COMMUNICATION

Synthesis, structure and reactivity of a 1-bromoalumole

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A stable 1-bromoalumole has been synthesized by the reaction of a 1,4-dilithio-1,3-butadiene derivative with AlBr$_3$. The 1-bromoalumole was found to exist as a dimeric structure in the crystalline state. Reaction of the 1-bromoalumole with Mes*Li afforded the corresponding Mes*-substituted alumole (Mes* = 2,4,6-(t-Bu)$_3$C$_6$H$_2$), demonstrating the potential of the 1-bromoalumole for the functionalization of alumoles.

Heteroles of group 13 elements are expected to possess unique optical and electronic properties owing to the orbital interactions between the vacant p orbital of the group 13 elements with the π* orbitals of the butadiene moieties.[1] In particular, boroles have received considerable attention from the viewpoint of not only fundamental chemistry but also material science.[2] On the other hand, the heavier element analogues of boroles, such as alumoles, remain underdeveloped so far.[3,4] Recently, we have reported the synthesis of the first stable Lewis-base-free alumole **1** by using the bulky Mes* group (Mes* = 2,4,6-(t-Bu)$_3$C$_6$H$_2$) (Figure 1).[5] Alumole **1** can be reduced to the corresponding dianionic species, indicating the possible use of alumole derivatives for electron accepting materials. In order to extensively elucidate the properties of alumoles and utilize them for the key components of functional materials, facile and versatile synthetic methods of alumoles bearing various functional groups should be of importance.
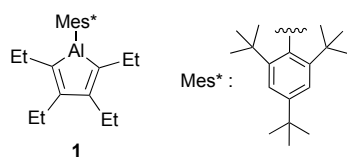

**Figure 1.** The first Lewis base free alumole **1**.

The research groups of Braunschweig and Piers reported the usability of isolable 1-haloboroles as synthetic precursors of functionalized borole derivatives.[6,7] For instance, the nucleophilic substitution at the boron atom of 1-chloroborole **I** afforded the corresponding 1-aminoborole **II** (Scheme 1).[6c] Such distinctive reactivities of 1-haloboroles suggest that their aluminium analogues, *i.e.*, 1-haloalumoles, would be promising modular synthetic precursors of functionalized alumole derivatives.[8,9] In addition, the

1-haloalumoles should exhibit unique characters owing to the electron-withdrawing and mesomeric effects of the halogeno group on the aluminium atom. Here, we report the synthesis, structure, and properties of 1-bromoalumole **2**, the first example of a stable 1-haloalumole derivative.
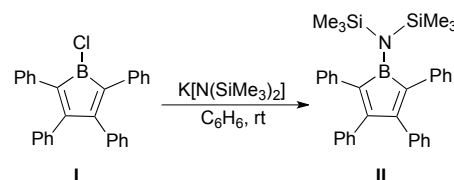
Scheme 1. Functionalization of a borole skeleton by using 1-chloroborole **I** as a borole source.[6c]

1-Bromoalumole **2** was obtained as a colourless solid in 64% yield by the treatment of AlBr$_3$ with 1,4-dilithio-1,3-butadiene derivative **3**[10] in toluene at room temperature (Scheme 2). Interestingly, Robinson et al. reported that the reaction of GaCl$_3$ with 1,4-dilithiotetraphenylbutadiene under similar reaction conditions afforded not the corresponding 1-chlorogallole but the first "spirogallane" derivative.[11] Compound **2** was found to undergo facile decomposition to give 4,5-diethyl-3,5-octadiene upon exposure to air and moisture even in the solid state. Compound **2** is thermally stable under an inert atmosphere either in the solid state (decomposed at 158 ºC) or in solution (toluene-d_8, at 100 ºC for 1 d in a sealed tube).
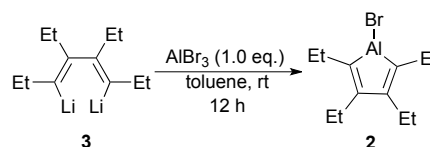
Scheme 2. Synthesis of 1-bromoalumole **2**.

X-Ray crystallographic analysis revealed that 1-bromoalumole **2** exists as a dimer in the crystalline state. In the unit cell, two crystallographically independent dimers of **2** were found, and each dimer unit has a crystallographic C_2 axis. The structure of one of the two independent dimers is shown in Figure 2. It should be noted that the Al1–C1 bond length (2.192(3) Å) is substantially elongated compared with those of alumole **1** (Al–C(ring) 1.952(2)–1.955(2) Å)[5] and the Al1–C4 bond length (1.944(3) Å). Meanwhile, the Al1–

C1* bond length (2.052(3) Å) lies between those of the Al1–C1 and Al1–C4 bonds. The geometries at the C2, C3, and C4 atoms are nearly trigonal planar, whereas the C1 atom adopts a distorted tetrahedral environment. The C1–C2 bond length (1.388(5) Å) is slightly longer than the typical value for a double bond, suggesting somewhat weakened C1–C2 bond. The Al1–Al1* distance (2.5881(18) Å) is close to those of the dimers of triorganoaluminium compounds (*e.g.*, Al_2Me_6: Al–Al 2.606(2) Å)[12] and those of the Al–Al single bonds of dialumanes (*e.g.*, Bbp(Br)Al–Al(Br)Bbp (Bbp = 2,6-$[CH(SiMe_3)_2]_2C_6H_3$): Al–Al 2.592(3) Å).[13] On the basis of these structural features, the bonding situation in the dimer unit can be interpreted in terms of multicentre bonding between the Al1, Al1*, C1, and C1* atoms, as in the case of triorganoaluminium compounds.[14] The crystal structure of the dimer of **2** was reproduced by density functional theory (DFT) calculations (see the Electronic Supplementary Information for detail).[15]
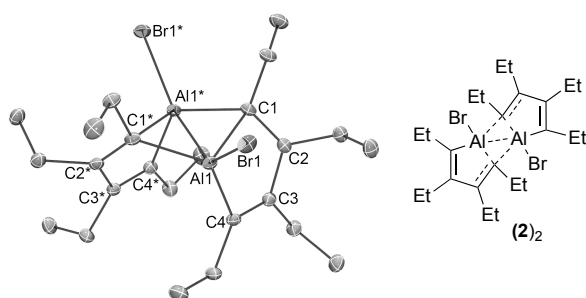
Figure 2. Dimeric structure of 1-bromoalumole **2** in the crystalline state (thermal ellipsoids at the 50% probability level). One of the two crystallographically independent molecules is shown here. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [º]: Molecule **A**: Al1–Al1* 2.5881(18), Al1–Br1 2.3056(10), Al1–C1 2.192(3), C1–C2 1.388(5), C2–C3 1.490(3), C3–C4 1.352(5), Al1–C4 1.944(3), Al1–C1* 2.052(3), C1–Al1–C4 89.43(14), Al1–C1–C2 92.1(2), C1–C2–C3 120.8(3), C2–C3–C4 117.2(3), C3–C4–Al1 106.3(2), Al1–C1–Al1* 75.07(11), C1–Al1–C1* 101.15(12), C1–Al1–Br1 104.75(9), C4–Al1–Br1 122.64(11); Molecule **B**: Al1–Al1* 2.5988(19), Al1–Br1 2.3096(10), Al1–C1 2.193(3), C1–C2 1.375(5), C2–C3 1.494(5), C3–C4 1.348(5), Al1–C4 1.948(3), Al1–C1* 2.052(3), C1–Al1–C4 88.97(14), Al1–C1–C2 91.8(2), C1–C2–C3 120.6(3), C2–C3–C4 116.7(3), C3–C4–Al1 106.3(2), Al1–C1–Al1* 75.48(12), C1–Al1–C1* 100.05(13), C1–Al1–Br1 106.39(10), C4–Al1–Br1 120.93(11).

1-Bromoalumole **2** in solution was characterized by using variable-temperature (VT) NMR spectroscopy. At 25 °C, the ^{1}H NMR spectrum of compound **2** exhibited one sharp triplet and two broad signals (Figure 3). Cooling this sample to –60 °C resolved these signals into four triplet and seven multiplet signals. Similarly, the ^{13}C NMR spectrum at –60 °C showed four signals attributable to the sp[2] carbon atoms in the alumole ring, these chemical shifts of which were well reproduced by the GIAO calculations on the DFT-optimized structure of the 1-bromoalumole dimer. The ^{13}C NMR signal corresponding to the C2 nucleus in Figure 2 appeared in a characteristic low-field region (δ = 201.6 ppm), indicating the decrease in the electron density of the C2 atom. The vinylic carbon atoms in the β-positions to the aluminium atoms in dimeric alkenylaluminium compounds are known to exhibit characteristic lower-field shifted resonances in the ^{13}C NMR spectra.[16] Accordingly, the dimeric form should be kept in solution at the low temperature. At 100 °C, the ^{1}H NMR spectrum exhibited two triplets and two quartet signals corresponding to the methyl and methylene

protons of the ethyl substituents, respectively, and only two signals were observed for the alumole ring carbon atoms in the ^{13}C NMR spectrum. These VT-NMR spectroscopic data could be accounted for by the rapid site exchange of the α-carbon atoms in the dimeric structure (*i.e.*, C1 and C4 atoms in Figure 2) and/or by the monomer-dimer equilibrium.
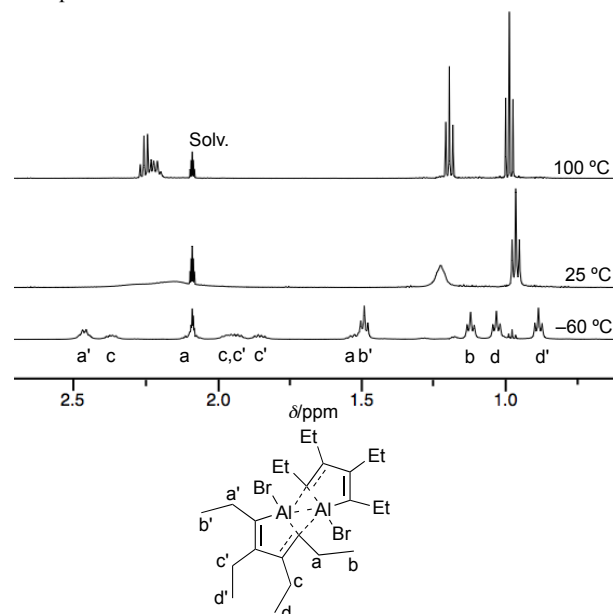

Figure 3. Variable-temperature (VT) ^{1}H NMR spectra of 1-bromoalumole **2** in toluene-d_8.

At room temperature, addition of excess amount of THF to the C_6D_6 solution of 1-bromoalumole **2** quantitatively afforded 1-bromoalumole–THF adduct **4** as a colourless solid (Scheme 3). Adduct **4** was characterized by the ^{1}H and ^{13}C NMR spectroscopies.
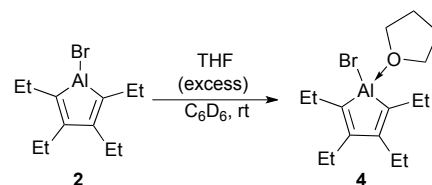
Scheme 3. Complexation of 1-bromoalumole **2** with THF.

Finally, a nucleophilic substitution reaction on the aluminium atom of 1-bromoalumole **2** was preliminarily examined. Reaction of **2** with equimolar quantity of Mes*Li[17] in C_6D_6 was completed after 48 h at 60 °C to afford the expected Mes*-substituted alumole **1** as a sole product.[5] Alumole **1** was isolated as colourless crystals in 48% yield after recrystallization from hexane (Scheme 4). This preliminary result demonstrated that 1-bromoalumole **2** should be a promising building block for novel functionalized alumole derivatives.
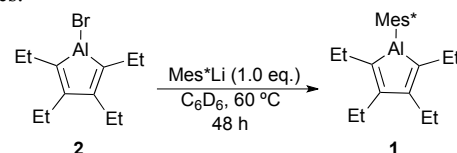
Scheme 4. Reaction of 1-bromoalumole **2** with Mes*Li.

In summary, we have succeeded in the synthesis of 1-bromoalumole **2**, the first alumole derivative bearing a halogen substituent on the aluminium atom. It was revealed that 1-bromoalumole **2** exhibits its unique dimeric structure in the crystalline state. Treatment of 1-bromoalumole **2** with Mes*Li afforded the corresponding Mes*-substituted alumole **1**, demonstrating the potential of **2** as a modular-precursor of functionalized alumole derivatives.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, spectroscopic and crystallographic data, and computational data. CCDC 974827. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c000000x/.

‡ Crystal data for **1**: $C_{24}H_{40}Al_2Br_2$, M_r = 542.34, colourless block, size $0.02 \times 0.01 \times 0.01$ mm^3, λ = 0.85000 Å, T = −170 °C, monoclinic, space group $P2/n$ (#13), a = 17.8044(1) Å, b = 8.4388(1) Å, c = 17.8350(1) Å, β = 100.7991(3)°, V = 2632.21(4) Å^3, Z = 4, $\mu(\lambda$ = 0.85000 Å) = 4.991 mm^{-1}, total reflections 22610, independent reflections 4671, parameters 262, R_{int} = 0.0412, θ_{max} = 31.00°, R_1 [$I > 2\sigma(I)$] = 0.0489, wR_2 (all data) = 0.1333, GOF 1.050.

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