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New route to alkylaluminum hydroxides via hydrolysis of cyclopentadienylaluminum complexes

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Abstract

A novel, very simple and effective synthetic method for the formation of alkylaluminum complexes with terminal hydroxy group via hydrolysis of cyclopentadienylaluminum compounds has been found. Investigations of the hydrolysis of cyclopentadienylaluminum complexes (L)Al(Me)Cp (**1**) and (L)Al(Et)Cp (**2**) (L = HC[(CMe)(2,6-$^{i}Pr_2C_6H_3N$)]$_2$) have shown that the reaction leads to the formation of (L)Al(Me)OH (**3**) and (L)Al(Et)OH (**4**), respectively. The high selectivity of the hydrolysis was revealed. The crystal structures of **1**, **2** and **4** were determined.

Keywords: Alkylaluminum hydroxides; Cyclopentadienylaluminum; β-Diketiminate; Hydrolysis; Structure

1. Introduction

The research on the controlled hydrolysis of organoaluminum derivatives has attracted great attention as this reaction can lead to the formation of alumoxanes [1], compounds containing Al–O–Al units, being active catalysts and cocatalysts for a wide variety of organic monomers [2]. Moreover, the hydrolysis generates products used as precursors for nanomaterials [3]. The hydrolysis of simple organoaluminum species R_3Al to alumoxanes $[RAl(\mu\text{-}O)]_n$ undergoes through the intermediates $[R_3Al \cdot H_2O]$, $[R_2Al(\mu\text{-}OH)]_n$ [4]. Despite the fact that the formation of very reactive $[R_3Al \cdot H_2O]$ adducts was confirmed based on the low-temperature ^{1}H NMR spectra almost thirty years ago [4], the first such a complex, $[(C_6F_5)_3Al \cdot H_2O]$, was structurally characterized in 2003 only [5]. The investigation on the controlled hydrolysis of organoaluminum compounds resulted in isolation of several alumoxanes and hydroxyalumoxanes, showed that the conditions of the hydrolysis process such as temperature, source of water, solvent and so on, have the strong influence on the products [6]. The hydrolysis of halogeno complexes of aluminum stabilized by β-diketiminate ligand L (where L = HC[(CMe)(2,6-$^{i}Pr_2C_6H_3N$)]$_2$) carried out in sophisticated two phase system consisting of liquid ammonia and toluene in the presence of KH and KOH containing small amounts of water allowed to obtain aluminum monohydroxide (L)Al(Me)OH, dihydroxide $(L)Al(OH)_2$ [7] and alumoxane $[(L)(OH)Al]_2(\mu\text{-}O)$ [8,9]. These compounds were found to be stable at ambient conditions and successfully applied as precursors for heterobimetallic species and alumoxanes [10–12]. The reaction of $(L)AlCl_2$ or (L)Al(I)Cl with stoichiometric amounts of water in the presence of *N*-heterocyclic carbene was previously used for preparation of aluminum hydroxides such as $(L)Al(OH)_2$ and $[(L)Al(\mu\text{-}OH)Cl]_2$ [13–15]. These very sophisticated and complicated procedures cause that the synthesis of

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hydroxyaluminum compounds still is considered as a challenge. Nevertheless, it was recently shown that the reaction of $LAl(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with water at low temperature resulted in ring cleavage yielding the monomeric aluminumalkenyl hydroxide $LAl(OH)\text{–}[C(SiMe_3)CH(SiMe_3)]$ [16].

Herein, we report a novel, very simple and effective synthetic method for the formation of the terminal alkylaluminum hydroxides (L)Al(Me)OH (**3**), (L)Al(Et)OH (**4**) via hydrolysis of easy to obtain cyclopentadienylaluminum compounds (L)Al(Me)Cp (**1**) and (L)Al(Et)Cp (**2**).

2. Results and discussion

2.1. Alkylaluminumcyclopentadienyl complexes

The reaction of dicyclopentadienylaluminum alkyls with β-diketimine (LH), where $L = HC[(CMe)(2,6\text{-}^{i}Pr_2C_6H_3N)]_2$ offers a convenient route to appropriate alkyl cyclopentadienylaluminum β-diketiminato complexes

$$\begin{aligned} &RAlCp_2 + LH \rightarrow (L)Al(R)Cp + CpH \\ &R = Me, Et \end{aligned} \qquad (1)$$

The compounds (L)Al(Me)Cp (**1**) and (L)Al(Et)Cp (**2**) were obtained in toluene at room temperature, according to Eq. (1), with about 80% yield. The reaction proceeds selectively with the elimination of CpH only. It is in accordance with our previous study on the reaction of protonolysis of cyclopentadienylaluminum derivatives [17].

Compounds **1** and **2** are air and moisture sensitive. The complexes **1** and **2** were isolated from hexane or hexane/toluene mixture as colorless crystals and characterized by ^1H, ^{13}C NMR and elemental analysis. Further, their crystal structure has been determined by X-ray crystallography. To our best knowledge there is no evidence about the structure of alkylaluminumcyclopentadienyl complexes with *N*,*N*′-chelating ligands in the literature. The crystals of **1** and **2** are isotypic and crystallize in the orthorhombic space group *Pnma*. The molecular structures of **1** and **2** are

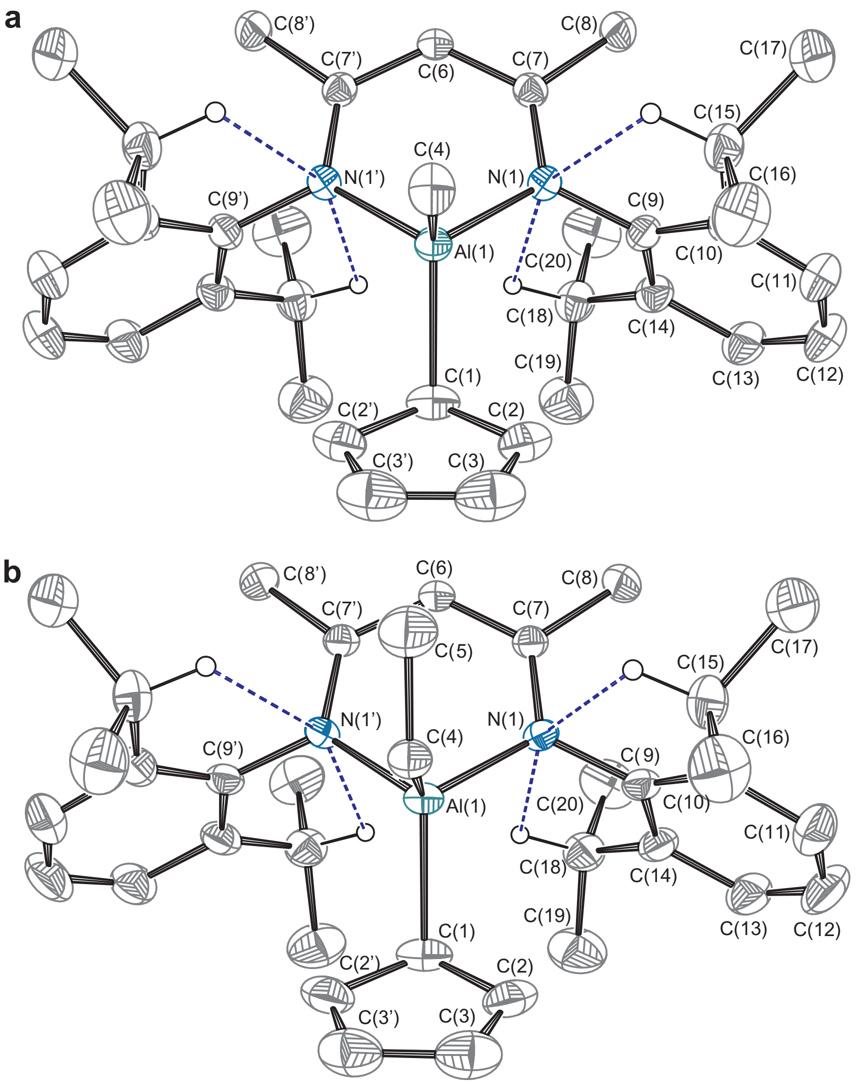

Fig. 1. ORTEP [18] diagrams of complexes (L)Al(Me)Cp (**1**) (a) and (L)Al(Et)Cp (**2**) (b) with atoms numbering scheme. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms, except those engaged in C–H…N intramolecular H-bonds (dashed lines), are omitted for clarity.