

Review

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

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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, {^tBu₄M₂[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 ^tBu₂M with Me₂M units (transmetallation reaction) is presented as another method of mixed-complex synthesis.

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

Abbreviations: [diol-(H)], mono-deprotonated diolate ligand (HOC_n-H_mO)⁻; [diol-(2H)], di-deprotonated diolate ligand (OC_nH_mO)²⁻

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

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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

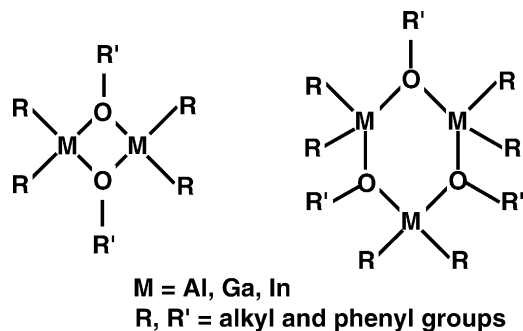
for metal organic chemical vapour deposition (MOCVD) [3], and precursors for sol–gel processes for materials and new materials [4]. Numerous examples of alane, -gallane, and -indane complexes with diacids, diamines, amino alcohols, and amino acids have been synthesized and characterized [5]. Aliphatic 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 ($M = \text{Al, Ga, In}$; $R = \text{alkyl or aromatic group}$) 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, $[\text{Me}_5\text{Al}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2]$ **1**, was synthesized by Pasykiewicz



Scheme 1.

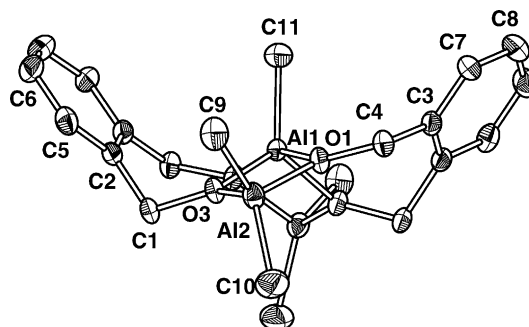
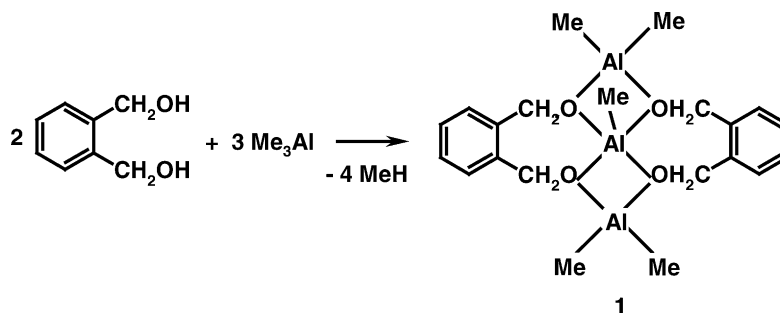


Fig. 1. Crystal structure of the trialuminum complex $[\text{Me}_5\text{Al}_3(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})_2]$ (**1**). All hydrogen atoms are omitted for clarity [10].

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].

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

During the last decade numerous trialuminum compounds, $[\text{R}_5\text{Al}_3(\text{diol}-(2H))_2]$, have been obtained as a result of reactions of R_3Al ($R = \text{Me, Et, }^i\text{Bu}$) with aliphatic diols



Scheme 2.

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