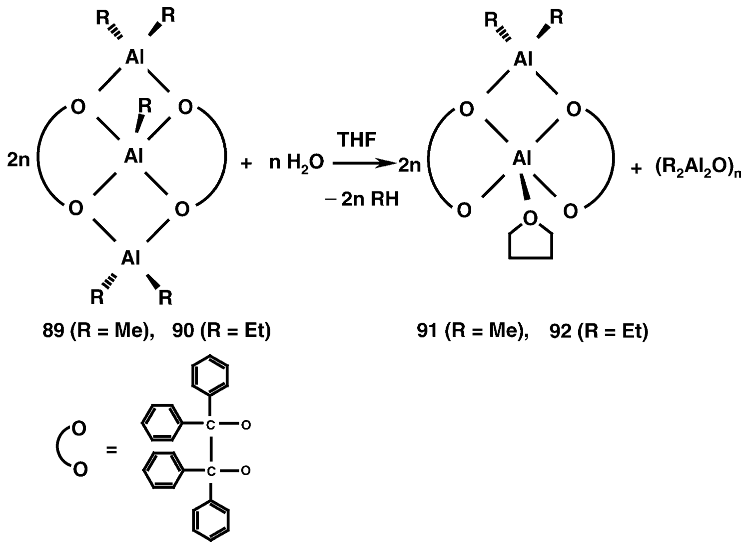
Alkylaluminum 1,1,2,2-tetraphenyl-ethane-1,2-diolates (benzopinacolates) are an example of group 13 1,2-diolates with bulky electron-withdrawing substituents introduced into diolate units not only as steric hindrances but also as an electronic factor weakening Al–O bonds. Reaction of three equivalents of $\mathrm{R_3Al}$ with two equivalents of benzopinacol yields a typical trimetallic product, $\{\mathrm{R_5Al_3[OC(C_6H_5)_2C(C_6H_5)_2O]_2}\}$ [where R = Me (**89**), R = Et (**90**)], in high yield [38]. The CO carbon signals in ^{13}C NMR spectra are dramatically shifted downfield (93.43 and 93.30 ppm for **89** and **90**, respectively) in comparison with those of other aliphatic alane diolates (60–75 ppm), which is due to the electron-withdrawing effect of aromatic rings.

Alane benzopinacolates **89** and **90** are the first diolates to undergo selective hydrolysis with the formation of unique bimetallic complexes of the formula $\{\mathrm{R_2Al_2(THF)[OC(C_6H_5)_2C(C_6H_5)_2O]_2}\}$ [where R = Me (**91**), R = Et (**92**)] and mixtures of alumoxanes (Scheme 30) [38]. Water plays essentially the role of a factor eliminating a $\mathrm{R_3Al}$ molecule from the trinuclear compounds **89** and **90**. The crystal structure of methyl alane derivative **91** shows that the five-coordinate aluminum atom is bonded to four oxygen atoms of the diolate units and to the THF molecule (Fig. 11).

Complexes **91** and **92** show efficient catalytic activity towards ring-opening polymerization of ε-caprolactone (ε-CL), which is very probably the result of the electron-



Scheme 29.



Scheme 30.

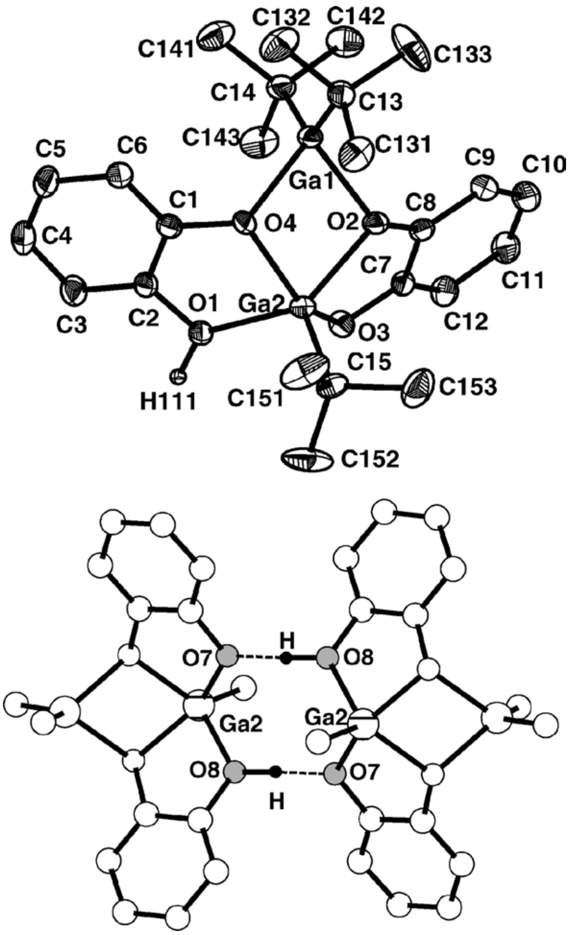


Fig. 10. (Top) Crystal structure of $[{}^{t}\mathrm{Bu_3Ga_2(OC_6H_4O)(OC_6H_4OH)}]$ (**86**). All hydrogen atoms (besides of OH) are omitted for clarity [37]. (Bottom) View of two molecules of **86** showing the intermolecular hydrogen O–H · · · O bonds. Aromatic hydrogen atoms and methyl groups were omitted for clarity [37].

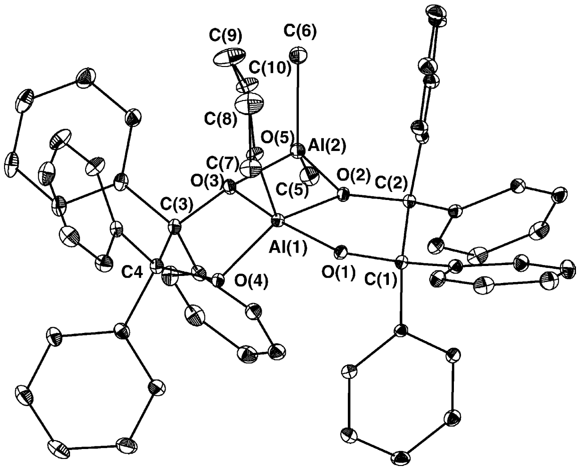


Fig. 11. Crystal structure of $\{\mathrm{Me_2Al_2(THF)[OC(C_6H_5)_2C(C_6H_5)_2O]_2}\}$ (**91**). All hydrogen atoms are omitted for clarity [38].

withdrawing effect of phenyl groups facilitating the insertion of ε-caprolactone into Al–O bonds due to the weakening of these bonds. The presence of a THF molecule coordinated to the aluminium atom may also play an important role, as it can easily be replaced with an ε-CL molecule. It seems that benzopinacolates of group 13 are promising catalysts for the polymerization of cyclic esters.

5. Conclusions

Group 13 diolates are mainly synthesized via reactions of diols with group 13 metallanes. The reaction courses and structures of products depend on steric repulsion between ligands, the length of the diolate backbone, the bulkiness of alkyl groups bonded to metal atoms, and the steric and electronic effects of diolate units. Several group 13 diolates have been used as catalysts in polymerization and organic synthesis. Alane bisphenolates, biphenolates, and benzopinacolates are promising catalysts for the polymerization of cyclic esters. Dimeric alane alkoxy bisphenolates catalyse MPV hydrogen transfer reactions of aldehydes and ketones. Until now, diolates have not been used as a route for the preparation of aluminum-, gallium-, and indium oxides as nanosized particles. However, it seems that some group 13 diolates, especially glycolates, propane-1,3-diolates, and butane-1,4-diolates, may be used as precursors of nanosized metal oxides due to good solubility in common organic solvents, the presence of oxygen atoms bonded to the metal atoms, low molecular weight, and ability to easily undergo hydrolysis.

Acknowledgement

Financial support for this work is provided by the State Committee for Scientific Research (Grant No. 3 T08E 02627).

References

[1] (a) M.P. Coles, R.F. Jordan, J. Am. Chem. Soc. 119 (1997) 8125;
(b) R.-C. Yu, C.-H. Hung, J.-H. Huang, H.-Y. Lee, J.-T. Chen, Inorg. Chem. 41 (2002) 6450;
(c) C.-H. Huang, F.-C. Wang, B.-T. Ko, T.-L. Yu, C.-C. Lin, Macromolecules 34 (2001) 356;
(d) M.R. Mason, A.M. Perkins, J. Organomet. Chem. 599 (2000) 200;
(e) X. Bi, D. Wang, Z. Wu, J. Mol. Cat. A 179 (2002) 53;
(f) C.P. Radano, G.L. Baker, M.R. Smith III, J. Am. Chem. Soc. 122 (2000) 1552;
(g) L.M. Alcazar-Roman, B.J. O'Keefe, M.A. Hillmyer, W.B. Tolman, Dalton Trans. (2003) 3082.

[2] (a) C.-H. Lin, L.-F. Yan, F.-C. Wang, Y.-L. Sun, C.-C. Lin, J. Organomet. Chem. 587 (1999) 151;
(b) J. Blum, J.A. Katz, N. Jaber, M. Michman, H. Schumann, S. Schutte, J. Kaufmann, B.C. Wassermann, J. Mol. Cat. A 165 (2001) 97;
(c) M. Shibasaki, H. Sasai, T. Arai, Angew. Chem. Int. Ed. Engl. 36 (1997) 1236.

[3] (a) D.C. Bradley, Polyhedron 13 (1994) 1111;
(b) R.C. Mehrotra, A. Singh, S. Sogiani, Chem. Rev. 94 (1994) 1643;
(c) C.D. Chandler, C. Roger, M.J. Hampden-Smith, Chem. Rev. 93 (1993) 1205;
(d) M. Veith, S. Mathur, C. Mathur, Polyhedron 17 (1998) 1005;
(e) D. Barreca, G.A. Battiston, R. Gerbasi, E. Tondello, J. Mater. Chem. 10 (2000) 2127;
(f) W. Koh, S.-J. Ku, Y. Kim, Thin Solid Films 304 (1997) 222;
(g) T.-Y. Chou, Y. Chi, S.-F. Huang, C.-S. Liu, Inorg. Chem. 42 (2003) 6041;
(h) Y. Chi, T.-Y. Chou, Y.-J. Wang, S.-F. Huang, A.J. Carty, L. Scoles, K.A. Udachin, S.-M. Peng, G.-H. Lee, Organometallics 23 (2004) 95.

[4] (a) Y. Kimura, A. Nischimura, T. Shimooka, I. Taniguchi, Macromol. Chem. Rapid Commun. 6 (1985) 247;
(b) Y. Kimura, S. Sugaza, T. Ichimura, I. Taniguchi, Macromolecules 20 (1987) 2329;
(c) Y. Kimura, M. Furukawa, H. Yamane, T. Kitao, Macromolecules 22 (1989) 79;
(d) H. Morita, H. Yamane, Y. Kimura, T. Kitao, J. Appl. Polym. Sci. 40 (1990) 753;
(e) R.L. Callender, C.J. Harlan, N.M. Shapiro, C.D. Jones, D.L. Callahan, M.R. Wiesner, D.B. Macqueen, R. Cook, A.R. Barron, Chem. Mater. 9 (1997) 2418;
(f) R.L. Callender, A.R. Barron, J. Mater. Sci. 36 (2001) 4977;
(g) K.A. DeFriend, A.R. Barron, J. Mater. Sci. 37 (2002) 2909;
(h) K.A. DeFriend, A.R. Barron, J. Mater. Sci. 38 (2003) 927;
(i) K.A. DeFriend, A.R. Barron, J. Mater. Sci. 38 (2003) 2673.

[5] (a) C.C. Landry, A. Hynes, A.R. Barron, Polyhedron 15 (1996) 381;
(b) A. Keys, S.G. Bott, A.R. Barron, Polyhedron 17 (1998) 3121;
(c) C.N. McMahon, J.A. Francis, S.G. Bott, A.R. Barron, J. Chem. Soc., Dalton Trans. (1999) 67;
(d) C.N. McMahon, A.R. Barron, J. Chem. Soc., Dalton Trans. (1998) 3703;
(e) A. Keys, T.J. Barbarich, S.G. Bott, A.R. Barron, J. Chem. Soc., Dalton Trans. (2000) 577;
(f) M.S. Hill, A.R. Hutchison, T.S. Keizer, S. Parkin, M.A. VanAelstyn, D.A. Atwood, J. Organomet. Chem. 628 (2001) 71;
(g) M.A. Munoz-Hernandez, S. Parkin, B. Yearwood, P.R. Wei, D.A. Atwood, J. Chem. Cryst. 30 (2000) 215;
(h) D.A. Atwood, M.J. Harvey, Chem. Rev. 101 (2001) 37;
(i) N.J. Hardman, C. Cui, H.W. Roesky, W.H. Fink, P.P. Power, Angew. Chem. Int. Ed. Engl. 40 (2001) 2172;
(j) D. Chakraborty, S. Horchler, R. Kratzner, S.P. Varkey, J. Pinkas, H.W. Roesky, I. Uson, M. Noltemeyer, H.G. Schmidt, Inorg. Chem. 40 (2001) 2620;
(k) W.J. Zheng, H. Hohmeister, N.C. Mosch-Zanetti, H.W. Roesky, M. Noltemeyer, H.G. Schmidt, Inorg. Chem. 40 (2001) 2363;
(l) J. Lewinski, I. Justyniak, J. Zachara, E. Tratkiewicz, Organometallics 22 (2003) 4151;
(m) J. Lewinski, J. Zachara, K.B. Starowieyski, Z. Ochal, I. Justyniak, T. Kopec, P. Stolarzewicz, M. Dranka, Organometallics 22 (2003) 3773;
(n) J. Lewinski, J. Zachara, T. Kopec, K.B. Starowieyski, J. Lipkowski, I. Justyniak, E. Kolodziejczyk, Eur. J. Inorg. Chem. (2001) 1123;
(o) C.S. Branch, J. Lewinski, I. Justyniak, S.G. Bott, J. Lipkowski, A.R. Barron, J. Chem. Soc., Dalton Trans. (2001) 1253;
(p) J. Lewinski, I. Justyniak, J. Lipkowski, J. Zachara, Inorg. Chem. Commun. 3 (2000) 700;
(q) J. Lewinski, I. Justyniak, Z. Ochal, J. Zachara, J. Chem. Soc., Dalton Trans. (1999) 2909;
(r) J. Lewinski, J. Zachara, K.B. Starowieyski, J. Chem. Soc., Dalton Trans. (1997) 4217;
(s) J. Lewinski, J. Zachara, T. Kopec, Z. Ochal, Polyhedron 16 (1997) 1337;
(t) L.-C. Liang, M.-H. Huang, C.-H. Huang, Inorg. Chem. 43 (2004) 2166;
(u) S. Szumacher, I. Madura, J. Zachara, A.R. Kunicki, J. Organomet. Chem. 613 (2000) 119.

[6] (a) T. Iida, N. Yamamoto, S. Matsunaga, H.-G. Woo, M. Shibasaki, Angew. Chem. Int. Ed. 37 (1998) 2223;
(b) M. Takamura, Y. Hamashima, H. Usuda, M. Kanai, M. Shibasaki, Angew. Chem. Int. Ed. 39 (2000) 1650;
(c) K.B. Simonsen, P. Bayon, R.G. Hazell, K.V. Gothelf, K.A. Jorgensen, J. Am. Chem. Soc. 121 (1999) 3845;
(d) K.B. Jensen, M. Roberson, K.A. Jorgensen, J. Org. Chem. 65 (2000) 9080;
(e) F.C. Holger, P.B. Rheiner, D. Seebach, Chem. Eur. J. 6 (2000) 3692;
(f) Y.-M. Lin, I.-P. Fu, B.-J. Uang, Tetrahedron: Asymmetry 12 (2001) 3217;
(g) C. Bolm, O. Beckmann, C. Palazzi, Can. J. Chem. 79 (2001) 1593;
(h) K. Maruoka, A.B. Concepcion, H. Yamamoto, Bull. Chem. Soc. Jpn. 65 (1992) 3501;
(i) K. Maruoka, Y. Hoshino, T. Shirasaka, H. Yamamoto, Tetrahedron Lett. 29 (1988) 3967;

(j) K. Maruoka, H. Yamamoto, J. Am. Chem. Soc. 111 (1989) 789;
(k) K. Maruoka, T. Itoh, Y. Araki, T. Shirasaka, H. Yamamoto, J. Am. Chem. Soc. 110 (1988) 310;
(l) A. Graven, M. Johannsen, K.A. Jorgensen, Chem. Commun. (1996) 2373;
(m) K. Maruoka, T. Ooi, Chem. Eur. J. 5 (1999) 829;
(n) T. Ooi, D. Uraguchi, N. Kagoshima, K. Maruoka, J. Am. Chem. Soc. 120 (1998) 5327;
(o) D.P. Heller, D.L. Goldberg, W.D. Wulf, J. Am. Chem. Soc. 119 (1997) 10551;
(p) K.B. Simonsen, N. Svestrup, M. Roberson, K.A. Jorgensen, Chem. Eur. J. 6 (2000) 123;
(q) J.D. White, Y. Choi, Org. Lett. 2 (2000) 2373;
(r) B. Wang, X. Feng, X. Cui, H. Liu, Y. Jiang, Chem. Commun. (2000) 1605;
(s) M. Roberson, A.S. Jepsen, K.A. Jorgensen, Tetrahedron 57 (2001) 907;
(t) T. Arai, M. Bougauchi, H. Sasai, M. Shibasaki, J. Org. Chem. 61 (1996) 2926;
(u) T. Yamagishi, T. Yokomatsu, K. Suemune, S. Shibuya, Tetrahedron 55 (1999) 12125;
(v) R. Noyori, Tetrahedron 50 (1994) 4259;
(w) T. Arai, H. Sasai, K. Aoe, K. Okamura, T. Date, M. Shibasaki, Angew. Chem. Int. Ed. Engl. 35 (1996) 104;
(x) M. Shibasaki, H. Sasai, T. Arai, Angew. Chem. Int. Ed. Engl. 36 (1997) 1236.

[7] (a) L. Pu, Chem. Rev. 98 (1998) 2405;
(b) H. Groeger, Chem. Rev. 103 (2003) 2795;
(c) Y. Chen, S. Yekta, A.K. Yudin, Chem. Rev. 103 (2003) 3155;
(d) A. Singh, R.C. Mehrotra, Coord. Chem. Rev. 248 (2004) 101;
(e) L.G. Hubert-Pfalzgraf, Coord. Chem. Rev. 178–180 (1998) 967.

[8] For the synthesis, structure and characterisation of dialkyl alkoxides of group 13 see refs 1 and 2 of a paper W. Ziemkowska, M. Buzniak, S. Kwasniewska, K.B. Starowieyski, R. Anulewicz-Ostrowska, J. Organomet. Chem. 688 (2003) 246.

[9] S. Pasynkiewicz, W. Ziemkowska, J. Organomet. Chem. 423 (1992) 1.

[10] W. Ziemkowska, M. Buzniak, S. Kwasniewska, K.B. Starowieyski, R. Anulewicz-Ostrowska, J. Organomet. Chem. 688 (2003) 246.

[11] R. Koester, K. Angermund, J. Serwatowski, A. Sporzynski, Chem. Ber. 119 (1986) 1301.

[12] W. Ziemkowska, S. Pasynkiewicz, E. Kalbarczyk, J. Organomet. Chem. 465 (1994) 93.

[13] W. Ziemkowska, S. Pasynkiewicz, J. Organomet. Chem. 508 (1996) 243.

[14] W. Ziemkowska, S. Pasynkiewicz, T. Glowiak, J. Organomet. Chem. 562 (1998) 3.

[15] W. Ziemkowska, Polyhedron 21 (2002) 281.

[16] W. Ziemkowska, S. Kwasniewska, R. Wroblewski, R. Anulewicz-Ostrowska, J. Organomet. Chem. 651 (2002) 72.

[17] W. Uhl, R. Gerding, A. Vester, J. Organomet. Chem. 513 (1996) 163.

[18] S. Pasynkiewicz, W. Ziemkowska, J. Organomet. Chem. 437 (1992) 99.

[19] W. Ziemkowska, S. Pasynkiewicz, T. Skrok, Main Group Metal Chem. 21 (1998) 105.

[20] W. Ziemkowska, Inorg. Chem. Commun. 4 (2001) 757.

[21] (a) H. Schumann, M. Frick, B. Heymer, F. Girgsdies, J. Organomet. Chem. 512 (1996) 117;
(b) C.N. McMahon, S.G. Bott, A.R. Barron, J. Chem. Soc., Dalton Trans. (1997) 3129;
(c) C.N. McMahon, S.G. Bott, A.R. Barron, J. Chem. Soc., Dalton Trans. (1998) 3301;
(d) J. Ashenhurst, G. Wu, S. Wang, J. Am. Chem. Soc. 122 (2000) 2541;
(e) B. Luo, M. Pink, W.L. Gladfelter, Inorg. Chem. 40 (2001) 307.

[22] C.N. McMahon, L. Alemany, R.L. Callender, S.G. Bott, A.R. Barron, Chem. Mater. 11 (1999) 3181.

[23] W. Ziemkowska, R. Anulewicz-Ostrowska, J. Organomet. Chem. 686 (2004) 2056.

[24] C.N. McMahon, S.J. Obrey, A. Keys, S.G. Bott, A.R. Barron, J. Chem. Soc., Dalton Trans. (2000) 2151.

[25] S.J. Obrey, S.G. Bott, A.R. Barron, Inorg. Chem. 41 (2002) 571.

[26] M.R. Walawalkar, Organometallics 22 (2003) 879.

[27] C.-H. Lin, L.-F. Yan, F.-C. Wang, Y.-L. Sun, C.-C. Lin, J. Organomet. Chem. 587 (1999) 151.

[28] Y.-C. Liu, B.-T. Ko, C.-C. Lin, Macromolecules 34 (2001) 6196.

[29] M.-L. Hsueh, B.-H. Huang, C.-C. Lin, Macromolecules 35 (2002) 5763.

[30] Y.-C. Liu, B.-T. Ko, B.-H. Huang, C.-C. Lin, Organometallics 21 (2002) 2066.

[31] M.H. Chisholm, C.-C. Lin, J.C. Gallucci, B.-T. Ko, Dalton Trans. (2003) 406.

[32] F.A.R. Kaul, M. Tschinkl, F.P. Gabbai, J. Organomet. Chem. 539 (1997) 187.

[33] L.H. van Poppel, S.G. Bott, A.R. Barron, J. Am. Chem Soc. 125 (2003) 11006.

[34] L.H. van Poppel, S.G. Bott, A.R. Barron, J. Chem. Soc., Dalton Trans. (2002) 3327.

[35] W. Ziemkowska, Main Group Metal Chem. 23 (2000) 389.

[36] W. Ziemkowska, A. Sawicki, Main Group Metal Chem. 24 (2001) 111.

[37] W. Ziemkowska, P. Stella, R. Anulewicz-Ostrowska, J. Organomet. Chem. 690 (2005) 722.

[38] W. Ziemkowska, S. Kucharski, A. Kolodziej, R. Anulewicz-Ostrowska, J. Organomet. Chem. 689 (2004) 2939.