

Synthesis, molecular structure, and reactivity of an Li_2Br_4 octahedrally stabilized organoaluminium bromide dimer

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The synthesis, molecular structure, and reactivity of an unusual Li_2Br_4 octahedrally stabilized organoaluminium bromide dimer, $[(\text{Mes}_2\text{C}_6\text{H}_3)\text{AlBr}_3\text{Li}]_2$, is described.

Utilization of the sterically demanding 2,6-dimesitylphenyl ligand, $(\text{Mes}_2\text{C}_6\text{H}_3)$, with group 13 elements has afforded a number of interesting compounds in recent years. Monomeric compounds of boron, $(\text{Mes}_2\text{C}_6\text{H}_3)\text{BBR}_2$,¹ gallium, $(\text{Mes}_2\text{C}_6\text{H}_3)_2\text{GaX}$ ($X = \text{Cl}$,² Br),³ and indium $(\text{Mes}_2\text{C}_6\text{H}_3)_2\text{InBr}$,⁴ have been reported. Gallium and indium dimers such as $[(\text{Mes}_2\text{C}_6\text{H}_3)\text{GaCl}_2]_2$ and $[(\text{Mes}_2\text{C}_6\text{H}_3)\text{InCl}_2]_2$ ⁵ have also been prepared. It is particularly significant that this ligand system has been shown to stabilize cycloallenes, organometallic 2π -electron aromatic moieties, $\text{M}_2[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$ ^{6–9} ($\text{M} = \text{Na}, \text{K}$). In notable contrast, the corresponding organoaluminium chemistry of this ligand has proven considerably less fruitful. Reaction of Me_3SiCl with $[(\text{Mes}_2\text{C}_6\text{H}_3)\text{AlH}_3\cdot\text{LiOEt}_2]_n$ gives $(\text{Mes}_2\text{C}_6\text{H}_3)\text{AlCl}_2\cdot\text{OEt}_2$.¹⁰ Herein we report the synthesis,[†] molecular structure, and reactivity of the Li_2Br_4 octahedrally stabilized aluminium bromide dimer $[(\text{Mes}_2\text{C}_6\text{H}_3)\text{AlBr}_3\text{Li}]_2$ **1**. Reaction of **1** with lithium 2,6-diisopropylphenylamide, $\text{Li}[\text{N}(\text{H})(\text{Pr}^i_2\text{C}_6\text{H}_3)]$, affords $(\text{Mes}_2\text{C}_6\text{H}_3)\text{Al}[\text{N}(\text{H})(\text{Pr}^i_2\text{C}_6\text{H}_3)]_2$ **2**.

The structure of **1** (Fig. 1)[‡] which resides about a center of symmetry, may be described as an Li_2Br_4 octahedrally stabilized aluminium bromide dimer. The Li_2Br_4 octahedron is facilitated by the displacement of the lithium atoms from the *ipso*-carbon atoms of the ligands by AlBr_3 moieties. **1** is easily compared with the unsolvated (2,6-dimesitylphenyl)lithium dimer, $[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Li}]_2$.¹¹ Perhaps most interesting is the differences in lithium coordination of **1** compared to that of $[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Li}]_2$. In $[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Li}]_2$ the primary interaction between the lithium and the ligand involves the *ipso*-carbon

atoms. The $\text{Li}-\text{C}_{ipso}$ bond distances are 2.17(1) and 2.16(1) Å while the secondary lithium–carbon interactions (with the *ipso*-carbon atoms of the *o*-mesityl substituents) range from 2.51(1) to 2.56 Å. In striking contrast from $[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Li}]_2$, the lithium atoms in **1** only interact with the 2,6-dimesitylphenyl ligand in an η^6 -aryl ring fashion with lithium–carbon contacts ranging from 2.38(4) to 2.70(4) Å. In addition to the $\text{Li}-$ (η^6 -aryl) ring interaction, and quite unlike other reported lithium aryls, the core **1** is further stabilized by weak lithium–bromine contacts: 2.52(2), 2.67(3) and 2.80(3) Å. These distances are considerably longer than the corresponding value reported for gaseous LiBr (2.35 Å).¹² Furthermore, the $\text{Li}\cdots\text{Li}$ separation in **1** of 3.45(6) Å is considerably longer than the values reported for $[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Li}]_2$ (2.31, 2.27 Å). The environment about the aluminium atom may be described as distorted tetrahedral with bond angles ranging from 99.0(5) to 122.5(5)°. The $\text{Al}-\text{C}$ bond distance in **1** of 1.96(2) Å compares well with other four-coordinate aluminium compounds. The $\text{Al}-\text{Br}$ bond distances, 2.359(5), 2.285(6) and 2.398(5) Å, for $\text{Al}-\text{Br}(1)$, $\text{Al}-\text{Br}(2)$ and $\text{Al}-\text{Br}(3)$, respectively, are comparable to other reported $\text{Al}-\text{Br}$ distances.^{13–15}

The unusual structure of **1** underscores the often substantial differences in chemical behavior of organoaluminium moieties relative to other group 13 congeners. However, it is interesting that reaction of **1** with $\text{Li}[\text{N}(\text{H})(\text{Pr}^i_2\text{C}_6\text{H}_3)]$ proceeds in an expected manner affording **2**. The aluminium atom in **2** assumes a trigonal planar geometry [bond angles about Al: 127.3(5), 116.4(2) and 116.4(2)°] (Fig. 2) with generally unremarkable $\text{Al}-\text{Cl}$ [1.978(11) Å] and $\text{Al}-\text{N}$ [1.788(6) Å] bond distances. The $\text{Al}-\text{N}$ bond distance in **2** is quite comparable to values reported for $[\text{CpAl}-\text{N}(\text{Pr}^i_2\text{C}_6\text{H}_3)]_2$ [1.796(2) and 1.811(3) Å]¹⁶ while these are much shorter than the distances reported for $[(\text{Me}_3\text{CCH}_2)_2\text{Al}-\text{N}(\text{H})(\text{Pr}^i_2\text{C}_6\text{H}_3)]_2$ [2.013(5) and 2.007(5) Å].¹⁷ **2** contains a mirror plane which bisects the $\text{N}-\text{Al}-\text{N}$ bond

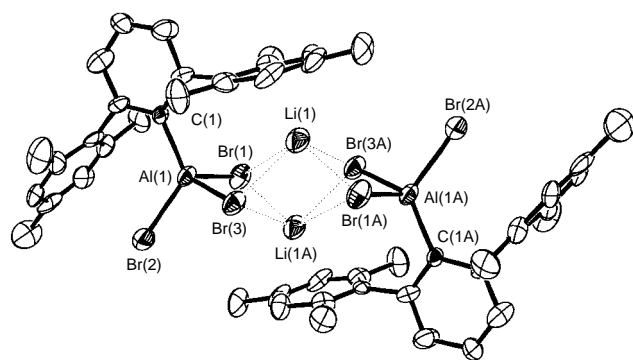


Fig. 1 Molecular structure of $[(\text{Mes}_2\text{C}_6\text{H}_3)\text{AlBr}_3\text{Li}]_2$ **1**. Selected bond distances (Å) and angles (°): $\text{Al}(1)-\text{C}(1)$ 1.96(2), $\text{Al}(1)-\text{Br}(1)$ 2.359(5), $\text{Al}(1)-\text{Br}(2)$ 2.285(6), $\text{Al}(1)-\text{Br}(3)$ 2.398(5), $\text{Br}(1)-\text{Li}(1\text{A})$ 2.67(3), $\text{Br}(3)-\text{Li}(1)$ 2.52(3), $\text{Br}(3)-\text{Li}(1\text{A})$ 2.80(3), $\text{Li}(1)-\text{Li}(1\text{A})$ 3.41(5), $\text{Li}(1)-\text{C}(7)$ 2.70(3), $\text{Li}(1)-\text{C}(8)$ 2.70(3), $\text{Li}(1)-\text{C}(9)$ 2.51(3), $\text{Li}(1)-\text{C}(10)$ 2.43(3), $\text{Li}(1)-\text{C}(11)$ 2.38(4), $\text{Li}(1)-\text{C}(12)$ 2.55(4), $\text{C}(1)-\text{Al}(1)-\text{Br}(1)$ 111.1(5), $\text{C}(1)-\text{Al}(1)-\text{Br}(2)$ 122.2(5), $\text{C}(1)-\text{Al}(1)-\text{Br}(3)$ 115.5(5), $\text{Br}(2)-\text{Al}(1)-\text{Br}(1)$ 106.2(2), $\text{Br}(2)-\text{Al}(1)-\text{Br}(3)$ 99.0(2), $\text{Br}(1)-\text{Al}(1)-\text{Br}(3)$ 100.0(2), $\text{Al}(1)-\text{Br}(1)-\text{Li}(1\text{A})$ 88.5(7), $\text{Al}(1)-\text{Br}(3)-\text{Li}(1)$ 106.1(8), $\text{Al}(1)-\text{Br}(3)-\text{Li}(1\text{A})$ 84.9(7), $\text{Li}(1)-\text{Br}(3)-\text{Li}(1\text{A})$ 79.6(9).

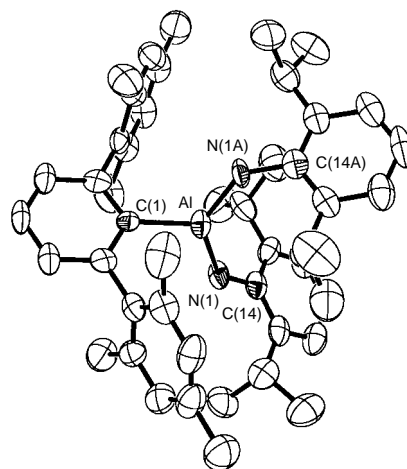


Fig. 2 Molecular structure of $(\text{Mes}_2\text{C}_6\text{H}_3)\text{Al}[\text{N}(\text{H})(\text{Pr}^i_2\text{C}_6\text{H}_3)]_2$ **2**. Selected bond distances (Å) and angles (°): $\text{Al}(1)-\text{C}(1)$ 1.978(11), $\text{Al}(1)-\text{N}(1)$ 1.788(6), $\text{N}(1)-\text{C}(14)$ 1.436(10), $\text{N}(1)-\text{Al}(1)-\text{C}(1)$ 116.4(2), $\text{N}(1)-\text{Al}(1)-\text{N}(1\text{A})$ 127.3(5), $\text{C}(14)-\text{N}-\text{Al}(1)$ 138.1(6).

angle while containing atoms Al, C(1) and C(4). The central phenyl ring of the ligand resides at an angle of 63.2° relative to the aluminium trigonal plane [C–Al(N)–N]. Indeed, significant π -bonding would appear to be precluded in **2** by the fact that both nitrogen trigonals [C–N(H)–Al] are twisted at an angle of 23.1° relative to the aluminium trigonal plane.

The formation of **2** suggests that **1** may be utilized in a variety of reactions as a means to approach other interesting derivatives.

Notes and References

† *Synthesis*: **1** a solution of (Me₂C₆H₃)Li (0.80 g, 2.5 mmol) in diethyl ether (40 ml) was added over a period of 10 min to an ether (30 ml) solution of AlBr₃ (0.67 g, 2.5 mmol) at –78 °C. The reaction mixture was stirred for 3 h and allowed to warm to room temp. over a period of 2 h. The resulting solution became yellow and was stirred for additional 30 h. After filtration, the solution was concentrated. Cooling this solution to –25 °C for several days afforded **1** (0.78 g) as colorless crystals. Yield: 53%, mp 67 °C. ¹H NMR (300 MHz, 298 K, [²H₈]THF): δ 1.92 (s, 12 H, *o'*-CH₃), 1.98, (s, 12 H, *o'*-CH₃), 2.13 (s, 6 H, *p'*-CH₃), 2.17, (s, 6 H, *p'*-CH₃), 6.65–6.73 [m, 6 H, CH(aromatic)], 6.76 [s, 8 H, *m'*-CH (aromatic)]. ¹³C NMR (300 MHz, 298 K, [²H₈]THF): δ 19.91, 20.06, 20.48, 20.62, 20.81 (methyl C); 125.90, 126.32, 126.68, 126.86–134.02, 139.23, 142.12, 145.98 (aromatic C).

2: an ether (50 ml) solution of Li[N(H)(Pr₂C₆H₃)] (0.22 g, 1.5 mmol), prepared from (Pr₂C₆H₃)NH₂ and *n*-C₄H₉Li, at 0 °C in ether, was slowly added to an ether (30 ml) solution of **1** (0.42 g, 0.70 mmol) at –78 °C. The reaction mixture was stirred for 3 h and allowed to warm to room temp. over a period of 2 h, and stirred for additional 30 h. After filtration, the solvent of the yellow solution was evaporated *in vacuo*. The residue was extracted with hexane (50 ml). The volume of the solution was reduced *in vacuo* to ca. 15 ml. Cooling the concentrated solution at –25 °C for a week afforded colorless needle crystals of **2**. X-Ray quality crystals were grown from diethyl ether–hexane (1 : 1). Yield: 78%. mp. 154 °C. ¹H NMR (300 MHz, 298 K, C₆D₈): δ 1.07 [d, 12 H, CH(CH₃)₂], 1.2 [d, 12 H, CH(CH₃)₂], 1.90 (s, 6 H, *o'*-CH₃), 1.93 (s, 6 H, *o'*-CH₃), 2.04 (s, 3 H, *p'*-CH₃), 2.08 (s, 3 H, *p'*-CH₃), 3.24–3.29, [m, 4 H, CH(CH₃)₂], 4.39 (s, 2 H, NH), 6.63–6.69 [m, 12 H, CH (aromatic)], 6.71–6.73 [m, 4 H, *m'*-CH (aromatic)]. ¹³C NMR (300 MHz, 298 K, C₆D₈): δ 8.18, 8.26, 16.38, 18.10, 18.38, 18.65, 19.91, 20.17 (alkyl C), 123.20, 123.42, 124.09, 124.75, 124.98–141.2, 142.87, 144.50, 145.96 (aromatic C).

‡ *Crystallographic data* for **1** and **2**: colorless cubic crystals of **1** (0.2 × 0.1 × 0.1 mm) and **2** (0.2 × 0.2 × 0.1 mm) were mounted in glass capillaries under an atmosphere of N₂ in a drybox. Single crystal X-ray intensity data were collected on a Siemens P4 diffractometer (50 kV/40 mA), with graphite-monochromated Mo-K α radiation (λ = 0.710 73 Å) at 21 °C, using the ω scan technique to a maximum 2θ value of 45°. Cell parameters and an orientation matrix for data collection were obtained from a least-squares analysis of the setting of up to 30 carefully centered reflections in the range 15.0° < 2θ < 30.0°. Absorption corrections were carried out using the empirical ψ -scan method. The structures were solved by direct methods using the SHELXTL 5.0¹⁸ software package. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms

were placed at ideal positions riding on the attached carbon and nitrogen atoms without further refinement.

Crystal data: **1**: a = 9.982(8), b = 10.179(2), c = 12.948(3) Å, α = 95.30(2), β = 94.90(4), γ = 107.70(2)°, V = 1239.0(11) Å³, D_c = 1.574 g cm^{–3}, Z = 1 for triclinic space group $P\bar{1}$. Refinement converged at $R1$ = 0.070, $wR2$ = 0.20 using the F^2 refinement for 2150 observed reflections. Data collection and refinement for **2** proceeded in a fashion similar to that described for **1**.

2: a = 24.604(14), b = 10.312(5), c = 18.173(8) Å, β = 115.50(5)°, V = 4161.8(34) Å³, D_c = 1.106 g cm^{–3}, Z = 4 for monoclinic space group $C2/c$. Refinement converged at $R1$ = 0.097, $wR2$ = 0.23 using the F^2 refinement for 1449 observed reflections. CCDC 182/851.

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