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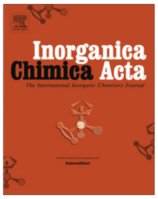

Research paper

Synthesis, characterization, and catalytic performance of aluminum and Tin(II) compounds supported by β-diketiminato ligands

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ABSTRACT

The four-coordinated bis(benzyl sulfide) complex $L^1Al(SCH_2Ph)_2$ (**1**) was synthesized in good yield by reacting one equivalent of L^1AlH_2 (L^1 = HC(CMeNAr)$_2$, Ar = 2,4,6-Me$_3$C$_6$H$_2$) with two equivalents of benzyl mercaptan. The reactions of L^2Li (L^2 = HC(CMeNAr)$_2$, Ar = 2-^{i}PrC$_6$H$_4$) with $SnCl_2$ and $AlCl_3$ in a molar ratio of 1:1 were carried out at room temperature, resulted in two new compounds, CH{(CH$_3$)CN-2-^{i}PrC$_6$H$_4$}$_2$SnCl (**2**) and CH{(CH$_3$)CN-2-^{i}PrC$_6$H$_4$}$_2$AlCl$_2$ (**3**). All compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, single crystal X-ray structural analysis and elemental analysis. The efficient catalytic performances of **1**–**3** for the hydroboration of organic compounds with carbonyl groups were investigated.

1. Introduction

Organoboranes are important synthetic intermediates in various organic chemical reactions. In recent years, boron-containing products have aroused increasing attention because of their ability to be converted into many functional groups [1]. The major synthetic routes of preparing organoboranes are hydroboration in the presence of metal catalysts. Compared with some toxic and expensive transition metals [2], main group compounds have got more and more applications on laboratory level for its low price and non-toxicity **[3]**. It has been reported that low-valent germanium(II) and tin(II) hydride compounds (DipNacnac)MH (DipNacnac = (DipNCMe)$_2$CH$^-$, Dip = C$_6$H$_3$Pr$^i_2$-2,6, M = Ge or Sn) have a remarkable catalytic effect on hydroboration of a series of unactivated aldehydes and ketones with HBpin [4]. The Lewis acidity and steric effect of the ligand around the metal center seems to play a vital role in the activation of carbonyl. Owing to this reactivity, bulky ligands with β-diketiminate substituents exhibit prominent performances for metal-mediated catalysis [5]. Furthermore, our group has demonstrated that functionalized LAlH$_2$ (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) types such as LAlH(OTf) can be applied to facilitate the hydroboration and hydrosilylation in high yield, which functions like a transition-metal catalyst [6].

Pioneering research stimulated us to think about the design of organometallics containing β-diketiminate ligands by conferring a higher positive charge to the metal center and stabilizing of electron-deficient functional groups [7]. Herein, we report on the synthesis of three new aluminum and tin (II) compounds supported by β-diketiminato ligands and their application in catalytic hydroboration of selected aldehydes and ketones.

2. Results and discussion

The reaction of L^1AlH_2 with benzyl mercaptan (Scheme 1) in a molar ratio of 1:2 resulted in the products $L^1Al(SCH_2Ph)_2$ (**1**). Compound **2** was prepared from the reaction of L^2H with *n*-BuLi and SnCl$_2$ in a molar ratio of 1:1, while compound **3** was prepared from L^2H with *n*-BuLi and AlCl$_3$ in a molar ratio of 1:1. Compound **1** and **3** were isolated after growing colorless crystals from a concentrated *n*-hexane solution and compound **2** from a concentrated toluene solution, respectively. All crystals are highly soluble in common organic solvents such as toluene, dichloromethane, and tetrahydrofuran, respectively.

Compounds **1**–**3** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy in CDCl$_3$ solution as well as by elemental analysis. In the ^{1}H NMR spectra, compound **1** shows the CH$_2$S-Ar resonances at δ 3.23 ppm in a 4:1 ratio to that of the γ-H proton at δ 5.1 ppm. The disappearance of the NH resonance (δ 12.14 ppm) of L^1 and (δ 12.85 ppm) of L^2, shows that the center metal is added to the ligand.

X-ray quality single crystals of **1** and **3** were obtained in hexane solution while **2** in toluene at low temperature. The molecular structures as well as the selected bond lengths and angles are shown in the captions of Figs. 1–3, respectively. The X-ray single-crystal structures **1**–**3** show that all compounds belong to

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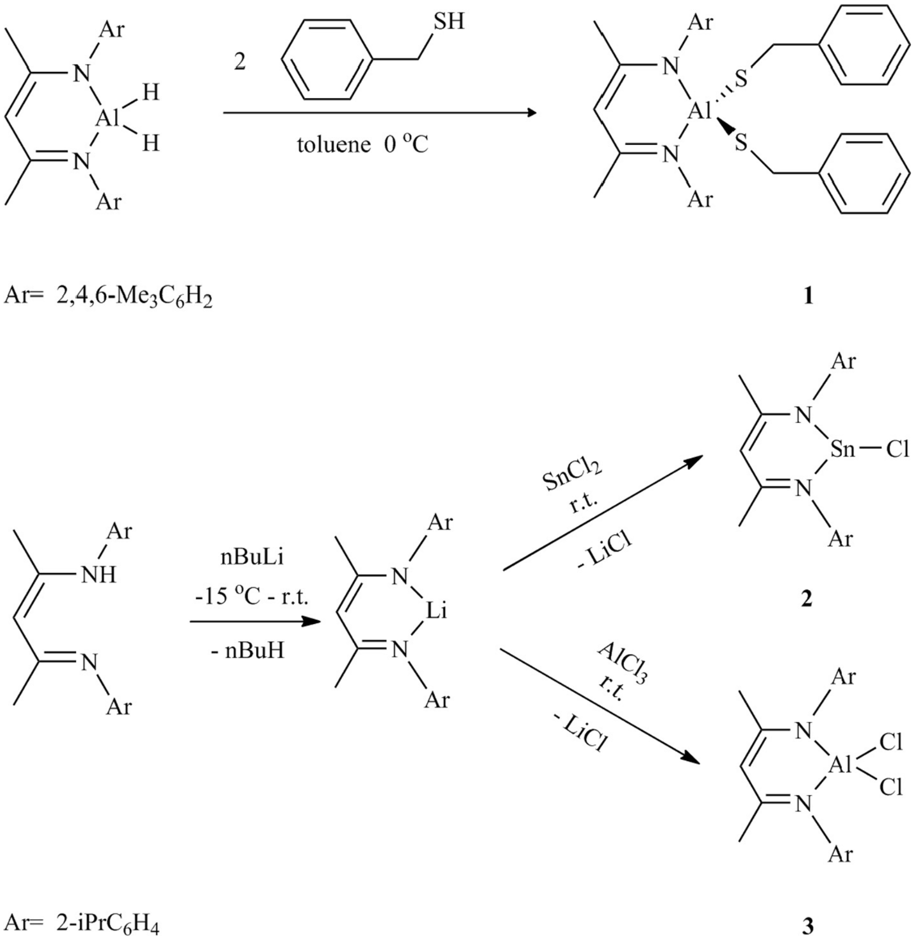

Scheme 1. Preparation of compounds **1**, **2**, and **3**.

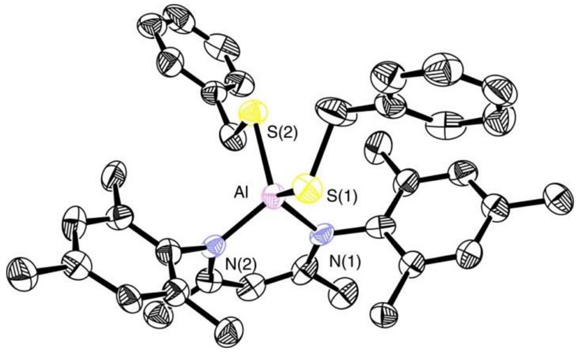

Fig. 1. Molecular structure of **1** in crystals. Thermal ellipsoids are drawn at 30% level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al–N(1) 1.901(8), Al–N(2) 1.881(8), Al–S(1), 2.209(4), Al–S(2) 2.241(4); N(2)–Al–N(1) 96.9(3), S(1)–Al–S(2) 110.57(14), N(1)–Al–S(1) 113.1(3), N(1)–Al–S(2) 111.1(3), N(2)–Al–S(1) 112.3(3), N(2)–Al–S(2) 112.3(2).

the monoclinic crystal system and exhibit a symmetric arrangement.

For the structure of **1**, the aluminum center exhibits a distorted tetrahedral geometry including two nitrogen atoms of the ligand and two sulfur atoms. The Al-S bond lengths (av. 2.225 Å) are quite close to those (av. 2.225 Å) in NacNacAl(SPh)$_2$ reported by Terry Chu and co-workers [8]. In compound **2**, the tin (II) atom has a pyramidal coordination sphere, which is surrounded by one chlorine and two nitrogen atoms. The bond angle of N(1)-Sn-N(2) (84.22(14)°) is smaller than that in (HC-(CMeNAr)$_2$)SnCl (Ar =

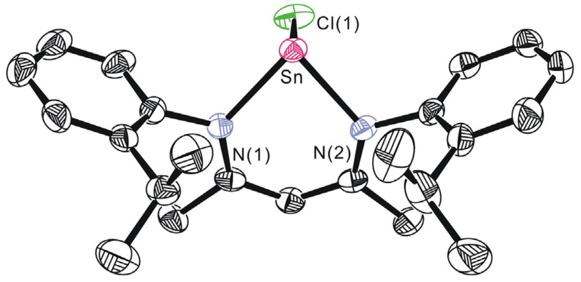

Fig. 2. Molecular structure of **2** in crystals. Thermal ellipsoids are drawn at 30% level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Sn–N(1) 2.173(4), Sn–N(2) 2.173(3), Sn–Cl(1) 2.4848(14), N(1)–Sn–N(2) 84.22(14), N(1)–Sn–Cl(1) 92.06(11), N(2)–Sn–Cl(1) 91.29(10).

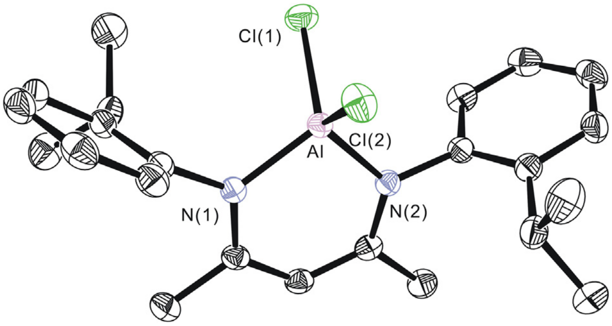

Fig. 3. Molecular structure of **3** in crystals. Thermal ellipsoids are drawn at 30% level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al–N(1) 1.8633(14), Al–Cl(1) 2.1290(7); N(1)–Al–N(1) 99.59(9), N(1)–Al–Cl(1) 113.54(4), Cl(1)–Al–Cl(2) 107.73(4).