

A Seven-Membered Aluminum Sulfur Allenyl Heterocycle Arising from the Conversion of an Aluminacyclopropene with CS₂

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There is a widespread interest in main group heterocyclic compounds due to their applications in pharmaceutical, agrochemical, and material science.¹ In recent years, the number of group 13 metal heterocycles has increased. Within the heterocycles, those containing multiple bonds have shown interesting structural features and properties. MⁿN₂C₂ (M = Al, Ga, In, *n* = 2; M = Ga, *n* = 1, 3)^{2,3} and MC₃N₂ (M = Al, Ga)⁴ heterocycles with C=C or C=N double bonds exhibit high electron density. The three-membered AlC₂ ring with a C=C bond shows a highly strained structure and good reactivity.⁵ Nonetheless, such species are rare, and the heteroatoms within the cycle are limited to C, N, and O elements due to the lack of appropriate synthetic routes. Herein we report on a seven-membered Al₂C₃S₂ heterocycle bearing a C=C=C allenyl group prepared from the reaction of an aluminacyclopropene, LAl[η²-C₂(SiMe₃)₂] (**1**, L = HC(CMeNAr)₂, Ar = 2,6-*i*Pr₂-C₆H₃)^{5b} with carbon disulfide. Interestingly, the unusual formation of the allenyl group, to the best of our knowledge, is hitherto unknown in organoaluminum chemistry.

The addition of neat carbon disulfide to the solution of **1** in toluene was carried out at -78 °C. In the course of warming the solution to room temperature, the color changed from red-black to green, to yellow green, and finally to yellow. Additional stirring for 12 h resulted in the formation of **2**.

The initial reaction of **1** with CS₂ closely resembles that of **1** with CO₂,^{5b} resulting in the generation of the five-membered heterocycle LAl[SC(S)C₂(SiMe₃)₂] (**A**). Obviously, **A** further interacts with a second molecule of **1** at the donor exocyclic S atom in **A** and the acceptor Al center in **1** to give intermediate **B**. The fact that use of either 1 equiv or an excess of CS₂ led to isolation of only product **2** indicates a stronger competitive reaction of **A** with **1** than with CS₂. **B** reacts further under elimination of one molecule of Me₃SiCCSiMe₃ due to the weak Al-η²-C_{alkyne} bonding (the bond dissociation energy of Al-η²-C₂ is only 95.8 kJ/mol and therefore much less than that of Al-C_{methyl} in AlMe₃⁶ (*D*_{average}, 281.4 kJ/mol; see Experimental Section II.1). Free Me₃SiCCSiMe₃ was detected in the ¹H NMR kinetic study. An easy migration of one Me₃Si group⁷ and rearrangement of C=S_{exo} and μ-S-C bonds led to the unique formation of the thioallenyl functional group and the final product **2**. A proposed mechanism for the formation of **2** is given in Scheme 1. A parallel investigation of **1** with S₈ resulted in the formation of a dimer [LAlS]₂ (see Experimental Section I.3). Evidently, the bulky β-diketiminato ligand with the steric and electronic stabilizing properties acts as an optimal skeleton for the aluminum center throughout the reaction process.

Compound **2** was obtained as yellow crystals, which were characterized by spectroscopy and by X-ray crystallography.^{8a} The structural analysis of **2** reveals a novel heterocyclic molecule (Figure

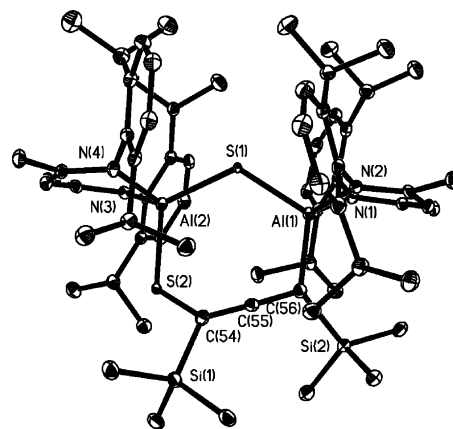
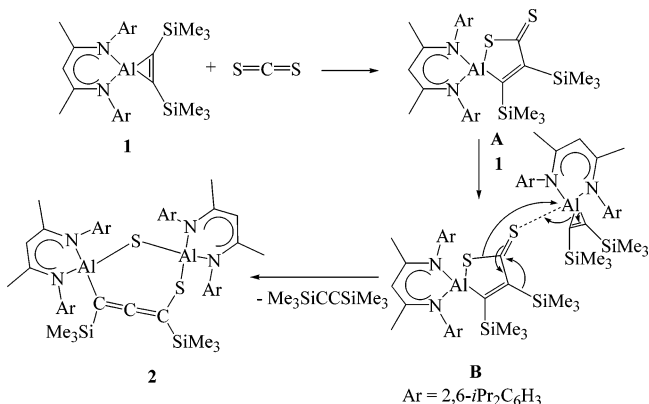


Figure 1. Molecular structure of **2** (without H atoms). Selected bond lengths (Å) and angles (deg): Al(1)–S(1) 2.2298(11), Al(1)–C(56) 1.990(3), Al(2)–S(1) 2.2188(11), Al(2)–S(2) 2.2270(11), S(2)–C(54) 1.809(3), C(54)–C(55) 1.325(4), C(55)–C(56) 1.316(4); Al(1)–S(1)–Al(2) 122.57(4), C(54)–C(55)–C(56) 178.0(3).

Scheme 1. Proposed Mechanism for the Conversion of **1** with CS₂ to **2**



1), which is in sharp contrast to those of known dinuclear aluminum sulfides or thiolates. Each aluminum atom is chelated by a β-diketiminato ligand to form LAl moieties. Between the two LAl, one S atom and one SC(SiMe₃)CC(SiMe₃) group each form a bridge. The bond lengths of Al–S_{bridge} (2.2188(11), 2.2298(11) Å) and Al–S_{thioallenyl} (2.2270(11) Å) are in the range (2.10–2.30 Å) of dinuclear aluminum sulfides.⁹ However, the bond angle of Al(1)–S(1)–Al(2) (122.57(4)°) is the widest among those of dinuclear aluminum sulfides or thiolates (78.1–117.5°).^{9,10} The two central Al atoms, the μ-S atom and the SCCC group constitute one seven-membered Al₂C₃S₂ ring, of which S(2), Al(2), S(1), Al(1), and C(56) are arranged within a plane (mean deviation Δ = 0.0375 Å), while the C(56)C(55)C(54) group is located outside of this

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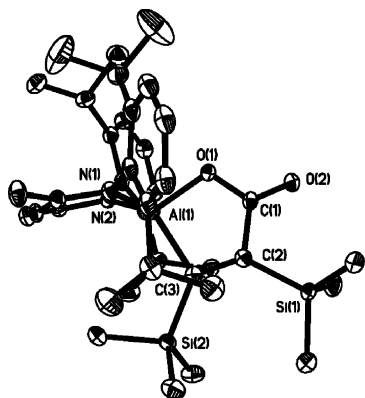


Figure 2. Molecular structure of **3** (without H atoms). Selected bond lengths (Å) and angles (deg): Al(1)–O(1) 1.7696(12), Al(1)–C(3) 1.9891(17), C(1)–O(1) 1.331(2), C(1)–O(2) 1.218(2), C(1)–C(2) 1.530(2), C(2)–C(3) 1.364(2); O(1)–C(1)–O(2) 121.78(15).

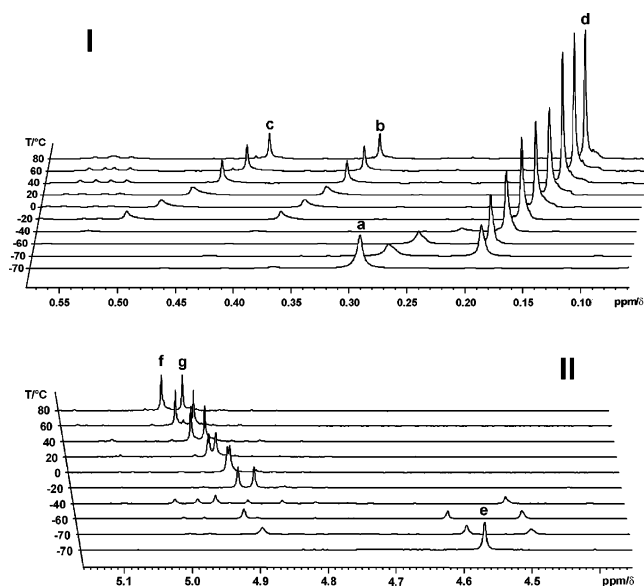


Figure 3. Variable-temperature ^1H NMR kinetic studies of the reaction of **1** with excess CS_2 in $[\text{D}_8]$ toluene. (I) Resonances of SiMe_3 (0.10–0.55 ppm), which correlate with changes of the $\eta^2\text{-C}_2(\text{SiMe}_3)_2$ group, and (II) resonances of $\gamma\text{-CH}$ protons (4.4–5.1 ppm) directly with the changes of LAl moieties (a and e correspond to **1**, b, c, f, and g to **2**, and d to free $\text{Me}_3\text{SiCCSiMe}_3$).

plane. The remarkable feature of **2** is the $\text{SC}(\text{SiMe}_3)\text{CC}(\text{SiMe}_3)$ group. The similar adjacent C–C bond distances (1.316(4), 1.325–(4) Å) and the almost linear C–C–C angle (178.0(3) $^\circ$) indicate the C=C=C allenyl functionality. A comparable example is only observed in *trans*- $\text{Rh}[\eta\text{-C}(\text{CH}=\text{CH}_2)=\text{C}=\text{CPh}_2](\text{CO})(\text{P}i\text{Pr}_3)_2]$ (1.308(6) and 1.332(6) Å and 177.5(5) $^\circ$).¹¹ The IR spectrum shows one weak band (1840 cm^{-1}) assignable to this bridged thioallenyl group. The deliberate ^{13}C NMR spectral studies give an unambiguous assignment of such allenyl ($\text{Al}-\text{C}(\text{SiMe}_3)=\text{C}=\text{C}(\text{SiMe}_3)\text{S}$) carbon resonances (δ 212.70 (=C=); 80.60, broad ($\text{Al}-\text{C}$); 59.94 ppm (=C–S)).

The crystal structure evidence of $\text{LAl}[\text{OC}(\text{O})\text{C}_2(\text{SiMe}_3)_2]$ (**3**)^{5b,8b} may approach that of **A** (Figure 2). As expected, the CO_2 was inserted into one of the Al–C bonds to form a five-membered AlC_3O planar ring with an *exo* C=O group ($\Delta = 0.0199$ Å). The longer bond distances and weaker bond strength of CS_2 than those of the corresponding CO_2 ^{12,13} might give rise to further interaction of **A** with **1** and rearrangement of the $\text{C}=\text{S}_{\text{exo}}$ unit.

The variable-temperature ^1H NMR kinetic study of this reaction (Figure 3) reveals the gradual consumption of **1** (a) and formation of **2** (b and c), including the byproduct $\text{Me}_3\text{SiCCSiMe}_3$ (d) in I. In II, this process is accompanied by the occurrence and quick disappearance of some resonances, indicating that this conversion proceeds via the proposed intermediates **A** and **B** to completion.

Thus, an unusual conversion of **1** with CS_2 to **2** has been shown, where the search of sterically and energetically favored unsaturated substrate CS_2 is crucial. An investigation on such selenium- or tellurium-containing heterocycles is in progress.

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Supporting Information Available: Experimental Section, including detailed synthetic procedures, analytical and spectral characterization data, and DFT calculations (PDF), as well as CIF data for **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) (a) Crystallographic data for **2**·0.55 toluene·0.45 ether with $\text{Cu K}\alpha$ ($\lambda = 1.54178$ Å) radiation at 133(2) K: $a = 18.903(4)$, $b = 18.624(4)$, $c = 20.125(4)$ Å, $\beta = 94.36(3)^\circ$, monoclinic, space group Cc , $Z = 4$, $R_1 = 0.0339$, $wR_2 = 0.0728$ for 8416 ($I > 2\sigma(I)$) data, and $R_1 = 0.0421$, $wR_2 = 0.0761$ for all (9398) data. (b) Crystallographic data for **3**·0.89 ether·0.11 toluene with $\text{Cu K}\alpha$ ($\lambda = 1.54178$ Å) radiation at 100(2) K: $a = 10.166(2)$, $b = 12.781(3)$, $c = 17.393(4)$ Å, $\alpha = 77.19(3)$, $\beta = 87.82(3)$, $\gamma = 81.06(3)^\circ$, triclinic, space group $P-1$, $Z = 2$, $R_1 = 0.0357$, $wR_2 = 0.0885$ for 5857 ($I > 2\sigma(I)$) data, and $R_1 = 0.0368$, $wR_2 = 0.0895$ for all (6103) data.
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