Aluminum Compounds

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# Ring Expansion to 1-Bromo-1-alumacyclonona-2,4,6,8-tetraene by Insertion of Two Alkyne Molecules into the Al–C Bonds**

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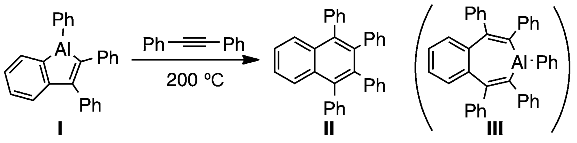
**Abstract:** *Treatment of 1-bromo-2,3,4,5-tetraethylalumole (**1**) with 3-hexyne afforded the corresponding product 1-bromo-1-alumacyclonona-2,4,6,8-tetraene (**2**), accompanied by the formation of hexaethylbenzene. In the crystalline state, **2** forms a Br-bridged dimer with a pseudo $C_2$-symmetric and twisted $AlC_8$ nine-membered ring. Deuterium-labeling experiments and DFT calculations on the reaction of **1** with 3-hexyne suggested that 1-bromo-1-alumacyclohepta-2,4,6-triene, which is formed by the insertion of one molecule of 1-hexyne into the Al–C bond of alumole **1**, is the key intermediate for the generation of **2** as well as hexaethylbenzene.*

Reactions of heteroles with compounds containing carbon–carbon multiple bonds, such as alkynes, are useful methods to construct new heterocyclic skeletons with specific structures and properties. For instance, reactions of pentaarylboroles with internal alkynes afforded various cyclic boranes including 7-borabicyclo[2.2.1]hepta-2,5-diene and borepin derivatives.[1] In contrast, reactivities of heavier Group 13 heteroles toward unsaturated compounds have been little unexplored to date.[2] Eisch and Kaska investigated the reaction of benzoalumole **I**,[3] which was generated in situ from $AlPh_3$ and diphenylacetylene, with diphenylacetylene (Scheme 1).[4] At 200 °C, benzoalumole **I** was reported to react with diphenylacetylene to give a mixture of products containing naphthalene derivative **II**. Formation of **II** was explained in terms of the generation of compound **III** as the intermediate, though the reaction mechanism has not been elucidated. Furthermore, aluminum-containing heterocyclic compounds were not obtained in this reaction.

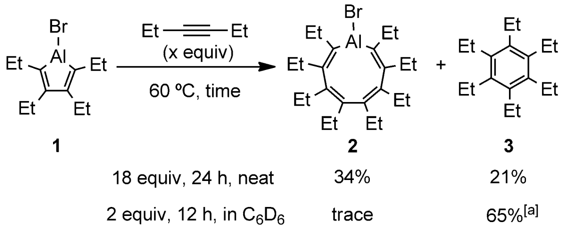


*Scheme 1.* Reaction of benzoalumole **I** with diphenylacetylene.[4]

In the course of our studies on heavier Group 13 heteroles,[5] we have recently reported the synthesis, structure, and some reactivities of 1-bromo-2,3,4,5-tetraethylalumole (**1**).[6] Owing to the electron-withdrawing bromo group on the aluminum center, the electrophilic character of **1** would be enhanced, and thus **1** is expected to show a unique reactivity pattern toward alkynes. In this Communication, we describe the formation of 1-bromo-1-alumacyclonona-2,4,6,8-tetraene (**2**) by the reaction of **1** with 3-hexyne. The structure and formation mechanism of **2** are also discussed.

A mixture of 1-bromo-2,3,4,5-tetraethylalumole (**1**) and 3-hexyne (18 equiv) was stirred at 60 °C for 1 d. Complete consumption of **1** and generation of **2** and hexaethylbenzene (**3**) were shown by a $^1H$ NMR spectrum of the crude reaction mixture (Scheme 2). Compound **2** is sparingly soluble in 3-hexyne and hexane, and thus **2** could be easily isolated as a colorless, thermally stable solid (m.p. 134–135 °C) by washing the crude material with cold hexane. In contrast, reaction of **1** with 2 equivalents of 3-hexyne in $C_6D_6$ at 60 °C afforded **3** as the major product (65 %, estimated by $^1H$ NMR spectroscopy), and only a trace amount of **2** was detected. In both experiments, aluminum-containing products except for **2** could not be characterized.

The molecular structure of **2** was elucidated by X-ray crystallographic analysis (Figure 1).[7] In the crystalline state, **2** formed a Br-bridged dimer with a crystallographic center of symmetry. The Al–Br bond lengths (2.5453(11) and 2.4694(12) Å) are comparable to those of the previously reported Br-bridged bromoalumane dimer $[Tip_2Al(\mu\text{-}Br)]_2$



*Scheme 2.* Reaction of alumole **1** with 3-hexyne. [a] Yield estimated using $^1H$ NMR spectroscopy.

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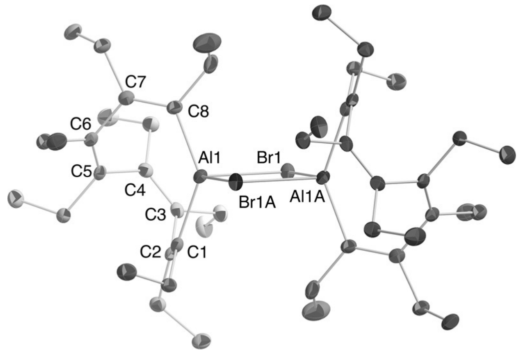
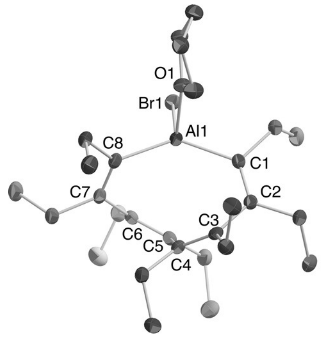
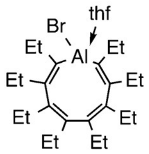


*Figure 1.* Crystal structure of **2** (thermal ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], bond angles [°], and torsion angles [°]: Al1–Br1 2.5453(11), Al1–Br1A 2.4694(12), Al1–C1 1.964(2), Al1–C8 1.959(2), C1–C2 1.346(3), C2–C3 1.498(3), C3–C4 1.352(3), C4–C5 1.516(3), C5–C6 1.347(3), C6–C7 1.490(3), C7–C8 1.343(3); C1-Al1-C8 139.31(10), C1-Al1-Br1 103.34(7), C1-Al1-Br1A 106.44(7), C8-Al1-Br1 101.67(7), C8-Al1-Br1A 106.22(8), Br1-Al1-Br1A 87.52(3), Al1-Br1-Al1A 92.49(3); C1-C2-C3-C4 −62.9(3), C3-C4-C5-C6 122.9(2), C5-C6-C7-C8 −54.5(3).





**4**

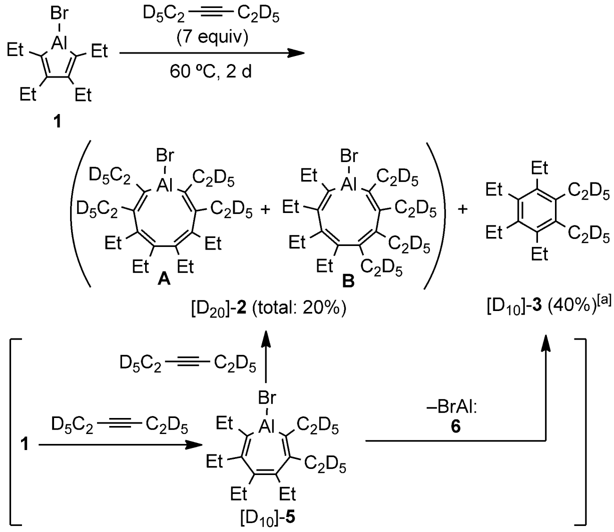
*Figure 2.* Crystal structure of complex **4** (thermal ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], bond angles [°], and torsion angles [°]: Al1–Br1 2.3722(5), Al1–O1 1.9381(12), Al1–C1 1.9736(16), Al1–C8 1.9772(17), C1–C2 1.352(2), C2–C3 1.497(2), C3–C4 1.348(2), C4–C5 1.507(2), C5–C6 1.356(2), C6–C7 1.490(3), C7–C8 1.347(2); C1-Al1-C8 135.41(7), C1-Al1-Br1 107.42(5), C1-Al1-O1 97.08(6), C8-Al1-Br1 109.47(5), C8-Al1-O1 102.16(6), O1-Al1-Br1 97.30(4); C1-C2-C3-C4 53.4(2), C3-C4-C5-C6 −125.37(17), C5-C6-C7-C8 63.3(2).

(Tip = 2,4,6-triisopropylphenyl; 2.500(3) and 2.475(4) Å).[8] The $AlC_8$ nine-membered ring of **2** exhibits a highly twisted, pseudo $C_2$-symmetric conformation. The torsion angles between the adjacent C=C double bonds are −62.9(3), 122.9(2), and −54.5(3)°. The twisted structure of **2** is corroborated by the DFT calculations on the parent compound $HAlC_8H_8$, which revealed that the twisted $C_2$-symmetic conformation corresponds to the energy minimum of the $AlC_8$ nine-membered ring.[9]

In the $^1$H NMR spectrum of **2**, the methylene protons of the ethyl substituents adjacent to the aluminum center (that is, the ethyl groups attached to the C1 and C8 atoms in Figure 1) exhibited an $ABX_3$ pattern signal, showing that these methylene protons are diastereotopic. Signals for the other methylene protons also showed complicated multiplet signals, probably because of the overlapping of $ABX_3$ patterns. The $^1$H NMR spectrum did not show notable changes between 25 and 60 °C in $C_6D_6$. These spectral data suggest that the pseudo $C_2$-symmetric structure of the $AlC_8$ nine-membered ring detected in the crystalline state is retained in solution and that ring inversion is slow on the NMR timescale.

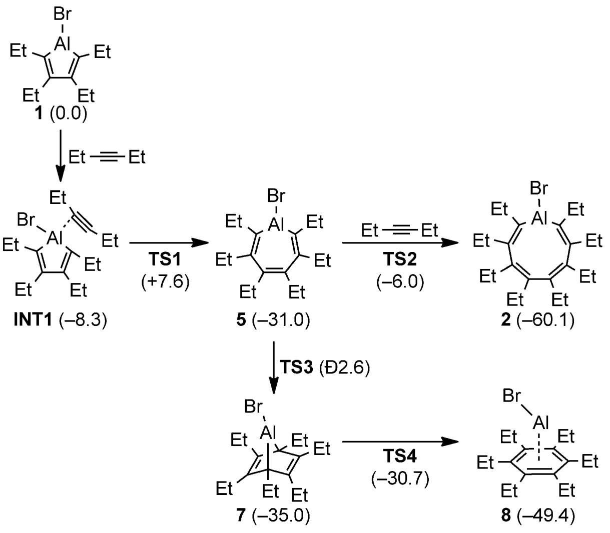
Treatment of **2** with THF afforded THF complex **4** as a colorless solid, and its structure was elucidated by single-crystal X-ray diffraction (Figure 2).[10] The Al1–O1 distance in **4** (1.9381(12) Å) is comparable to those detected for the THF complexes of sterically hindered alumanes $Mes_2RAl$ (R = Mes, 1.969(5) Å; R = Et, 1.934(4) Å; R = Cl, 1.890(5), 1.898(5) Å),[11] demonstrating the moderate Lewis acidity of **2**. Similarly to the case of **2**, the $AlC_8$ nine-membered ring of **4** exhibited a highly twisted conformation with a pseudo $C_2$-axis passing through the Al1 atom and the midpoint of the C4–C5 bond.

To obtain information on the mechanism of the formation of **2** and **3**, the reaction of **1** with $[D_{10}]$-3-hexyne was carried out. After heating the mixture at 60 °C for 2 days, the mass spectrum of the hydrolyzed reaction mixture suggested the generation of $[D_{20}]$-**2** and hexaethylbenzene $[D_{10}]$-**3** (Scheme 3). Resonance signals in the $^1$H NMR spectrum of $[D_{20}]$-**2** indicated that two compounds, **A** and **B**, were present in a 1:1 ratio. These experimental data can be explained by generation of the alumacycloheptatriene $[D_{10}]$-**5** as the key intermediate by the insertion of $[D_{10}]$-3-hexyne into an Al–C bond of alumole **1**.[4,12] Further reaction of $[D_{10}]$-**5** with the second molecule of $[D_{10}]$-3-hexyne affords $[D_{20}]$-**2** as a one-to-one mixture of **A** and **B**. Meanwhile, reductive elimination of $[D_{10}]$-**5** would afford $[D_{10}]$-**3** accompanied by the extrusion of the aluminum(I) species BrAl: (**6**).[13,14] Although attempts to trap transient species **6** have been unsuccessful so far, it might react with the alkyne to afford unidentified organoaluminum compounds.[15]



*Scheme 3.* Reaction of **1** with $[D_{10}]$-3-hexyne ($D_5C_2$-C≡C-$C_2D_5$). The scheme in square brackets shows the proposed reaction mechanism. [a] Yield estimated using $^1$H NMR spectroscopy.

The mechanism for the reaction of alumole **1** with 3-hexyne was further investigated by DFT calculations at the M06-2X/6-31G(d) level of theory.[16] The computed reaction profile is shown in Scheme 4. At the first stage, coordination of 3-hexyne to the aluminum center of **1** affords pre-reactive complex **INT1** through an exothermic reaction ($\Delta G = -8.3\ \text{kcal}\,\text{mol}^{-1}$). After the formation of **INT1**, insertion of the coordinated 3-hexyne into the Al–C bond results in the exothermic formation of key intermediate **5**, which proceeds through **TS1** with a reaction barrier of $15.9\ \text{kcal}\,\text{mol}^{-1}$. Nucleophilic attack and reaction of the second molecule of 3-hexyne with **5** affords **2** by means of a strongly exothermic reaction ($\Delta G = -29.1\ \text{kcal}\,\text{mol}^{-1}$) through a reaction barrier of $25.0\ \text{kcal}\,\text{mol}^{-1}$ (**TS2**). Meanwhile, **5** can isomerize to 7-bromo-7-alumabicyclo[2.2.1]hepta-2,5-diene (**7**), which is slightly more stable compared to **5**, with an isomerization barrier of $28.4\ \text{kcal}\,\text{mol}^{-1}$ (**TS3**). Retro [1+4] cycloaddition of bicyclic intermediate **7** results in the exothermic formation of aluminum–arene complex **8** ($\Delta G = -14.4\ \text{kcal}\,\text{mol}^{-1}$) through a low reaction barrier of $4.3\ \text{kcal}\,\text{mol}^{-1}$ (**TS4**). The structure of the $C_6Et_6$ moiety of complex **8** is nearly the same as that of free hexaethylbenzene (**3**), indicating that there is only a weak interaction between the $C_6Et_6$ and BrAl**:** moieties in **8**. Dissociation of complex **8** affords **3** as an isolable product, though the fate of the BrAl**:** moiety remained unclear. These calculation results can explain the concentration effect of 3-hexyne on the product ratio of **2**/**3** as shown in Scheme 2. Because the reaction barrier for the insertion of 3-hexyne into **5** ($25.0\ \text{kcal}\,\text{mol}^{-1}$) is slightly lower than that for the isomerization from **5** to **7** ($28.4\ \text{kcal}\,\text{mol}^{-1}$), **2** was preferentially obtained under the neat reaction conditions. When the amount and concentration of 3-hexyne are decreased, the reaction of intermediate **5** and 3-hexyne is less feasible. Therefore, the reaction of **1** with 2 equivalents of 3-hexyne in $C_6D_6$ afforded **3** as the major product, and **2** was generated as a trace product.



*Scheme 4.* Possible mechanism for the reaction of **1** with 3-hexyne. Relative Gibbs free energies ($\text{kcal}\,\text{mol}^{-1}$) were calculated at the M06-2X/6-31G(d) level of theory.

In conclusion, we have demonstrated that the reaction of alumole **1** with 3-hexyne affords **2** accompanied by the formation of benzene derivative **3**. Compound **2** is, to our knowledge, the first example of structurally characterized, stable alumacyclononatetraene derivative. The $AlC_8$ nine-membered ring of **2** exhibited a highly twisted, pseudo $C_2$-symmetric structure both in the crystalline state and in solution. The crystallographic analysis of THF complex **4** suggested that **2** had moderate Lewis acidity. Products **2** and **3** were likely formed from the common intermediate alumacycloheptatriene **5**, as suggested by deuterium-labeling experiments and DFT calculations.

## Experimental Section

Synthesis of 1-bromo-1-alumacyclonona-2,4,6,8-tetraene (**2**): A mixture of 1-bromoalumole (**1**; 0.521 g, 1.92 mmol) and 3-hexyne (2.85 g, 34.7 mmol) was stirred at 60 °C for 1 d. After cooling the reaction mixture to room temperature, crude precipitated product **2** was collected by filtration and washed with cold hexane to afford pure **2** as a colorless, crystalline solid (0.281 g, 0.647 mmol, 34 %).[17] An aqueous solution of $NaHCO_3$ was added to the filtrate and the organic layer was separated. The aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (using hexane as eluent) to afford hexaethylbenzene (**3**) as a colorless solid (0.101 g, 0.410 mmol, 21 %).[18]

**Keywords:** alkynes · aluminum · DFT calculations · ring expansion · structure elucidation

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