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Chiral dialkylaluminum 6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazol-7-olates: Synthesis, characterization and polymerization activity

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ABSTRACT

Reactions of the chiral alcohol rac 6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazol-7-ol [(R,S)-LH] with R_3Al (R = ^{t}Bu, Et) have been studied. An influence of reaction conditions on the product structures and distributions was found. The dimeric products ($Al_2R_4L_2$) [R = ^{t}Bu (**1**), R = Et (**2**)] were formed in the reactions of R_3Al with one equivalent of (R,S)-LH as mixtures of the heterochiral (R,S) and homochiral (R,R) and (S,S) diastereomers. The X-ray diffraction measurements of the (R,S)-**1** and (R,S)-**2** showed dinuclear complexes with bridging ON ligands and 10-membered $C_4N_2O_2Al_2$ central cycles. The molecules contain two chiral ligands demonstrating (R) and (S) configurations of CO carbon atoms. Polymerization tests showed that the complexes **1** and **2** have activity in the ROP of ε-caprolactone. Kinetic studies revealed first order reaction of polymerization.

1. Introduction

The metal complexes with optically active and chiral ligands are very interesting due to their application in asymmetric organic synthesis [1]. Recently, Horeglad and coworkers have reported an increase of the heteroselectivity of the ring opening polymerization (ROP) of rac-lactide in the presence of an excess of gallium and indium homochiral complexes [2]. The exclusive formation of the complex (R*R*)-[$Me_2Al(\mu$-OCH(Me)CO_2Et)]$_2$ in the reaction of rac-ethyl lactate with Me_3Al was firstly observed by Lewiński and coworkers [3]. Reactions of aluminum compounds with racemic chiral alcohols lead to a formation of the mixture of diastereoisomers. In the post reaction mixture of Cp_3Al with *rac*-1-phenyl-1-propanol, *rac*-2-phenyl-1-propanol and *rac*-1-phenyl-2-propanol, Kunicki found (R,S) and (R*,R*) diastereoisomers [4]. In the case of dialkylaluminum alkoxides derived from chiral donor-functionalized alcohols, the formation of dimeric species is often a highly stereoselective reaction [5]. Homochiral alcohols play important role in the synthesis of optically active organometallic complexes [6]. During the last decade, organoaluminum complexes with deprotonated natural alkaloid cinchonine were used as effective chiral building blocks for the construction of coordination polymers [7]. Herein, we present the study on the reactions of trialkyl aluminum compounds with rac 6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazol-7-ol as a chiral donor-functionalized alcohol. We show the formation of a mixture of heterochiral (R,S) and homochiral (R,R) and (S,S) organoaluminum dimers.

2. Results and discussion

The treatment of the chiral alcohol rac 6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazol-7-ol [(R,S)-LH] with one equivalent of ^{t}Bu$_3$Al·OEt$_2$ in CH_2Cl_2 afforded a product, whose characterizing data are consistent with a mixture of the heterochiral [(R,S)-**1**] of the formula ^{t}Bu$_4$Al$_2$[(R)-L][(S)-L], and homochiral [(R,R) (S,S)-**1**] of the formulae ^{t}Bu$_4$Al$_2$[(R)-L]$_2$ and ^{t}Bu$_4$Al$_2$[(S)-L]$_2$ dimers (Scheme 1). A crystallization from the cyclohexane solution of the mixture at 10 °C led to the precipitation of a crystalline solid of the pure heterochiral [(R,S)-**1**] isomer containing two ligands with R and S configurations of CO carbons. The structure of the (R,S)-**1** compound was determined by means of NMR spectroscopy, elemental analysis and X-ray diffraction studies. The ^{1}H NMR spectrum (see

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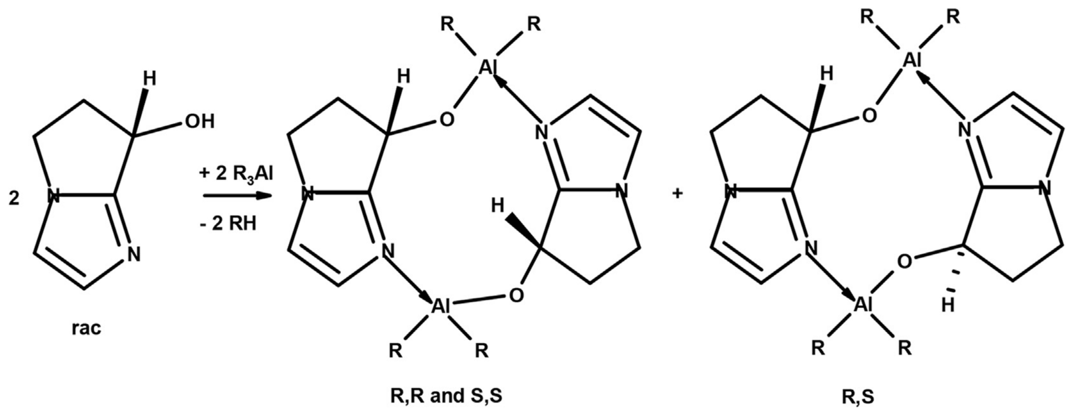

Scheme 1. Reactions of rac 6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazol-7-ol with R_3Al (R = ^{t}Bu, Et).

Figs. 1S and 2S in the Supporting information) showed two signals of $(CH_3)_3Al$ protons at 1.05 and 0.69 ppm with an integration ratio of 1:1, which indicated non-equivalence of ^{t}Bu groups bonded to the aluminum atoms. Two doublets at 7.20 and 6.95 ppm with 2.8 Hz coupling constants were assigned to the signals of *cis* HC=CH protons. The integration ratio of the HC=CH proton signals at 7.20 and 6.95 ppm, and $(CH_3)_3Al$ proton signals at 1.05 and 0.69 ppm equaling 1:1:9:9 indicated two ^{t}BuAl groups per one ligand.

The molecular structure of (R,S)-**1** was determined on the basis of X-ray diffraction studies and is shown in Fig. 1. Details of data collection and structure analysis are summarized in Table 1. Molecular studies showed that a molecule of (R,S)-**1** is dinuclear and centrosymmetric. The molecule consists of two chiral 6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazol-7-olate ligands demonstrating (R) and (S) configurations of C(1) atoms and two $^tBu_2Al$ units. The ligands act as a NO bridges. The N(1), C(6), C(1) and O(1) and Al(1) atoms form ten-membered cycle $C_4N_2O_2Al_2$ in a shape of a distorted chair. The rings larger than the eight-membered are rare in aluminum complexes chemistry. A 32-membered ring complex obtained in the reaction of Me_3Al with 2,2-diphenylglycine [6], 12-membered ring in the organoaluminum benzoate [8], a 34-membered ring in the aluminum diglycolate [9], a 14-membered ring in the aluminum hippurate [9] and 16-membered ring complex obtained in the reaction of $^tBu_3Al$ with 2-mercaptobenzoxazole [10] are the only examples with large rings. Each of aluminum atoms Al(1) is tetra-coordinated and bonded to two ^{t}Bu groups, one oxygen atom O(1) and one nitrogen atom N(1) originating from two ligands. The bond length of Al(1)–N(1) [1.975(2) Å] demonstrates a coordinating character of the bond.

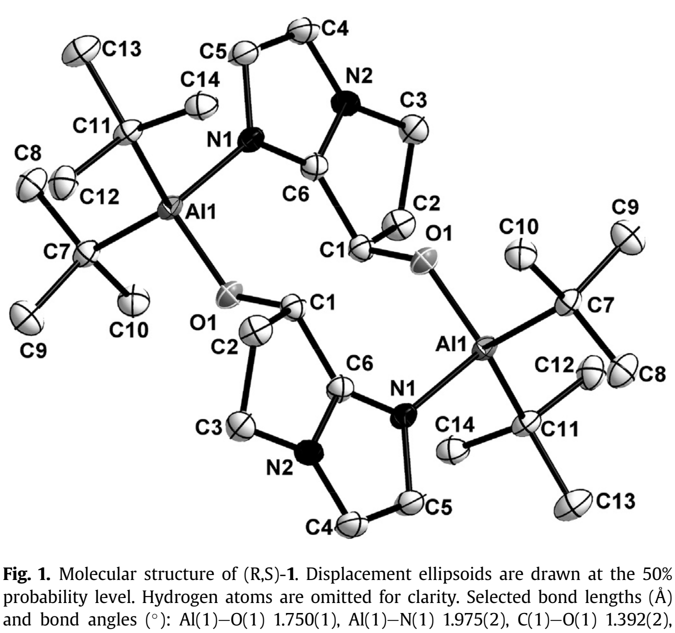

Fig. 1. Molecular structure of (R,S)-**1**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al(1)–O(1) 1.750(1), Al(1)–N(1) 1.975(2), C(1)–O(1) 1.392(2), C(1)–C(6) 1.516(3), C(1)–C(2) 1.556(3), C(2)–C(3) 1.530(3), C(3)–N(2) 1.461(2), C(4)–C(5) 1.351(3), C(4)–N(2) 1.363(2), C(5)–N(1) 1.401(2), C(6)–N(1)–1.332(2), C(6)–N(2) 1.341(2), O(1)–Al(1)–N(1) 103.7(1), O(1)–C(1)–C(6) 110.0(2), N(1)–C(6)–N(2) 110.7(2), N(1)–C(6)–C(1) 138.6(2), N(2)–C(6)–C(1) 110.7(2), C(6)–N(1)–C(5) 104.6(2), C(6)–N(1)–Al(1) 128.2(1), C(5)–N(1)–Al(1) 126.4(1), C(6)–N(2)–C(4) 109.1(2), C(6)–N(2)–C(3) 113.5(2), C(4)–N(2)–C(3) 137.5(2), C(1)–O(1)–Al(1) 134.3(1).

The isolation of the pure homochiral [(R,R) (S,S)-**1**] diastereomers failed, therefore they were mainly characterized by the ^{1}H NMR analysis of the mixture of the heterochiral [(R,S)-**1**] and homochiral [(R,R) (S,S)-**1**] diastereomers obtained after removal of a solvent from the post reaction mixture of the alcohol with $^tBu_3Al\cdot OEt_2$. Besides the signals of (R,S)-**1** protons, the ^{1}H NMR spectrum revealed the following proton signals of the homochiral [(R,R) (S,S)-**1**]: two doublets at 7.06 and 6.91 ppm assigned to the HC=CH protons and two singlets at 0.79 and 0.73 ppm representing signals of protons of two inequivalent $(CH_3)_3CAl$ groups (see Figs. 3S and 4S in the Supporting information). Similarly to the (R,S)-**1**, in the [(R,R) (S,S)-**1**] an integration ratio of the signals at 7.06, 6.91, 0.79 and 0.73 equaling 1:1:9:9 showed one ligand moiety per two ^{t}BuAl groups. The presence of two signals of $(C\underline{H}_3)_3CAl$ protons at 0.79 and 0.73 ppm indicated an inequivalence of ^{t}Bu groups bonded to Al atoms. According our recent studies [11] inequivalent alkyl groups in the R_2Al moieties are present in the monomeric complexes $R_2Al(L)$, therefore we have considered the structure of the [(R,R) (S,S)-**1**] as a mixture of two monomeric isomers $^tBu_2Al[(S)\text{-}L]$ and $^tBu_2Al[(R)\text{-}L]$ (where L = alcoholate moiety). However, despite the inequivalence of ^{t}BuAl groups, molecular weight measurements by cryoscopic methods in benzene indicated the dimeric character of (R,S)-**1** and (R,R) (S,S)-**1** products. The calculated molecular weight for dimeric structures (529 g/mol) was similar to the average molecular weights for the mixture consisting of 58% of (R,S)-**1** and 42% of (R,R) (S,S)-**1** (515 g/mol), and for the mixture consisting of 35% of (R,S)-**1** and 65% of (R,R) (S,S)-**1** (521 g/mol). The mixture compositions for the molecular weight measurements were determined on the basis of an integration ratio of HC=CH proton signals of the (R,S)-**1** and (R,R) (S,S)-**1** products at 7.20 and 7.06 ppm equaling 1.4:1 and 0.55:1, respectively.

In time, the product molar ratio of (R,S)-**1**: (R,R) (S,S)-**1** remained the same, which indicated the stability of the compounds and lack of transformation of one isomer into another.

Similarly to the reaction of $^tBu_3Al$, the reaction of Et_3Al with an equimolar amount of [(R,S)-LH yielded the mixture of (R,S)-**2** and