

The First Structurally Characterized Aluminum Compound with Two SH Groups: $[\text{LAl}(\text{SH})_2]$ ($\text{L} = \text{N}(\text{Ar})\text{C}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})$, $\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) and the Catalytic Properties of the Sulfur $\text{P}(\text{NMe}_2)_3$ System

Vojtech Jancik, Ying Peng, Herbert W. Roesky,* Jiyang Li, Dante Neculai, Ana M. Neculai, and Regine Herbst-Irmer

Institute of Inorganic Chemistry, University of Goettingen, Tammannstrasse 4, D-37077 Goettingen, Germany

Received October 3, 2002; E-mail: hroesky@gwdg.de

Organoaluminum chalcogenides have attracted great attention in recent years as important precursors in chemical vapor deposition (CVD) and catalysts.¹ Our success in preparing the unique monomeric $[\text{LAl}(\text{SeH})_2]$, where L is the β -diketiminato ligand $\text{N}(\text{Ar})\text{C}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$)² led us to explore new species of this kind including sulfur analogues. In fact, aluminum hydrides form aluminum sulfides with S_8 , H_2S , or $\text{S}(\text{SiMe}_3)_2$, that are either dimeric, tetrameric, or hexameric in the solid state in which sulfur acts as a μ or μ_3 ligand.³ Nonetheless, there are no reports on organoaluminum compounds with Al–SH bonds. Only few examples of structurally known species are those of transition-metal complexes (Pd, Pt, Ru, Rh, Re, Cr, Fe, Ni, Ti, and Zr) containing two terminal hydrogen sulfide groups.⁴ Among the main group metals, only Ge has been reported to yield the stable $(\text{C}_6\text{H}_{11})_3\text{GeSH}$ derivative,⁵ while Ga forms the dimeric $[\text{t-Bu}_2\text{Ga}(\mu\text{-SH})_2]$.⁶

Thus, LAlH_2 (**1**), prepared from LH and $\text{AlH}_3 \cdot \text{NMe}_3$,² reacted with elemental sulfur to give a mixture of several products. However, a small amount of $[\text{LAl}(\text{SH})_2]$ (**2**) formed after a reaction time of 72 h at ambient temperature. Addition of a small amount of $\text{P}(\text{NMe}_2)_3$ significantly increased the reaction rate. After 5 h, the reaction was complete, and the yield of **2** increased to 90% (Scheme 1).⁷ Furthermore, **2** was unexpectedly thermal stable—no changes were observable after 3 h of heating at 80 °C. This can be explained by the steric and electronic stabilizing properties of the bulky β -diketiminato ligand.

Compound **2** was characterized by analytical, spectroscopic and single-crystal X-ray diffraction studies. The ^1H NMR spectrum of **2** showed a high-field singlet (δ –0.88 ppm) which can be, by comparison with the selenium analogue, assigned to the SH protons. The IR spectrum exhibited a weak peak at 2549 cm^{-1} that is comparable with the stretching bands of S–H in other metal–SH bonded complexes (2520–2596 cm^{-1}),^{4c–e,g,h} but it is significantly lower than the literature data for H_2S (2615 cm^{-1}).⁸ The mass spectrum gave the molecular ion peak at $m/e = 510$.

The unambiguous molecular geometry of **2** was determined by X-ray crystallography. The pale yellow crystals of **2** were obtained by slow cooling of its saturated solution in toluene. The structure of **2** is shown in Figure 1.

Compound **2** is isostructural to the Se analogue. Taking the difference in covalent radii (0.14 Å)⁹ into account, the Al–S bonds (2.223 and 2.217 Å) are comparable with the Al–Se bonds (2.331 and 2.340 Å). Furthermore, the angle S–Al–S (105.4°) is very similar to the Se–Al–Se angle (103.7°).² The Al–S bond distances are also comparable with those of bridging aluminum-(μ -S)-sulfides, and the S–Al–S angle is in the range of those reported in the literature.^{3a,c–f} The S–H bond (1.2 Å) falls in the range (0.99–1.40 Å) of those for terminal S–H groups in other metal complexes.^{4d–f,5} SCF/3-21G* calculations for monomeric H–S–

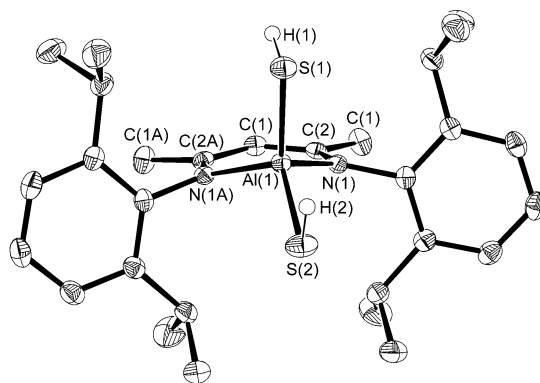
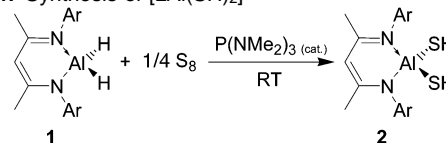


Figure 1. Molecular structure of **2**. Hydrogen atoms with the exception of the protons of the SH units, are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al(1)–N(1) 1.891(1), Al(1)–S(1) 2.223(1), Al(1)–S(2) 2.217(1), S(1)–H(1) 1.20(2), S(2)–H(2) 1.21(3); N(1)–Al(1)–N(1A) 97.3(1), N(1)–Al(1)–S(1) 114.3(1), N(1)–Al(1)–S(2) 112.9(1), S(1)–Al(1)–S(2) 105.4(1), Al(1)–S(1)–H(1) 97(1), Al(1)–S(2)–H(2) 91(2).

Scheme 1. Synthesis of $[\text{LAl}(\text{SH})_2]$



Al=S give the values for Al–S(H) (2.160 Å), S–H (1.33 Å), and Al–S–H (96.0°), respectively.¹⁰ The latter angle is almost similar to those in **2** (97 and 91°).

To investigate the role of phosphine in the reaction, the ^1H and ^{31}P NMR spectroscopy was periodically monitored. From the ^1H NMR kinetic studies, it is evident that the reaction proceeds via an unstable reactive intermediate $[\text{LAl}(\text{H})\text{SH}]$ to completion (Figure 2).

The ^{31}P NMR spectrum showed that all of the phosphine is immediately oxidized to $\text{SP}(\text{NMe}_2)_3$ (^{31}P NMR δ 82.4 ppm; literature¹² 81.5 ppm), indicating its role as a catalyst in the reaction. This hypothesis was confirmed by carrying out another experiment directly with $\text{SP}(\text{NMe}_2)_3$ as a catalyst, instead of $\text{P}(\text{NMe}_2)_3$, and conversion of **1** to **2** was observed. However, no reaction between **1** and $\text{SP}(\text{NMe}_2)_3$ occurred when the components are used in a molar ratio of 1:2 without adding additional sulfur. Therefore, we believe that $\text{SP}(\text{NMe}_2)_3$ reacts in the first step by a [2 + 1] cycloaddition with sulfur to form the reactive intermediate $(\text{S}_2)\text{P}(\text{NMe}_2)_3$. Formation of such a species is also favored from theoretical calculations for the model compound SPH_3 using the RHF/3-21 G* method, where ΔE is –183.0 kJ/mol for the reaction of SPH_3 and S to $(\text{S}_2)\text{-PH}_3$. It is most likely that $(\text{S}_2)\text{P}(\text{NMe}_2)_3$ forms a complex with **2** by opening the S–S bond and, consequently, inserts into one of the Al–H bonds to yield $[\text{LAl}(\text{H})\text{-S-P}(\text{SH})(\text{NMe}_2)_3]$ as an inter-

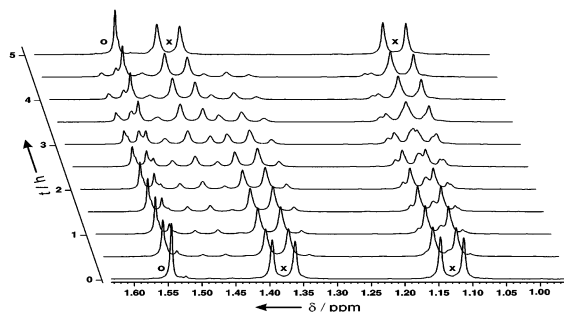
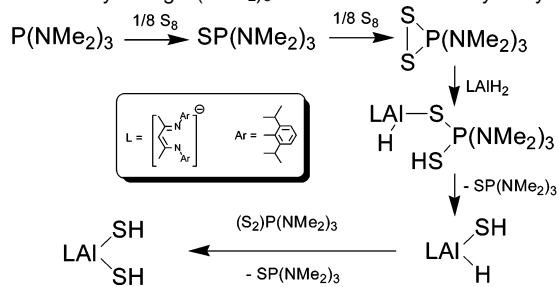


Figure 2. ^1H NMR kinetic study of the conversion of **1** to $[\text{Al}(\text{SH})_2]$ (**2**). Resonances between δ 1.5 and 1.55 ppm are assigned to the backbone methyl groups (O), and the doublets belong to the anisotropic methyl groups of the *i*-Pr moieties (X).

Scheme 2. Proposed Mechanism for Insertion of Sulfur into the Al–H Bonds by Using $\text{P}(\text{NMe}_2)_3$ and Sulfur as a Catalytic System



mediate. In the latter step, an “umpolung” of the hydridic to the protonic form of the hydrogen atom takes place. Finally, a proton transfer occurs from one sulfur atom to another, and thus the catalyst is regenerated (Scheme 2).

To sum up, this work constitutes the first report on the synthesis and structural characterization of species containing Al–SH units of which we are aware. This work could be developed into new strategies for the synthesis of mixed metal organometallics, due to the latent acidic nature of the SH protons, and preparation of aluminum sulfide clusters. Since $\text{SP}(\text{NMe}_2)_3$ was found to be an excellent catalyst for the insertion of sulfur into Al–H bonds, further investigations of this catalyst on insertion reactions of sulfur into metal–hydrogen bonds, instead of the reaction with toxic H_2S , is therefore warranted. Such studies are currently underway in our laboratories.

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Supporting Information Available: Full experimental data for compound **2** (PDF), and details of the X-ray structure determination of **2** (CIF). This material is available free of charge via Internet at <http://pubs.acs.org>.

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- (7) Toluene (15 mL) was added to a mixture of **1** (1.063 g, 2.230 mmol) and sulfur (0.147 g, 4.572 mmol), and after complete dissolution of the sulfur, $\text{P}(\text{NMe}_2)_3$ (0.03 mL, 0.02 mmol) was added. The reaction mixture was stirred for an additional 5 h, concentrated to ~ 3 mL, and stored overnight at -32°C . The resulting pale yellow crystals of **2** were filtered off, washed with cold toluene (1 mL), and dried in vacuo. Yield 1.09 g (90%); mp 218°C dec; ^1H NMR (benzene- d_6 , 200.131 MHz): δ 7.13–7.11 (m, 6H; Ar-H), 4.88 (s, 1H; γ -H), 3.47 (sept, 4H, $^3J_{\text{H-H}} = 6.8$ Hz; CHMe_2), 1.51 (s, 6H; Me), 1.44 (d, 12H, $^3J_{\text{H-H}} = 6.7$ Hz; CHMe_2), 1.10 (d, 12H, $^3J_{\text{H-H}} = 6.8$ Hz; CHMe_2), -0.88 (s, 2H; SH). ^{13}C NMR (benzene- d_6 , 50.325 MHz): δ 171.43 (CN), 144.44, 138.74, 127.51, 124.54 (Ar), 98.70 (γ -C), 28.59 (CHMe_2), 25.49 (CHMe_2), 24.69 (CHMe_2), 23.96 (Me).
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