New route to alkylaluminum hydroxides via hydrolysis of cyclopentadienylaluminum complexes

Kinga Leszczyńska, Izabela D. Madura, Antoni R. Kunicki *, Janusz Zachara, Magdalena Łoś

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

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$_2$C$_6$H$_3$N)]$_2$) 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.
© 2007 Elsevier B.V. All rights reserved.

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$_3$Al to alumoxanes [RAl(μ-O)]$_n$ undergoes through the intermediates [R$_3$Al · H$_2$O], [R$_2$Al(μ-OH)]$_n$ [4]. Despite the fact that the formation of very reactive [R$_3$Al · H$_2$O] adducts was confirmed based on the low-temperature ^{1}H NMR spectra almost thirty years ago [4], the first such a complex, [(C$_6$F$_5$)$_3$Al · H$_2$O], 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$_2$C$_6$H$_3$N)]$_2$) 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]$_2$(μ-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-(μ-OH)Cl]$_2$ [13–15]. These very sophisticated and complicated procedures cause that the synthesis of

---

* Corresponding author. Tel.: +48 22 6605581; fax: +48 22 6605462.
 *E-mail address:* kunicki@ch.pw.edu.pl (A.R. Kunicki).

hydroxyaluminum compounds still is considered as a challenge. Nevertheless, it was recently shown that the reaction of LAl(η^2-Me$_3$SiC$_2$SiMe$_3$) with water at low temperature resulted in ring cleavage yielding the monomeric aluminumalkenyl hydroxide LAl(OH)–[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-^{i} Pr$_2$C$_6$H$_3$ N)]$_2$ offers a convenient route to appropriate alkyl cyclopentadienylaluminum β-diketiminato complexes

$$RAlCp_2 + LH \rightarrow (L)Al(R)Cp + CpH$$
$$R = Me, Et \tag{1}$$
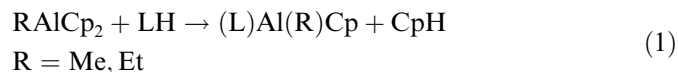
The compounds (L)Al(Me)Cp (**1**) and (L)Al(Et)Cp (**2**) were obtained in toluene at room temperature, according to Eq. (1), with about 80% yield. The reaction proceeds selectively with the elimination of CpH only. It is in accordance with our previous study on the reaction of protonolysis of cyclopentadienylaluminum 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 ^{1}H, ^{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
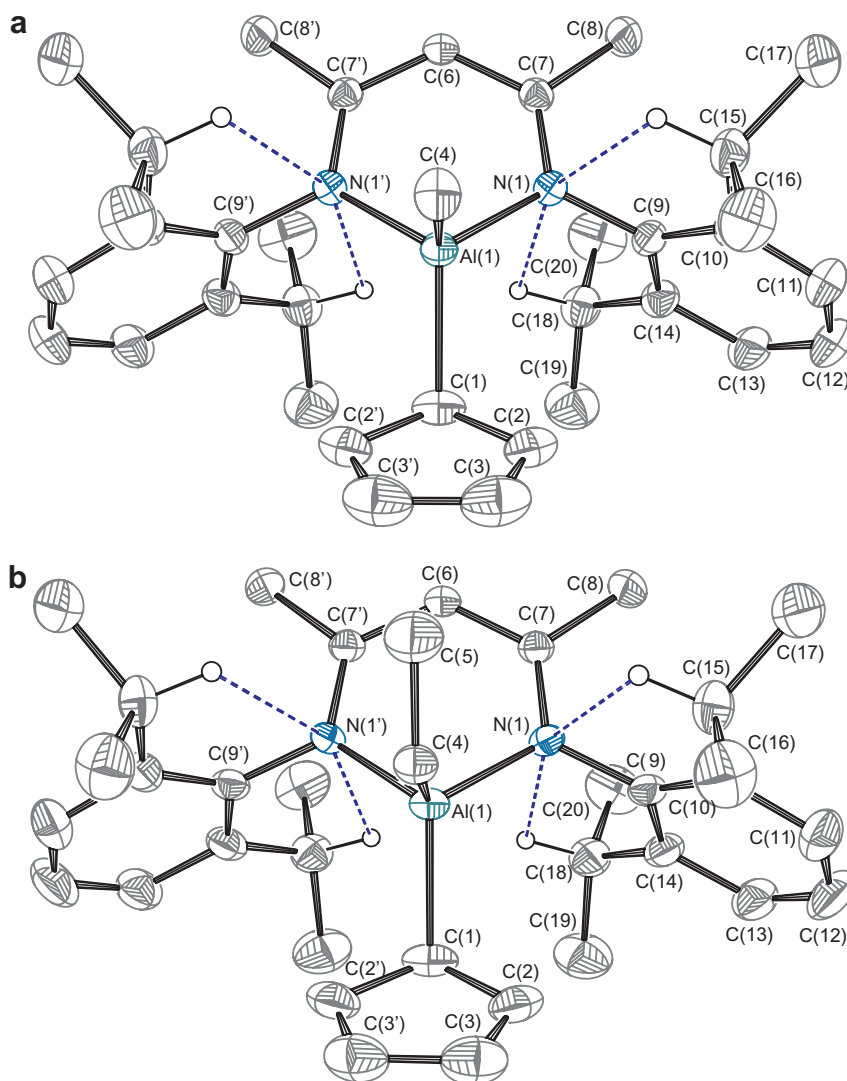
Fig. 1. ORTEP [18] diagrams of complexes (L)Al(Me)Cp (**1**) (a) and (L)Al(Et)Cp (**2**) (b) with atoms numbering scheme. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms, except those engaged in C–H...N intramolecular H-bonds (dashed lines), are omitted for clarity.

Table 1
Selected geometrical parameters for compounds **1** and **2**

	1	**2**
Distances (Å)		
Al(1)–N(1)	1.923(1)	1.927(3)
Al(1)–C(1)	2.034(3)	2.036(5)
Al(1)–C(4)	1.950(2)	1.955(5)
Angles (°)		
N(1)–Al(1)–N(1′)	95.92(8)	95.8(2)
N(1)–Al(1)–C(1)	108.81(7)	109.2(2)
N(1)–Al(1)–C(4)	111.21(6)	113.0(1)
C(1)–Al(1)–C(4)	118.5(1)	114.9(3)

Symmetry operation for equivalent atoms denoted with prime (′) : $x, 1/2 − y, z$.

shown in Fig. 1a and b, respectively, while selected distances and bond angles are collected in Table 1.

Both compounds exist in the solid state as monomeric four-coordinate chelate complexes. The overall molecular symmetry is crystallographically constrained as the molecules reside on the mirror plane passing through the Al(1), C(1), C(4) and C(6) atoms. Thus, the chelate ligands bound the metal centers in a symmetrical fashion and both the Al–N distances are the same and equal 1.923(1) and 1.927(3) Å for **1** and **2**, respectively. They are slightly shorter than the mean value (1.930 Å) observed for the Al–N bond lengths in the (L)AlMe$_2$ complex [19], and elongated comparing to the mean value of corresponding bonds in (L)AlCl$_2$ (1.875 Å) [20], (L)Al(Me)Cl (1.897 Å) [21] or (L)Al(Me)F (1.891 Å) [21]. It is consistent with our previous conclusions, that the exchange of Cp ligand by Me group cause the lowering of the aluminum center acidity, while halogen ligands work in opposite way. That is, the Cp$^−$ shows intermediate basicity between Cl$^−$ (F$^−$) and Me$^−$ ligands. In both **1** and **2**, the aluminum center shows a distorted tetrahedral geometry with bond angles ranging from 95.92(8)° to 118.5(1)° and from 95.8(2)° to 114.9(3)°, respectively. The most acute angle in each case is associated with the bite of the chelating ligand. The six-membered Al(1)N(1)C(7)C(6)C(7′)N(1′) chelate rings in **1** and **2** adopt a conformation close to the flattened boat with the Al(1) and C(6) atoms perched from a plane defined by the remaining atoms. The aluminum atom is displaced by 0.6617(7) and 0.614(2) Å, while C(6) atom by 0.123(2) Å and 0.120(5) Å in **1** and **2**, respectively. The chelate ring conformation is alike to the observed for analogous (L)Al(R)X complexes [21]. Contrary to the (L)Al(Me)F and (L)Al(Me)Cl molecules the alkyl group in **1** and **2** occupy the axial position of the ring. The preferred conformation results from different size of Cp and alkyl ligands. For comparison, the similar size of the Cl and Me ligands in (L)Al(Me)Cl causes the presence of both conformers in the crystal. Hence, in both **1** and **2** molecules the cyclopentadienyl ligand occupies equatorial position. Symmetrically located Cp-ring is $\eta^1(\sigma)$ bonded to the Al center with the ring-slippage parameter [22] equal to 1.822 Å and 1.846 Å, in **1** and **2**, respectively.

A detailed inspection of the crystal structures of compounds **1** and **2** revealed the presence of weak intra- and intermolecular hydrogen bonds. The geometry of H-bonds is summarized in Table 2. As depicted in Fig. 1, isopropyl groups of the chelate ligand are engaged in weak C–H...N hydrogen bonds. This interaction is typical for Al–L complexes as well as is observed in uncomplexed LH moiety [23]. Moreover, in both **1** and **2** crystals the adjacent monomeric moieties are linked by the intermolecular C–H...π bonds between C(6)–H(6) donor group and Cp-ligand acting as a π-acceptor to form an infinite 1D chain running along the *a* axis, as depicted in Fig. 2.

The ^1H, ^{13}C NMR spectra of **1** and **2** in C$_6$D$_6$ are consistent with their solid state structures being retained in solution. Slow aryl rotation around C–N bond and the presence of different ligands at the Al center results in asymmetrical environments of ^{i}Pr groups. That is why in ^1H NMR spectra two ^{i}Pr methine signals and four ^{i}Pr methyl signals are observed. ^{13}C NMR spectra confirm non equivalence of ^{i}Pr groups as well as the non equivalence of carbon atoms of aryl ring [4d]. The presence of hydrogen atoms and carbon atoms of the Cp ligand in ^1H, ^{13}C NMR spectra of **1**, **2** as a single resonance line confirms rapid in the NMR time-scale rotation of the Cp ring on Al atom [24].

2.2. Alkylaluminum hydroxides

We have found that hydrolysis of **1** and **2** carried out according to Eq. (2) results in the formation of aluminum

Table 2
The geometry of intra- and intermolecular H-bonds in crystals of **1**, **2**, **3**[a] and **4**[b]

	d(H...A)	d(C...A)	∠C–H...A
1			
C(15)–H(15)...N(1)	2.49	2.972(2)	110
C(18)–H(18)...N(1)	2.46	2.914(2)	108
C(6)–H(6)...Cg[#1]	2.95(2)	3.881(2)	172(2)
2			
C(15)–H(15)...N(1)	2.47	2.963(5)	111
C(18)–H(18)...N(1)	2.45	2.904(5)	108
C(6)–H(6)...Cg[#1]	2.99(3)	3.934(5)	173(3)
3[a]			
C(13)–H(14)...N(1)	2.47	2.965(7)	110
C(16)–H(21)...N(1)	2.44	2.905(7)	108
C(25)–H(31)...N(2)	2.42	2.917(7)	110
C(28)–H(38)...N(2)	2.45	2.944(7)	111
4			
C(26)–H(26)...O(1)	2.58	3.374(3)	138
C(14)–H(14)...N(1)	2.47	2.957(3)	110
C(17)–H(17)...N(1)	2.47	2.878(3)	105
C(26)–H(26)...N(2)	2.45	2.951(3)	111
C(29)–H(29)...N(2)	2.42	2.922(3)	111
C(11)–H(11)...O(1)[#2]	2.55	3.445(3)	162

Symmetry codes: #1: $1/2 + x, 1/2 − y, 1/2 − z$; #2: $−x, −1/2 + y, 1/2 − z$.
[a] Crystal data taken from CSD: refcode NAHYIF [7].
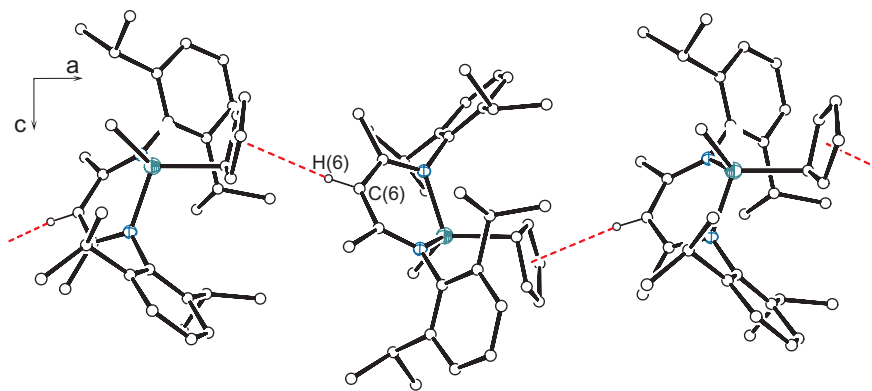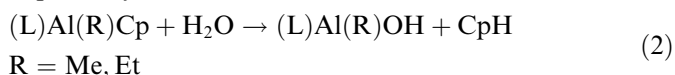[b] Cg denotes a center of gravity of the Cp ring.

Fig. 2. Supramolecular chain-structure formed by C–H...π hydrogen bonds in the crystals of complex (L)Al(Me)Cp (**1**). Analogous structure is observed in isotypic crystals of (L)Al(Et)Cp (**2**).

alkyl hydroxides (L)Al(Me)OH (**3**) and (L)Al(Et)OH (**4**), respectively.

$$(L)Al(R)Cp + H_2O \rightarrow (L)Al(R)OH + CpH$$
$$R = Me, Et \tag{2}$$

The ^{1}H NMR spectra of the post-reaction mixtures pointed out high selectivity of the studied hydrolysis reaction (Eq. (2)). Small amount (∼10%) of the protonated ligand L–H was only detected. Besides the spectra show the presence of unreacted substrates **1** or **2** at the level of 10%. We found that the use of small excess (∼15%) of water improves the reaction selectivity. It should be emphasized that analogous hydrolysis reaction of chloromethylaluminum derivative, (L)Al(Me)Cl, leads to the complete L–H elimination yielding insoluble aluminum oxide(hydroxide) [7]. On the other hand, dimethylaluminum complex, {HC[(CMe)(4-MeC₆H₄ N)]₂}AlMe₂, does not hydrolyze even at room temperature, while at higher temperature hydrolyzes slowly yielding L–H and uncharacterized aluminum species [25]. We have stated that the presence of the Cp ligand is essential for the selective formation of aluminum hydroxides using the simple hydrolysis procedure. The observed difference in the susceptibility of Al–R bond (where R = Me, Cl or Cp) towards hydrolysis can be explained as a result of different polarization of the Al–R bond. However, the structure of the Cp-ligand is unique, thus the protonation of Cp-ring carbon atoms not bonded to the aluminum atom is very likely. The reaction path of an attack of proton on the Cp-ring is under investigation [26].

The spectral data (^{1}H NMR and IR) for the obtained complex **3** are consistent with the results reported previously [7]. The compound **4** was found to be stable in the solid state and in toluene, CH₂Cl₂ or hexane solution at room temperature under an inert atmosphere. The complex **4** was structurally characterized by X-ray diffraction studies and by ^{1}H, ^{13}C NMR, IR, EI-MS and elemental analysis. Single crystals of **4**, suitable for X-ray structural analysis were obtained from reaction (Eq. (2)) with small
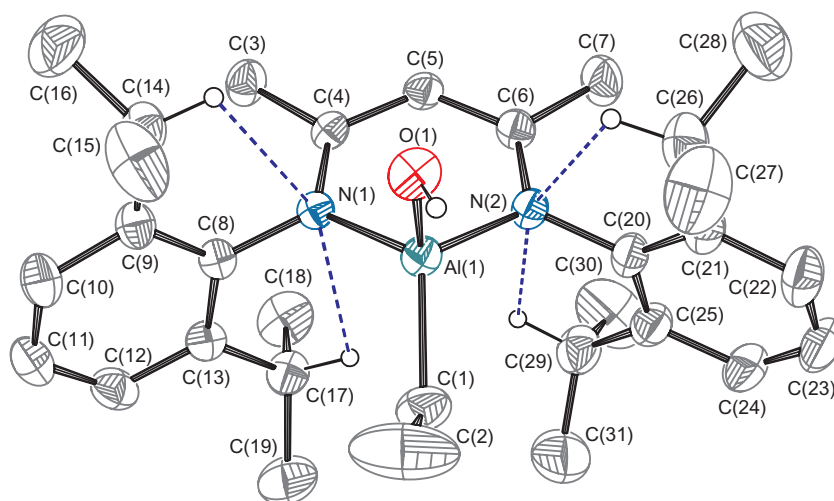

Fig. 3. ORTEP [18] diagram of ethylaluminum hydroxide complex (L)Al(Et)OH (**4**) with atoms numbering scheme. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms except those engaged in intramolecular H-bonds (dashed lines) are omitted for clarity.

Table 3
Selected geometrical parameters for compounds 3[a], and 4

	3[a]	4
Distances (Å)		
Al(1)–N(1)	1.904(3)	1.907(2)
Al(1)–N(2)	1.907(3)	1.909(2)
Al(1)–O(1)	1.731(3)	1.725(2)
Al(1)–C(1)	1.961(3)	1.958(2)
Bond angles (°)		
N(1)–Al(1)–N(2)	96.3(1)	95.82(7)
N(1)–Al(1)–O(1)	105.8(1)	105.57(8)
N(1)–Al(1)–C(1)	115.0(1)	115.69(9)
N(2)–Al(1)–O(1)	108.1(1)	108.19(8)
N(2)–Al(1)–C(1)	113.0(1)	114.62(10)
O(1)–Al(1)–C(1)	116.6(2)	114.97(10)

[a] Values taken from Ref. [7]. The atom numeration is changed to be the same as in 4.

excess of water by maintaining the reaction mixture in hexane/toluene at 5 °C for 1 week. Compound 4 crystallizes in the monoclinic space group $P2_1/c$ and it is not isotypic with the reported crystal structure of 3 [7]. The molecular structure of 4 is shown in Fig. 3. For comparison the selected bond lengths and bond angles for 4 and 3 [7] are collected together in Table 3.

The compound 4 is a monomeric aluminum hydroxide with a four-coordinated Al center of a distorted tetrahedral geometry. The geometrical parameters are the same within the error margin as that found in 3 [7]. The Al–N bond lengths are ∼0.02 Å shorter than those observed in the substrate 2. The analysis of short intra- and intermolecular contacts in 4 revealed that the hydroxy group is not engaged in any hydrogen bond as a donor (Table 2). The same situation we have also found in the crystal structure of complex 3. Nevertheless, in 4 the weak intermolecular C–H...O interaction between aryl hydrogen and the oxygen atom of adjacent molecules related by the 2_1 screw-axis are formed. These interactions arrange molecules into H-bonded helices propagating along b axis. In case of 3 no such interactions are observed.

The EI mass spectrum of 4 shows the molecular peak of low intense at m/z 490 (>1) [M$^+$], the most intense peak at m/z 461 assigned to the fragment [M$^+$−Et] and the peak at 443 (9%) [M$^+$−Et−H$_2$O]. Similar fragmentation was previously found for 3 [7]. The IR spectrum of 4 exhibits a sharp band at 3734 cm^{-1} attributed to the terminal hydroxy group. The similar absorption frequency reported for terminal OH was found in 3 (3728 cm^{-1}) [7], (L)Al(OH)$_2$ (3727 cm^{-1}) [7], and [(L)(OH)Al]$_2$(μ-O) (3716 cm^{-1}) [8]. The ^{1}H, ^{13}C NMR spectra of 4 are consistent with solid state structure being retained in solution. The NMR spectra of 4 (^{1}H, ^{13}C) show slow aryl rotation around Ar–N bond. The observed chemical shift of hydroxy group in ^{1}H NMR for 4 (0.63 ppm) is close to that reported for other organoaluminum derivatives with the terminal OH group: (L)AlMe(OH) (0.53 ppm) [7] and [(L)(OH)Al]$_2$ (μ-O) (−0.30 ppm) [8].

In summary, we have shown that the hydrolysis of cyclopentadienylaluminum complexes is a convenient method of the synthesis of hydroxyaluminum compounds. The reaction runs selectively and the pure products are easy to isolate. The research on using this method to synthesize another hydroxyaluminum complexes and alumoxanes are in progress. We are continuing to explore the reactivity of Cp–Al labile bond toward a number of Broenstead acids, such as water, alcohols, carboxylic and organic phosphoric acids, for explaining the mechanisms of CpH elimination.

3. Experimental

3.1. General remarks

All organometallic compounds were prepared and manipulated under dry argon atmosphere using standard Schlenk techniques. Solvents were distilled over potassium benzophenone ketyl. MeCl$_2$Al, EtCl$_2$Al were purchased from Aldrich and used without further purification. CpNa was synthesized in the reaction of freshly distilled cyclopentadiene with sodium in xylene. MeCp$_2$Al and EtCp$_2$Al were prepared from MeCl$_2$Al or EtCl$_2$Al, respectively and CpNa in toluene. Pro-ligand LH was synthesized according to the procedure previously given [23] and crystallized from ^{i}PrOH before use. NMR spectra were recorded on Varian-Mercury (^{1}H 400.09 MHz, ^{13}C 100.60 MHz, ^{27}Al 104.25 MHz) using d_6-benzene solutions. All chemical shifts are reported in ppm and referenced to solvent (^{1}H, ^{13}C) or Al(OH)$_6^{3+}$ (^{27}Al, external reference, $\delta = 0$ ppm). Infrared spectra were recorded on a Perkin Elmer 2000 FT IR spectrophotometer in Nujol. Mass spectra were recorded on AMD 604 mass spectrometer using EI-MS method.

3.2. Synthesis of (L)Al(Me)Cp (1)

A solution of L–H (0.50 g, 1.2 mmol) in 5 ml of toluene was added via syringe to the cooled to −20 °C solution of MeAlCp$_2$ (0.21 g, 1.2 mmol) in 10 ml of toluene. The reaction mixture was warmed to room temperature and stirred for additional 3 days, then the solvent was evaporated to give white solid, which was dissolved in the mixture hexane/toluene. Crystallization at room temperature afforded colorless crystals with 74% yield (0.47 g, 0.90 mmol). ^{1}H NMR (C$_6$D$_6$): $\delta = -0.95$ (s, 3H, AlMe), 1.06 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 1.12 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 1.37 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 1.41 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 1.52 (s, 6H, β-Me), 3.10 (sept, $^3J_{HH} = 6.8$ Hz, 2H, CHMe$_2$), 3.62 (sept, $^3J_{HH} = 6.8$ Hz, 2H, CHMe$_2$), 4.81 (s, 1H, γ-CH), 5.87 (s, 5H, Al-Cp), 7.10–7.25 (m, 6H, Ar–H). ^{13}C NMR (C$_6$D$_6$): $\delta = -16.2$ (AlMe), 23.8, 24.2, 24.8, 25.3, 25.6, 27.7, 29.2 (CH(CH_3)$_2$, β-Me), 97.6 (γ-C), 112.1 (Cp), 124.3, 125.1, 127.5, 141.5, 143.2, 145.8 (Ar–C), 170.3 (CN). Elemental Anal. Calc. for C$_{35}$H$_{49}$AlN$_2$ (524.76 g mol^{-1}): C, 80.1; H, 9.4; Al, 5.1; N, 5.3. Found: C, 79.8; H, 9.2; Al, 5.0; N, 5.2%.

3.3. Synthesis of (L)Al(Et)Cp (2)

The compound **2** was prepared by a method analogous to that for compound **1** using EtAlCp$_2$ (0.26 g, 1.4 mmol) and L–H (0.59 g, 1.4 mmol). The product **2** crystallized from toluene at 5 °C as a colorless solid. Yield 81% (0.61 g, 1.1 mmol). ^{1}H NMR (C$_6$D$_6$): $\delta = -0.31$ (q, $^3J_{HH} = 8$ Hz, 2H, AlCH_2Me), 1.09 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 1.20 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 1.26 (t, $^3J_{HH} = 8$ Hz, 3H, AlCH$_2Me$), 1.39 (d, $^3J_{HH} = 6.8$Hz, 6 H, CHMe_2), 1.42 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 1.50 (s, 6H, β-Me), 3.24 (sept, $^3J_{HH} = 6.8$ Hz, 2H, CHMe$_2$), 3.57 (sept, $^3J_{HH} = 6.8$ Hz, 2H, CHMe$_2$), 4.73 (s, 1H, γ-CH), 5.87 (s, 5H, Al-Cp), 7.12–7.23 (m, 6H, Ar–H). ^{13}C NMR (C$_6$D$_6$): $\delta = 9.5$ (AlCH$_2Me$), 23.9, 24.7, 25.0, 25.1, 25.2, 27.3, 29.1 (CH(CH$_3$)$_2$, β-Me), 98.6 (γ-C), 112.1 (Cp), 124.5, 125.0, 127.6, 141.7, 143.4, 145.8 (Ar-C), 171.0 (CN). Elemental Anal. Calc. for C$_{36}$H$_{51}$AlN$_2$ (538.79 g mol^{-1}): C, 80.3; H, 9.5; Al, 5.0; N, 5.2. Found: C, 80.2; H, 9.4; Al, 4.9; N, 5.2%.

3.4. Synthesis of (L)Al(Me)OH (3)

H$_2$O (12 μL, 0.67 mmol) was added via syringe to the cooled to −78 °C solution of **1** (0.35 g, 0.67 mmol) in 10 ml of toluene. The reaction mixture was slowly warmed to room temperature and stirred for additional 3 h. Then the solvent was evaporated to give white solid (0.31 g). Compound **3** was characterised by ^{1}H NMR and IR (nujol). Data for **3** are consistent with previously given [7]. ^{1}H NMR

sample reveals peaks due to the contamination by about 10% of free LH and 10% of unreacted substrate **1**.

3.5. Synthesis of (L)Al(Et)OH (4)

H$_2$O (12 μL, 0.66 mmol) was added via syringe to the cooled to −78 °C solution of **2** (0.31 g, 0.58 mmol) in 10 ml of toluene. The reaction mixture was slowly warmed to room temperature and stirred for additional 3 h. Then the solvent was evaporated to give white solid, which was dissolved in the hexane. Crystallization at 5 °C afforded **4** as colorless crystals. Yield 70% (0.20 g, 0.41 mmol). ^{1}H NMR (C$_6$D$_6$): $\delta = -0.23$ (q, $^3J_{HH} = 8$ Hz, 2H, AlCH_2Me), 0.63 (s, 1H, Al–OH), 0.71 (t, $^3J_{HH} = 8$ Hz, 3H, AlCH$_2Me$), 1.06 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 1.20 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 1.33 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 1.34 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 1.57 (s, 6H, β-Me), 3.22 (sept, $^3J_{HH} = 6.8$ Hz, 2H, CHMe$_2$), 3.67 (sept, $^3J_{HH} = 6.8$ Hz, 2H, CHMe$_2$), 4.92 (s, 1H, γ-CH), 7.00–7.17 (m, 6 H, Ar–H). ^{13}C NMR (C$_6$D$_6$): $\delta = -2.4$ (AlCH$_2$Me), 9.3 (AlCH$_2Me$), 23.1, 24.0, 24.4, 24.9, 26.1, 27.8, 28.9 (CH(CH$_3$)$_2$, β-Me), 97.3 (γ-C), 123.8, 124.8, 127.3, 140.7, 143.4, 145.3 (Ar–C), 169.3 (CN). IR (Nujol): 3734, 1551, 1530, 1319, 1255, 1178, 1101, 1057, 1023, 985, 936, 876, 799, 759, 702, 695, 649, 601 cm^{-1}; EI-MS: m/z (%): 490 (>1) [M$^+$], 461 (100) [M$^+$−Et], 443 [M$^+$−Et−H$_2$O] (9). Elemental Anal. Calc. for C$_{31}$H$_{47}$AlN$_2$O (490.70 g mol^{-1}): C, 75.9; H, 9.7; Al, 5.5; N, 5.7. Found: C, 80.0; H, 9.8; Al, 5.3; N, 5.6%.

Table 4
Crystal data, data collection and refinement parameters for compounds **1**, **2** and **4**

	1	**2**	**4**
Empirical formula	C$_{35}$H$_{49}$AlN$_2$	C$_{36}$H$_{51}$AlN$_2$	C$_{31}$H$_{47}$AlN$_2$O
Formula weight	524.74	538.77	490.69
Radiation	Mo Kα ($\lambda = 0.71073$ Å), graphite-monochromated		
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pnma* (No. 62)	*Pnma* (No. 62)	*P*2$_1$/*c* (No. 14)
Z	4	4	4
a (Å)	16.035(3)	16.333(3)	10.643(2)
b (Å)	20.612(4)	20.522(5)	12.833(3)
c (Å)	9.870(2)	9.840(2)	22.858(5)
β (°)	90	90	97.69(3)
Volume (Å^3)	3262.1(11)	3298.2(13)	3093.9(11)
Calculated density (Mg m^{-3})	1.068	1.085	1.053
Absorption coefficient (mm^{-1})	0.086	0.087	0.089
Reflections collected	2961	2964	5714
Reflections with $I > 2\sigma(I)$	2090	1378	3905
Data/restraints/parameters	2961/0/191	2964/0/210	5401/0/330
Goodness-of-fit on F^{2a}	1.017	0.937	1.021
Final R indices ($I > 2\sigma(I)$)[b]	$R_1 = 0.0398$	$R_1 = 0.0615$	$R_1 = 0.0464$
	$wR_2 = 0.0997$	$wR_2 = 0.1279$	$wR_2 = 0.1203$
R indices (all data)[b]	$R_1 = 0.0641$	$R_1 = 0.1564$	$R_1 = 0.0695$
	$wR_2 = 0.1086$	$wR_2 = 0.1618$	$wR_2 = 0.1326$
Largest diffraction peak/hole (e Å^{-3})	+0.20/−0.23	+0.18/−0.19	+0.18/−0.23

[a] Goodness of fit $S = \{[w(F_o^2 - F_c^2)^2/(n - p)]\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.
[b] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_c|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

3.6. X-ray structure determination

The crystal data for compounds **1**, **2**, and **4** were collected on a Siemens P3 diffractometer at room temperature. The measured intensities were processed with the Lorentz and polarization effects and crystal decomposition. In case of **2** the crystal decomposition during data collection was over 20%. The structures were solved by direct methods (SHELXS-97) [27] and refined by the full-matrix least-squares method against F^2 using SHELXL-97 [28]. All non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically. The positions of H atoms attached to cyclopentadienyl C(1) atom in **1** and **2** were refined freely $[U_{iso}(H) = 1.2 \times U_{eq}(C)]$. The remaining H atoms were positioned geometrically and refined using a riding model. The methyl groups bonded to the Al atom in **1** and in the backbone of chelate in **4** (C(3) and C(7) atoms) were modeled as idealized disordered rotating groups with refined occupancy factors. The crystal data and structure refinement details are presented in Table 4. The geometrical parameters for structural analysis were calculated using the PLATON package [22].

4. Supplementary material

CCDC 636341, 636342 and 636343 contain the supplementary crystallographic data for **1**, **2** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk.

References

[1] (a) S. Pasynkiewicz, Polyhedron 9 (1990) 429;
(b) H.W. Roesky, M.G. Walawalkar, R. Murugavel, Acc. Chem. Res. 34 (2001) 201.
[2] (a) T.L. Feng, P.L. Gurian, M.D. Healy, A.R. Barron, Inorg. Chem. 29 (1990) 408;
(b) R.J. Wehmschulte, W.J. Grigsby, B. Schiemenz, R.A. Barlett, P.P. Power, Inorg. Chem. 35 (1996) 6694;
(c) M. Watanabi, C.N. McMahon, C.J. Harlan, A.R. Barron, Organometallics 20 (2001) 460;
(d) Y.V. Kissin, Macromolecules 36 (2003) 7413.
[3] (a) K.V.P.M. Shafi, A. Ulman, J. Lai, N.-L. Yang, M.-H. Cui, J. Am. Chem. Soc. 125 (2003) 4010;
(b) S. Liu, U. Fooken, C.M. Burba, M.A. Eatsman, R.J. Wehmschulte, Chem. Mat. 15 (2003) 2803;
(c) R. Loscutova, A.R. Barron, J. Mat. Sci. 41 (2006) 3391.
[4] (a) S. Pasynkiewicz, A. Sadownik, A. Kunicki, J. Organomet. Chem. 124 (1977) 265;

(b) M. Bolesławski, J. Serwatowski, J. Organomet. Chem. 255 (1983) 269;
(c) J. Storre, A. Klemp, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, R. Fleischer, D. Stalke, J. Am. Chem. Soc. 118 (1996) 1380;
(d) A.R. Kunicki, A. Chojecki, J. Zachara, M. Gliński, J. Organomet.Chem. 664 (2002) 136;
(e) A.R. Kunicki, S. Pasynkiewicz, J. Jankowski, M. Mańk, Pol. J. Chem. 78 (2004) 1857.
[5] D. Chakraborty, E.Y.-X. Chen, Organometallics 22 (2003) 207.
[6] (a) M.R. Mason, J.M. Smith, S.G. Bott, A.R. Barron, J. Am. Chem. Soc. 115 (1993) 4971;
(b) C.J. Harlan, M.R. Mason, A.R. Barron, Organometallics 13 (1994) 2957;
(c) C.C. Landry, C.J. Harlan, S.G. Bott, A.R. Barron, Angew. Chem., Int. Ed. 34 (1995) 1201;
(d) C.J. Harlan, S.G. Bott, A.R. Barron, J. Am. Chem. Soc. 117 (1995) 6465.
[7] G. Bai, Y. Peng, H.W. Roesky, J. Li, H.-G. Schmidt, M. Noltemeyer, Angew. Chem., Int. Ed. 42 (2003) 1132.
[8] G. Bai, H.W. Roesky, J. Li, M. Noltemeyer, H.-G. Schmidt, Angew. Chem., Int. Ed. 42 (2003) 5502.
[9] H.W. Roesky, Inorg. Chem. 43 (2004) 7284, and references therein.
[10] G. Bai, S. Singh, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, J. Am. Chem. Soc. 127 (2005) 3449.
[11] J. Chai, V. Jancik, S. Singh, H. Zhu, C. He, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, N.S. Hosmane, J. Am. Chem. Soc. 127 (2005) 7521.
[12] H.W. Roesky, S. Singh, V. Jancik, V. Chandrasekhar, Acc. Chem. Res. 37 (2004) 969.
[13] V. Jancik, L.W. Pineda, J. Pinkas, H.W. Roesky, D. Nuculai, A.M. Nuculai, R. Herbst-Irmer, Angew. Chem., Int. Ed. 43 (2004) 2142.
[14] H. Zhu, J. Chai, C. He, G. Bai, H.W. Roesky, V. Jancik, H.-G. Schmidt, M. Noltemeyer, Organometallics 24 (2005) 380.
[15] S. Singh, V. Jancik, H.W. Roesky, R. Herbst-Irmer, Inorg. Chem. 45 (2006) 949.
[16] X. Li, L. Duan, H. Song, Ch. Ni, Ch. Cui, Organometallics 25 (2006) 5665.
[17] (a) A. Cebulski, Ph.D. Thesis, Warsaw University of Technology, 2003;
(b) K. Leszczyńska, Ph.D. Thesis, Warsaw University of Technology, 2006.
[18] M.N. Burnett, C.K. Johnson, ORTEPIII, Report ORLN-6895, Oak Ridge National Laboratory, Oak Ridge TN, 1996.
[19] C.E. Radzewich, M.P. Coles, R.F. Jordan, J. Am. Chem. Soc. 120 (1998) 9384.
[20] M. Stender, B.E. Eichler, N.J. Hardman, P.P. Power, J. Prust, M. Noltemeyer, H.W. Roesky, Inorg. Chem. 40 (2001) 2794.
[21] S. Singh, H.-J. Ahn, A. Stasch, V. Jancik, H.W. Roesky, A. Pal, M. Biadene, R. Herbst-Irmer, M. Noltemeyer, H.-G. Schmidt, Inorg. Chem. 45 (2006) 1853.
[22] (a) Distance between perpendicular projection of heavy atom on Cp ring l.s.-plane and ring centroid: A.L. Spek, Acta Crystallogr., Sect. A 46 (1990) 34;
(b) A.L. Spek, PLATON – A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2000.
[23] M. Stender, R.J. Wright, B.E. Eichler, J. Prust, M.M. Olmstead, H.W. Roesky, P.P. Power, J. Chem. Soc., Dalton Trans. (2001) 3465.
[24] (a) See for example: J.D. Fisher, M.-Y. Wei, R. Willett, P.J. Shapiro, Organometallics 13 (1994) 3324;
(b) P.J. Shapiro, Coord. Chem. Rev. 189 (1999) 1.
[25] B. Qian, D.L. Ward, M.R. Smith III, Organometallics 17 (1998) 3070.
[26] I.D. Madura, Ph.D. Thesis, Warsaw University of Technology, 2006.
[27] G.M. Sheldrick, SHELXS-97, Program for structure solution, Acta Crystallogr., Sect. A 46 (1990) 467.
[28] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen, Göttingen, Germany, 1997.