

# Synthesis and crystal structures of three amidinatoaluminum compounds and their catalytic behavior in the Tishchenko reaction



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## ABSTRACT

Three amidinatoaluminum compounds,  $[\{\text{MeC}(\text{NCy})_2\}\text{AlMe}(\mu\text{-OMe})]_2$  (**1**),  $[\{(\text{PhN})\text{MeC}(\text{NCy})\}\text{AlMe}(\mu\text{-OMe})]_2$  (**2**) and  $[\{(\text{PhN})\text{MeC}(\text{N}^i\text{Bu})\}\text{AlMe}(\mu\text{-OMe})]_2$  (**3**), were prepared by the insertion reaction of oxygen with the corresponding aluminum amidinate in high yield and characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and single crystal X-ray diffraction analysis. **1–3** were used as pre-catalysts to catalyze the Tishchenko reaction and both **2** and **3** exhibited good to excellent catalytic activity under mild conditions.

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## 1. Introduction

Many natural products and synthetic pharmaceuticals contain amidine functional groups, which often play an essential role in their biological activities [1]. Amidinates  $[\text{R}^1\text{NC}(\text{R}^3)\text{NR}^2]^-$  ( $\text{L}^-$ ;  $\text{R}^1$ ,  $\text{R}^2 = \text{H}$ , alkyl, cycloalkyl, aryl or trimethylsilyl;  $\text{R}^3 = \text{H}$ , alkyl, or aryl) have been long studied as chelating ligands for main group, transition metal and lanthanide elements [2] due to their versatile steric and electronic properties [3], which can be easily tuned by changing the various  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  groups [4]. Large numbers of metal amidinate complexes have been synthesized and applied in many areas, including catalytic reactions, organic transformations and atomic layer deposition [5]. More specifically, aluminum amidinates are of interest as potential reagents in organic synthesis [6], as catalysts for olefin polymerization [7], and as precursors for thin film deposition [8], and have attracted increasing attention in recent years. Three major synthetic routes for *N,N*-disubstituted aluminum amidinates are (i) insertion of carbodiimides into Al–C bonds, (ii) condensation reactions of amidines with aluminum reagents and (iii) displacement reactions of amidino lithium compounds with aluminum halide [9]. For instance, Rowley et al. synthesized aluminum amidinates ( $[\text{CH}_3\text{C}(\text{N}^i\text{-Pr})_2]_2\text{AlCH}_3$ ,  $[\text{CH}_3\text{C}(\text{N}^i\text{-Pr})_2]_3\text{Al}$ ) containing two and three acetamidinate units via insertion of 2 or 3 equivalents of diisopropylcarbodiimide into trimethylaluminum [10].

Usually, aluminum(III) displays a high oxophilicity ability, several examples of the interaction of aluminum complexes with oxygen, as well as details of the reaction mechanism have been reported [11]. However, the insertion reaction of oxygen into aluminum amidinate alkyls has not been reported to date. To the best of our knowledge, the sole example,  $[\{\text{HC}(\text{NDipp})_2\}\text{AlMe}(\mu\text{-OMe})]_2$ , was synthesized and well characterized by Richards' group [7b], what is more, it was obtained unexpectedly by using an undried solvent. It is noteworthy that it was unsuccessfully synthesized by the addition of stoichiometric quantities of water or oxygen to anhydrous reactions. Here we report the synthesis and structures of three amidinatoaluminum compounds containing the  $\mu\text{-OCH}_3$  moiety, and their use as pre-catalysts for the dimerization of aldehydes to the corresponding carboxylic esters was also investigated.

## 2. Experimental

### 2.1. General remarks

All manipulations were performed under a nitrogen atmosphere with rigorous exclusion of oxygen and water using standard Schlenk and cannula techniques. All solvents were freshly distilled and stored over a potassium mirror or activated molecular sieves prior to use. The deuterated solvent  $\text{C}_6\text{D}_6$  was dried over activated molecular sieves (4 Å) and vacuum transferred before use.  $\text{CyN}=\text{C}=\text{NCy}$  ( $\text{Cy} = \text{cyclohexyl}$ , Alfa Aesar) and  $\text{AlMe}_3$  (2.0 M solution in hexane; Alfa Aesar) were obtained commercially and used

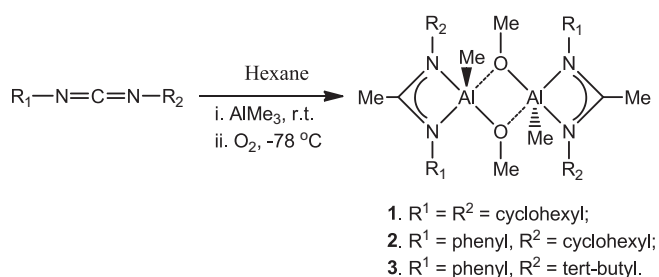
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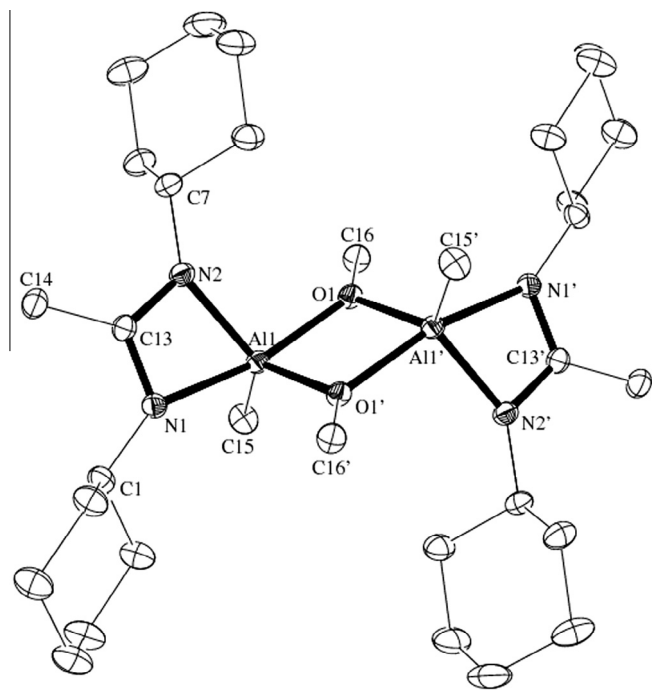
as received.  $\text{PhN}=\text{C}=\text{NCy}$  and  $\text{PhN}=\text{C}=\text{N}^t\text{-Bu}$  were prepared according to the literature procedures [12]. Glassware was oven-dried at 105 °C overnight.  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75 MHz) spectra of the compounds were recorded on a Bruker DRX 300 instrument and referenced internally to the residual solvent resonances (chemical shift data in  $\delta$ ). All NMR spectra ( $^1\text{H}$  and  $^{13}\text{C}$ ) were measured in  $\text{C}_6\text{D}_6$  at 298 K. Elemental analyses were performed on a Vario EL-III instrument. Crystallographic measurements were performed with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Bruker Smart Apex CCD diffractometer at 296(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. Details of the modeling of disorder in the crystals can be found in their CIF files.

## 2.2. Synthesis of **1**, $[\{\text{MeC}(\text{NCy})_2\}\text{AlMe}(\mu\text{-OMe})_2]$

To a stirred solution of *N,N'*-dicyclohexylcarbodiimide (0.62 g, 3.0 mmol) in hexane (20 mL) was added trimethylaluminum (1.50 mL of a 2.0 M solution in hexane, 3.0 mmol) dropwise at room temperature. After being stirred for 6 h, stoichiometric quantities of dry oxygen were introduced slowly into the solution via a syringe and the reaction was carried out for 30 min at  $-78 \text{ }^\circ\text{C}$ . The



**Scheme 1.** Synthetic routes to complexes **1–3**.

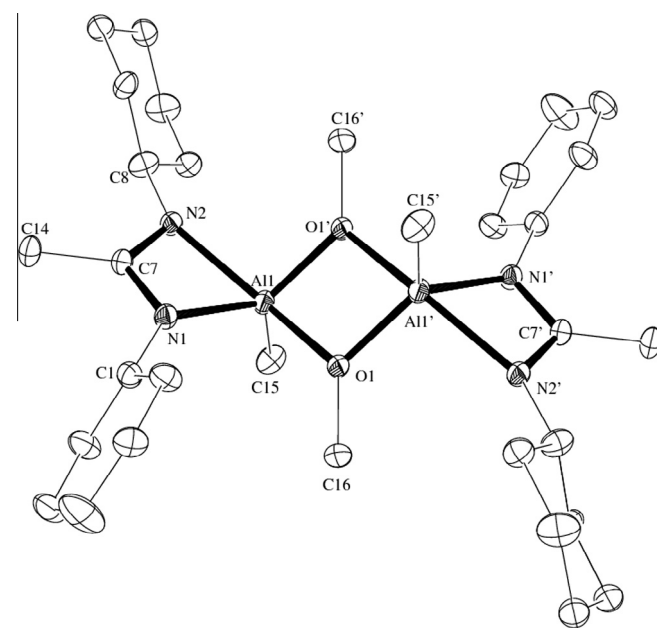


**Fig. 1.** Molecular structure of complex **1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. (Symmetry codes: '  $-x$ ,  $1 - y$ ,  $1 - z$ ).

**Table 1**  
Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for compound **1**.

|            |            |              |            |
|------------|------------|--------------|------------|
| Al1–O1     | 1.9190(11) | Al1–O1'      | 1.8270(11) |
| Al1–N1     | 2.0524(14) | Al1–N2       | 1.9280(14) |
| Al1–C15    | 1.9769(18) | Al1–Al1'     | 2.9418(9)  |
| N1–C13     | 1.318(2)   | N2–C13       | 1.339(2)   |
| N1–C1      | 1.460(2)   | N2–C7        | 1.460(2)   |
| O1–C16     | 1.4194(18) | O1–Al1'      | 1.8270(11) |
| O1–Al1–O1' | 76.53(5)   | O1–Al1–N1    | 160.97(6)  |
| O1'–Al1–N1 | 97.98(5)   | O1–Al1–N2    | 99.48(6)   |
| O1'–Al1–N2 | 117.51(6)  | N2–Al1–C15   | 121.20(8)  |
| O1–Al1–C15 | 121.06(7)  | O1'–Al1–C15  | 98.36(7)   |
| N1–Al1–N2  | 66.53(6)   | N1–Al1–C15   | 100.01(7)  |
| C1–N1–Al1  | 146.10(12) | C7–N2–Al1    | 143.04(11) |
| C13–N1–Al1 | 88.66(10)  | Al1–O1'–Al1' | 103.47(5)  |
| C16–O1–Al1 | 129.20(10) | C16'–O1'–Al1 | 124.48(10) |
| C1–N1–C13  | 122.39(14) | C7–N2–C13    | 123.28(14) |
| N1–C13–C14 | 124.83(15) | N2–C13–C14   | 124.42(15) |

Symmetry transformations used to generate equivalent atoms: '  $-x$ ,  $1 - y$ ,  $1 - z$ .



**Fig. 2.** Molecular structure of complex **2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. (Symmetry codes: '  $-x + 1$ ,  $-y$ ,  $-z$ ).

resulting mixture was then warmed to room temperature and stirred overnight. The white precipitate that formed was collected by filtration and extracted into tetrahydrofuran. The filtrate was concentrated to ca. 15 mL and stored at  $-10 \text{ }^\circ\text{C}$  for several days, yielding colorless crystals of **1**. Yield: 0.71 g, 80.4%. *Anal. Calc.* for  $\text{C}_{32}\text{H}_{62}\text{Al}_2\text{N}_4\text{O}_2$ : C, 65.92; H, 10.64; N, 9.03. Found: C, 65.77; H, 10.48; N, 9.24%.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C)  $\delta$  (ppm):  $-0.19$  (s, 6H,  $\text{AlCH}_3$ ),  $1.22\text{--}1.36$  (m, 8H,  $\text{C}_6\text{H}_{11}$ ),  $1.55$  (s, 6H,  $(\text{CyN})_2\text{CCH}_3$ ),  $1.59\text{--}1.72$  (m, 16H,  $\text{C}_6\text{H}_{11}$ ),  $1.86\text{--}1.97$  (m, 16H,  $\text{C}_6\text{H}_{11}$ ),  $3.10$  (m, 4H,  $\text{C}_6\text{H}_{11}$ ),  $3.68$  (s, 6H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C)  $\delta$  (ppm):  $-9.54$  ( $\text{OCH}_3$ ),  $10.31$  ( $\text{AlCH}_3$ ),  $25.26$ ,  $26.25$  ( $\text{C}_6\text{H}_{11}\text{NCCH}_3$ ),  $35.09$ ,  $35.43$ ,  $51.46$ ,  $54.55$  ( $\text{C}_6\text{H}_{11}$ ),  $170.95$  (NCN).

## 2.3. Synthesis of **2**, $[\{(\text{PhN})\text{MeC}(\text{NCy})\}\text{AlMe}(\mu\text{-OMe})_2]$

Compound **2** was isolated using the same procedures as described for compound **1**, except *N*-phenyl-*N'*-cyclohexylcarbodiimide was employed. Yield: 0.65 g, 74.9%. *Anal. Calc.* for  $\text{C}_{32}\text{H}_{52}\text{Al}_2\text{N}_4\text{O}_2$ : C, 66.78; H, 9.12; N, 9.48. Found: C, 66.59; H, 9.04; N, 9.63%.

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