ORGANOMETALLICS

Note

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Reactivity Studies of $LAlH_2$ (L = $HC(CMeNAr)_2$, Ar = 2,6-*i*$Pr_2C_6H_3$) with 2-Aminobenzenethiol, 2-Aminophenol, and 1,4-Dithiane-2,5-diol

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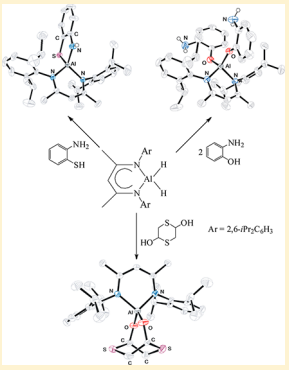
Supporting Information

ABSTRACT: The reaction of $LAlH_2$ (L = $HC(CMeNAr)_2$, Ar = 2,6-*i*$Pr_2C_6H_3$) (**1**) with 2-aminobenzenethiol, 2-aminophenol, and 1,4-dithiane-2,5-diol resulted in the compounds $LAl[(\mu\text{-}N)(\mu\text{-}S)](o\text{-}C_6H_4)$ (**2**), $LAl[(\mu\text{-}O)(o\text{-}C_6H_4)(NH_2)]_2$ (**3**), and $LAl(\mu\text{-}O)_2(p\text{-dithiane})$ (**4**), respectively. Compound **2** features an organic−inorganic hybrid containing an $NAlSC_2$ five-membered ring, while compound **3** exhibits a C−O−Al−O−C chain structure. Compound **4** forms a basket-like molecule with the C_4S_2 unit as the bottom part and O_2Al as the handle. Complexes **2**, **3**, and **4** were characterized by ^1H NMR, elemental analysis, and single-crystal X-ray diffraction studies.



INTRODUCTION

Owing to the strong Lewis acidity and inexpensiveness, the aluminum complexes attract considerable attention for organic synthesis[1] and polymerization.[2] Aluminum compounds containing Al−S−C moieties have not been well studied when compared with those containing Al−O−C cores. This is mainly due to the thermodynamic stability of the latter species. Aluminum sulfides with the $[AlS]_n$ core are either planar (n = 2), cubic (n = 4), or drum-like (n = 6) or possess more complex structures with an Al:S molar ratio different from that of 1:1.[3] In 2003 Jancik et al. reported on the preparation of the unique monomeric aluminum moiety comprising two terminal S−H groups.[4] Henceforth, more and more aluminum compounds containing the Al−S−C core were reported.[5] It is noteworthy to mention that aluminum nitrides possessing the Al−N−C core are associated with far-ranging applications such as Al−N-based semiconductors and Al−N-based ceramics.[6] However, compounds containing the S−Al−N moiety are very rare.[7−9] Thus, we became interested in preparing organoaluminum heterocycles containing both the Al−S−C core and the Al−N−C skeleton. Meanwhile, aluminoxane exhibits excellent initiator properties for the ring-opening polymerization of lactone.[10]

Main group metal hydrides supported by organic ligands are important in organometallic chemistry. Previously,[11−15] we reported on a series of organoaluminum heterocycles by the reaction of organic aluminum precursors with organic compounds containing reactive groups. Due to the converse polarity of the hydrides in **1** and the protons in C−XH (X = S, N, O), these systems facilitate reactions under hydrogen elimination. Herein, we report on three structures bearing the Al−X−C moiety by the reaction of **1** with 2-aminobenzenethiol, 2-aminophenol, and 1,4-dithiane-2,5-diol, respectively.

RESULTS AND DISCUSSION

The reaction of **1** with 2-aminobenzenethiol, 2-aminophenol, and 1,4-dithiane-2,5-diol (Scheme 1) in a molar ratio of 1:1, 1:2, and 1:1 resulted in products $LAl[(\mu\text{-}N)(\mu\text{-}S)](o\text{-}C_6H_4)$ (**2**), $LAl[(\mu\text{-}O)(o\text{-}C_6H_4)(NH_2)]_2$ (**3**), and $LAl(\mu\text{-}O)_2(p\text{-dithiane})$ (**4**), respectively. During the course of these reactions hydrogen gas evolution was observed, which proceeds under the elimination of 2 equiv of hydrogen. Compound **2** was crystallized from THF, **3** from toluene, and **4** from *n*-hexane. All products are soluble in toluene, benzene, THF, and trichloromethane, respectively.

Compounds **2**, **3**, and **4** were characterized by ^1H NMR investigation in $CDCl_3$ and by elemental analysis. The ^1H NMR spectra of **3** and **4** exhibit one set of resonances for the aryl group on sulfur, nitrogen, carbon, and the ligand, indicating symmetric molecules. The IR spectrum of compound **2** shows a strong absorption band at $\overline{\nu}$ 3309 cm^{-1}, which is quite close to that ($\overline{\nu}$ 3398 and $\overline{\nu}$ 3220 cm^{-1}) reported in refs 8 and 9 with the proton bound to nitrogen.

Compound **2** crystallizes in the orthorhombic space group *Cmca*, **3** in the monoclinic $P2_1/c$, and **4** in the orthorhombic *Pbca*. The molecular structures are shown in Figures 1, 2, and 3, respectively. For the structure of **2**, two carbon atoms, one aluminum atom, one nitrogen atom, and one sulfur atom form a five-membered planar C_2AlNS ring. The central aluminum

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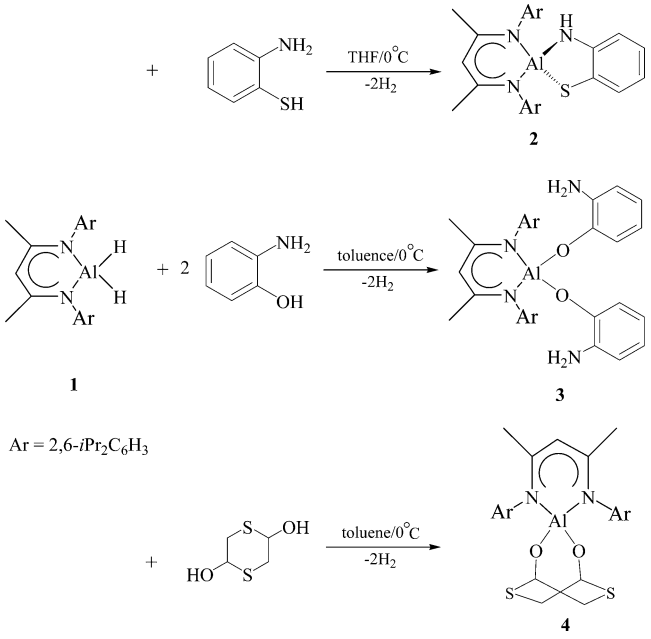
Scheme 1. Preparation of Compounds 2, 3, and 4



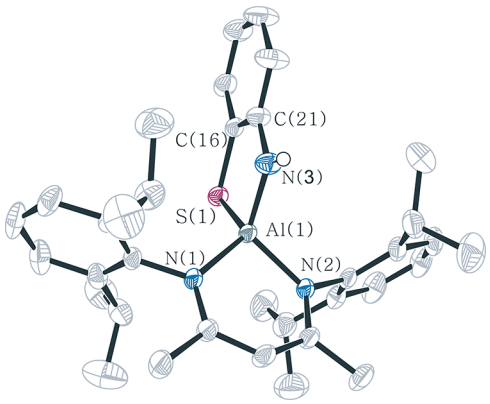


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% level. The solvent molecule and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)–N(1) 1.877(2), Al(1)–N(2) 1.877(2), Al(1)–N(3) 1.799(4), Al(1)–S(1) 2.2274(15), N(3)–C(21) 1.387(5), S(1)–C(16) 1.778(4), C(16)–C(21) 1.406(6); N(1)–Al(1)–N(2) 97.49(14), N(3)–Al(1)–N(1) 116.83(10), N(3)–Al(1)–N(2) 116.83(10), N(1)–Al(1)–S(1) 116.88(8), N(2)–Al(1)–S(1) 116.88(8), C(16)–S(1)–Al(1) 92.21(14), N(3)–Al(1)–S(1) 93.52(12), C(21)–C(16)–S(1) 118.5(3), C(21)–N(3)–Al(1) 116.8(3), N(3)–C(21)–C(16) 119.0(4).

atom is located in the spirocyclic center of the fused six-membered ring (C_3N_2Al) and the five-membered ring (C_2AlNS). The sum of the inner angles of the C_2AlO_2 five-membered ring in **2** is 539.99°, which is quite close to the ideal planar ring of 540°. Compound **3** exhibits a C–O–Al–O–C framework with the unreacted protons on the ortho-nitrogen atoms. The Al(1)–O(1) bond length of **3** (av 1.716 Å) is slightly longer when compared with the normal Al–OH bond distance (av 1.705 Å) in $LAl(OH)_2$.[16] It is interesting that the structure of **3** is quite different from that of **2**. This is independent of the precursor ratio of 1:1 or 1:2 (**1** to 2-aminobenzenethiol or 2-aminophenol). For this different behavior we assume that the thermodynamic Al–O bond

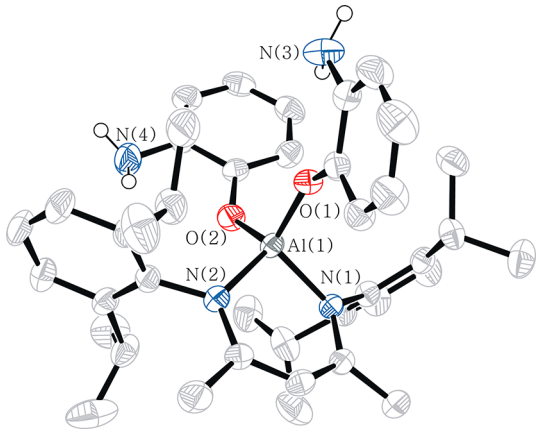


Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms attached to the benzene nitrogens are shown. Selected bond distances (Å) and angles (deg): Al(1)–N(1) 1.868(4), Al(1)–N(2) 1.878(4), Al(1)–O(1) 1.716(3), Al(1)–O(2) 1.705(3); O(1)–Al(1)–N(1) 111.26(18), O(1)–Al(1)–N(2) 114.93(18), O(2)–Al(1)–O(1) 109.80(18), O(2)–Al(1)–N(1) 113.18(18), O(2)–Al(1)–N(2) 108.80(18), N(1)–Al(1)–N(2) 98.53(17).

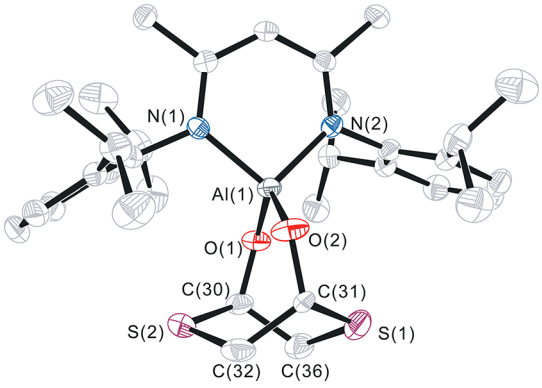


Figure 3. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% level. The solvent molecule and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)–N(1) 1.888(2), Al(1)–N(2) 1.892(2), Al(1)–O(1) 1.724(2), Al(1)–O(2) 1.730(2), O(1)–C(30) 1.375(8), O(2)–C(31) 1.405(17), C(31)–S(1) 1.853(15), C(36)–S(1) 1.811(6), C(30)–S(2) 1.816(7), C(32)–S(2) 1.822(7), C(32)–C(31) 1.573(16), C(30)–C(36) 1.542(8); O(1)–Al(1)–N(1) 111.40(10), O(2)–Al(1)–N(2) 112.74(11), O(1)–Al(1)–O(2) 111.67(10), N(1)–Al(1)–N(2), 96.74(10), C(30)–O(1)–Al(1) 127.6(3), C(31)–O(2)–Al(1) 125.2(8), O(1)–C(30)–C(36) 110.2(5), O(1)–C(30)–S(2) 112.9(5), C(36)–C(30)–S(2) 110.6(5), C(31)–C(32)–S(2) 115.4(8), O(2)–C(31)–C(32) 14.8(10), O(2)–C(31)–S(1) 110.5(10), C(32)–C(31)–S(1) 106.2(10), C(30)–C(36)–S(1) 113.4(4), C(36)–S(1)–C(31) 104.0(6), C(30)–S(2)–C(32) 101.2(3).

energy in **3** favors the formation of the two Al–O bonds, while in **2** the more flexible Al–S–C bond angle of 92.21(14)° prefers the formation of the five-membered $AlNC_2S$ ring. The formation of $LAl[(\mu\text{-}S)(o\text{-}C_6H_4)(NH_2)]_2$ instead of **2** was not observed. For comparing the rigid compounds **2** and **3** the product with the more flexible 1,4-dithiane-2,5-diol precursor was prepared. Compound **4** contains the organic–inorganic hybrid with the AlO_2C_3S seven-membered rings, which show a structure similar to a basket with the O–Al–O as the handle and C_4S_2 as the bottom. During the reaction the 2,5-dithiazole

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six-membered ring turned from the chair conformation to a boat configuration under elimination of hydrogen and formation of two Al−O bonds. The Al−O bond length in **4** (av 1.727 Å) is longer when compared with that of $LAl(OH)_2$ (av 1.705 Å). This might be due to the electron-donating ligand bound at the aluminum.

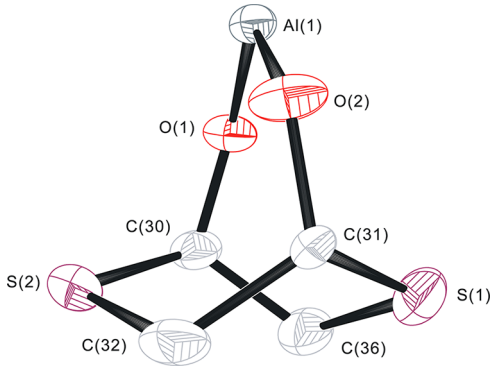

Figure 4. Core molecular structure of **4**. Thermal ellipsoids are drawn at the 50% level. The solvent molecule and the hydrogen atoms are omitted for clarity. The molecular structure of the latter shows as the lower part a basket-like arrangement.

SUMMARY

Three compounds containing the Al−X−C (X = S, N, O) structural motif have been prepared by the facile reaction of aluminum hydride with 2-aminobenzenethiol, 2-aminophenol, and 1,4-dithiane-2,5-diol, respectively. These compounds have novel aluminum-containing acyclic or cyclic building blocks with O, S, and N elements. Presently we are investigating their catalytic properties for ring-opening polymerization of cyclic esters and *rac*-lactide.

ASSOCIATED CONTENT

Supporting Information

Table, cif files for compounds **2**, **3**, and **4**, and full experimental procedures are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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