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Synthesis of $[LAl(\mu-S)_2AlL]$ (L = HC(CMeNAr)₂, Ar = 2,6-Et₂C₆H₃) with the insertion of sulfur into the Al-H bonds of LAlH₂ and its application in catalysis

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Synthesis of $[LAl(\mu-S)_2AlL]$ (L = HC(CMeNAr)₂, Ar = 2,6-Et₂C₆H₃) with the insertion of sulfur into the Al-H bonds of LAlH₂ and its application in catalysis

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Fax: (+86) 10-68911032; E-mail: <u>maxiaoli@bit.edu.cn</u>. zhiyang@bit.edu.cn **ABSTRACT:** Two aluminum complexes [LAl(μ -S)₂AlL] (1) and [LAl(SeH)₂] (2) were synthesized in good yield by reacting one equivalent of LAlH₂ (L = HC(CMeNAr)₂, Ar = 2,6-Et₂C₆H₃) with one equivalent of S and with two equivalents of Se without any catalysts, respectively. Complexes 1 and 2 have been characterized by ¹H and ¹³C NMR, elemental analyses, and single crystal X-ray structural analysis. Furthermore, the good catalytic activity of 1 as bimetallic Lewis acid catalyst for the addition reaction of TMSCN to aldehydes and aldimine condensation reactions, respectively, were investigated.

Keywords : aluminum complexes, bimetallic Lewis acid catalyst, addition reaction, aldimine condensation

Introduction

The Lewis acid properties of aluminum compounds for the mediation of various organic transformations have a long-standing tradition. Among those compounds, inorganic aluminum reagents such as AlCl₃ are primarily used for their Lewis acid properties. Poor selectivity and control of reactivity often the major issues in using these compounds.^{1,2} While are organoaluminum compounds such as alanes, AlR₃, and their derivatives combine a Lewis acidic character with an intrinsic nucleophilicity, which provides them with additional reactivity towards organic substrates.³⁻⁶ The majority of organic aluminum compounds applied in organic reactions are bearing multidentate ligands containing nitrogen and oxygen as hard donor atoms.⁷ In contrast, chelating ligands incorporating soft donors, which are coordinated to the aluminum center and function as catalysts are scarce.⁸ Even though, recent reports have shown that the use of ancillary ligands with softer donors could affect the Lewis acidity of the metal center, with remarkable effects on the catalytic performance.⁹

The advances that have been made in the chemistry of multiple bonding between main group elements compounds over the past two decades have been remarkable¹⁰. Since the first unique monomeric $[L^{Dipp}Al(SeH)_2]^{11}$ and $[L^{Dipp}Al(SH)_2]^{12}$ compounds $(L^{Dipp} =$ N(Ar)C(Me)CHC(Me)N(Ar) (Ar = 2,6-*i*-Pr₂C₆H₃)₂)) were reported, more

and more organoaluminum chalcogenides have been synthesized.¹³ Furthermore, organic aluminum compounds responsible for polymerization reactions exhibited bimetallic cooperative effects that can lead to higher catalytic activity than the corresponding mononuclear ones.¹⁴ However, bisaluminum compounds with chelating ligands incorporating soft donors that act as moderate and stable Lewis acid catalysts have never been reported. Recently, we reported on an aluminum(III) hydride as a main group catalyst based on the principles of transition-metal catalysts.¹⁵ Considering the distinct reactivity of [L^{Dipp}AlH₂], it can be used for the activation of element-element bonds and reduction of various polar functional and unsaturated substrates.^{11,12,16} Inspired by these results, we set out to investigate on the bulky aluminum dihydride for the activation of nonpolar element-element bonds to form bis-aluminum species. Herein, we report on the synthesis and structural characterization of bis-aluminum compounds with soft donor properties, as well as their catalytic activity in the addition reaction of TMSCN to aldehydes and as Lewis acid catalyst in aldimine condensation reaction.

EXPERIMENTAL SECTION

General Information: Unless otherwise noted, all manipulations were performed using a vacuum line and standard Schlenk techniques with an atmosphere of nitrogen or using glove box techniques (typically oxygen and

moisture were controlled at less than 1 ppm). All solvents including C_6D_6 and CDCl₃ were refluxed over the appropriate drying agent and distilled prior to use. Commercially available chemicals were purchased from J&K and used as received. $LAlH_2^{15a}$ was prepared as described in the literature. Elemental analyses were performed by Analysis & Testing Center of Beijing Institute of Technology. NMR spectra were recorded on a Bruker AM 400 spectrometer. Infrared spectra of **2** were recorded on a Perkin Elmer spectrophotometer. Melting points were measured in sealed glass tubes.

Synthesis of [LAl(μ -S)₂AlL] (1). A solution of LAlH₂ (0.390 g, 1.0 mmol) in THF (10 mL) was added drop by drop to a suspension of sulfur (0.032 g, 1.0 mmol) in THF (10 mL) at room temperature. After the addition was complete, stirring of the reaction mixture was continued overnight. Then the solvent was removed in *vacuo*. The solid was extracted with toluene (10 mL), and the extract was stored at -30 °C for 2d to afford **1** as pale yellow crystals. An additional crop of **1** was obtained from the mother liquor. Total yield: 0.359 g (85%), mp 175 °C (decomp). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.15-7.02 (m, 12 H, Ar–H), 4.89 (s, 2 H, γ –H), 3.03 (sept, ³*J*_{H–H} = 6.8 Hz, 8 H, C*H*₂Me), 2.57 (sept, ³*J*_{H–H} = 6.8 Hz, 8 H, C*H*₂Me), 1.44 (s, 12 H, *Me*), 1.22 (t, ³*J*_{H–H} = 6.8 Hz, 24 H, CH₂Me); ¹³C NMR (100.61 MHz, C₆D₆, 25 °C): δ = 170.85 (*C*N), 140.27, 139.14, 127.06, 126.17 (*C* of Ar),

97.75 (*γ*-*C*H), 24.52 (*C*H₂Me), 22.72, (*C*H₂Me) 13.87 (*Me*). C₅₀H₆₈Al₂N₄S₂

(843.16): calcd. C 71.39, H 7.91, N 6.66; found C 70.69, H 7.35, N 6.33.

Synthesis of [LAI(SeH)₂] (2). A solution of LAIH₂ (0.390 g, 1.0 mmol) in THF (10 mL) was added drop by drop to a suspension of selenium (0.156 g, 2.0 mmol) in THF (10 mL) at room temperature. After the addition was complete, stirring of the reaction mixture was continued overnight, and a light brown solution formed with trace amount of unchanged selenium. After filtration, the solvent was removed and the residue extracted with toluene (10 mL). The extract was stored at -30° C for 2 d to give yellow crystals of 2 (0.284, yield 52%), mp 223 °C (decomp). ¹H NMR (400 MHz, C₆D₆, 25 °C): $\delta = 7.15-7.09$ (m, 6 H, Ar–H), 4.91 (s, 1 H, γ –H), 3.05 (sept, ${}^{3}J_{H-H} = 6.8$ Hz, 4 H, CH_2 Me), 2.58 (sept, ${}^{3}J_{H-H}$ = 6.8 Hz,4 H, CH_2 Me), 1.44 (s, 6 H, Me), 1.21 (t, ${}^{3}J_{H-H} = 6.8$ Hz, 12 H, CH₂Me), -2.82 (s, 2 H, SeH); ${}^{13}C$ NMR $(100.61 \text{ MHz}, C_6D_6, 25^{\circ}\text{C}): \delta = 170.85 (CN), 140.28, 139.06, 127.15,$ 126.28 (C of Ar), 98.15 (y-CH), 24.92 (CH₂Me), 22.82 (CH₂Me), 13.98 (Me). C₂₅H₃₅AlN₂Se₂ (843.16): calcd. C 54.75, H 6.43, N 5.11; found C 53.86, H 6.70, N 5.74.

RESULTS AND DISCUSSION

LAlH₂ reacts smoothly with one equivalent of element sulfur at room temperature to afford [LAl(μ -S)₂AlL] (1) in high yield (Scheme 1). It is noteworthy that 1 is formed even when two equivalents of sulfur were used.

 $[LAl(\mu-Se)_2AlL]$ could not be obtained by using this protocol. The direct reaction of $LAlH_2$ with elemental Se led to $[LAl(SeH)_2]$ (2) (Scheme 1). The conversion of LAIH₂ to 2 demonstrates the umpolung from the hydridic to the protonic form of the hydrogen atoms. This assumption well explained our experimental results that compound 2 was always obtained as the product formed at room temperature, regardless of the amount of the selenium used. Note, this transformation proceeded in the absence of any promoter. Inoue and co-workers reported that dimeric imidazolin-2-iminato aluminum dihydride could be used for the activation of nonpolar element–element bonds without any catalyst.¹⁷ The crystals of **1** and **2** are soluble common organic slightly in solvents such as toluene, dichloromethane, and tetrahydrofuran, respectively. Furthermore, 1 is unexpectedly thermal stable no changes were observed after heating at 80 °C for 4 h, which is explained by the steric and electronic stabilizing properties of the bulky β -diketiminato ligand. Compounds 1 and 2 were characterized by analytical, spectroscopic, and single-crystal X-ray diffraction studies. The ¹H NMR spectrum of **2** shows a high-field singlet at $\delta = -2.82$ ppm, which was assigned to SeH.¹¹ The absorption of the Se-H stretching frequencies could not be observed in the IR spectrum. The molecular geometries of 1 and 2 were determined by X-ray crystallography. The pale yellow crystals of 1 and yellow crystals of 2 were obtained by slow cooling of their saturated

solutions in toluene, respectively. The molecular structures of **1** and **2** are shown in Figures 1 and 2. The four-membered Al₂S₂ ring is essentially planar, and the Al–S bond lengths are similar (2.2212(7) and 2.2224(8) Å). They are a little shorter with respect to those in the literature reported (2.237 and 2.245 Å).¹⁷ The S(1)–Al(1)–S(2) angle falls within the range of comparable compounds (95.9° to 101.9°).^{18,19,20} Unfortunately, the quality of crystals of **2** did not allow the location of the hydrogen atoms on the selenium atoms. The Al–Se bond lengths (2.349 and 2.376 Å) are nearly similar , when compared with those of the dimeric compound: [{[N(SiMe₃)C(Ph)C(SiMe₃)₂]AlSe}₂] (av 2.350 Å).²¹ The Al atom deviates slightly from the NCCCN plane of the ligand.

Recently our group reported on aluminum compounds with chelating ligands incorporating soft donors that exhibited good catalytic activity in addition reactions of aldehydes with trimethylsilyl cyanide (TMSCN). Herein, we used the bis-aluminum compound [LAl(μ -S)₂AlL] (1) as a bimetallic catalyst. To investigate the catalytic properties of compound 1, addition reactions were performed by adding TMSCN to aldehydes. As shown in Scheme 2, the reaction of TMSCN with benzaldehyde gives an almost quantitative yield of product within 4 h with 2 mol% loading of the catalyst at ambient temperature in CDCl₃. Excellent yield was also obtained when an aldehyde with electron-donating aromatic group was used (Scheme

2, product 2). Phenylacrolein and *o*-fluorobenzaldehyde were studied to show the electronic effect on the activation by using catalyst loadings of 2 mol% (Scheme 2, products 3 and 4). Under the same conditions, the reaction with aliphatic aldehyde exhibited lower yield than those with aromatic aldehydes (Scheme 2, product 5). The analogous reactions with substrates including heterocycles were also found to be less efficient than those with aromatic aldehydes (Scheme 2, products 6 and 7). The steric effect of the bulky groups on the Al center decrease the catalytic activity.⁹ However, the bimetallic cooperative effect may induce the high activity.²²

Imines are highly useful precursors for the synthesis of chiral amines, secondary amines, and important biological molecules.²³ Traditional imines are synthesized using a primary amine and a carbonyl compound that generally involves heating to reflux for an extended period of time to shift the equilibrium to the product side. This protocol often requires the use of materials such as molecular sieves (MS), titanium tetrachloride, CuSO₄, zinc dichloride, and alumina.²⁴ However, bimetallic compounds as moderate and stable Lewis acid catalysts used in this type of reaction have never been reported to the best of our knowledge. We found that **1** is an effective catalyst for aldimine condensation reaction. The reactions were carried out in CDCl₃ with 5 mol% loading of the catalyst at ambient temperature. The results are shown in Scheme 3 and indicate that these reactions give an

almost quantitative yield of product within 2 h. It is generally considered that using the catalyst in the reaction usually undergoes a preliminary coordinative interaction between the catalytic metal center and the carbonyl oxygen atom of the substrate followed by a nucleophilic attack.

CONCLUSION

In summary, we have prepared and structurally characterized two new thermally stable aluminum chalcogenides $[LAl(\mu-S)_2AlL]$ and $[LAl(SeH)_2]$. This work shows new strategies for the activation of element–element bonds by aluminum dihydride without any additional catalyst. Bis-aluminum compound **1** acts as a good bimetallic Lewis acid catalyst in addition reaction of TMSCN to aldehydes as well as in the aldimine condensation reactions.

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Scheme 2 Addition reactions of TMSCN to aldehyde catalyzed by 1^a



^aAldehyde, 1 mmol; TMSCN, 1 mmol; **1**, 0.02 mmol; in CDCl₃, at ambient temperature. Yield was obtained according to thin-layer chromatographic (TLC) and ¹H NMR spectral analysis.



Scheme 3 Aldimine condensation reaction catalyzed by 1^a

^aAmine, 1 mmol; Aldehyde, 1 mmol; **1**, 0.05 mmol; in CDCl₃, at ambient temperature. Yield was obtained according to thin-layer chromatographic (TLC) and ¹H NMR spectral analysis.



Fig. 1 Molecular structure of $LAl(\mu-S)_2AlL(1)$; hydrogen atoms and solvent molecules are omitted for clarity; selected bond lengths [Å] and angles [°]: Al(1)-S(1) 2.2212(7), Al(1)-S(2) 2.2224(8), S(1)-Al(1)-S(2) 99.60(3), Al(1)-S(1)-Al(2) 88.40(3), N(1)-Al(1)-N(2) 95.95(6)



Fig. 2 Molecular structure of $LAl(SeH)_2$ (2); hydrogen atoms and solvent molecules are omitted for clarity; selected bond lengths [Å] and angles [°]: Al(1)-Se(1) 2.349 (3), Al(1)-Se(2) 2.376 (2), Se(1)-Al(1)-Se(2) 105.6 (5), N(1)-Al(1)-N(2) 97.75(6)

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TOC

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[LAl(μ -S)₂AlL] (1) and [LAl(SeH)₂] (2) were synthesized and fully characterized. [LAl(μ -S)₂AlL] (1) as a bimetallic Lewis acid catalyst for addition reaction of TMSCN to aldehydes and aldimine condensation reaction were reported.

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Two aluminum complexes [LAl(μ -S)₂AlL] (1) and [LAl(SeH)₂] (2) were synthesized in good yield by reacting one equivalent of LAlH₂ (L = HC(CMeNAr)₂, Ar = 2,6-Et₂C₆H₃) with one equivalent of S and with two equivalents of Se without any catalysts, respectively. Complexes 1 and 2 have been characterized by ¹H and ¹³C NMR, elemental analyses, and single crystal X-ray structural analysis. Furthermore, the good catalytic activity of 1 as bimetallic Lewis acid catalyst for the addition reaction of TMSCN to aldehydes and aldimine condensation reactions, respectively, were investigated.