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Supplementary Information

Synthesis, structure and reactivity of a 1-bromoalumole

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General remarks

All the manipulations were performed under a dry argon atmosphere using standard Schlenk techniques or glove boxes. AlBr₃ was purchased from Sigma-Aldrich Japan K.K. and purified by sublimation under vacuum. Solvents were purified by the Ultimate Solvent System, Glass Contour Company (hexane, Et₂O, THF and toluene)^{S1} or by bulb-to-bulb distillation from a potassium mirror (C_6D_6 and toluene- d_8) prior to use. ¹H, ¹³C and ²⁷Al NMR spectra were measured on a JEOL AL-300 spectrometer or a Bruker Avance-600 spectrometer and referenced to SiMe₄ (¹H and ¹³C) or AlNO₃/D₂O (²⁷Al). Melting points were determined on a Yanaco micro melting point apparatus and uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory, Institute for Chemical Research, Kyoto University. 1,4-Dilithiobutadiene derivative **3** and Mes*Li were prepared according to literatures.^{S2,S3} We are grateful to Ms. K. Omine (JURC in the Institute for Chemical Research, Kyoto University) for the NMR measurements.

Synthesis of 1-bromoalumole 2: A toluene (50 mL) solution of 1,4-dilithiobutadiene derivative **3** (0.132 g, 0.741 mmol) and a solution of AlBr₃ (0.199 g, 0.746 mmol) were simultaneously added dropwise to a toluene (50 mL) at room temperature. The reaction mixture was stirred for 12 h at room temperature. The solvent was removed under reduced pressure, and the residue was dissolved in hexane and filtered. The filtrate was concentrated and stored at -35 °C to afford **2** as a colourless solid (0.128 g, 0.472 mmol, 64%).

mp 158 °C (dec.). ¹H NMR (600 MHz, toluene-*d*₈, 100 °C): $\delta = 0.99$ (t, *J* = 7.5 Hz, 6H, β-CH₂CH₃), 1.20 (t, *J* = 7.5 Hz, 6H, α-CH₂CH₃), 2.22 (q, *J* = 7.5 Hz, 4H, β-CH₂CH₃), 2.25 (q, *J* = 7.5 Hz, 4H, α-CH₂CH₃); ¹³C NMR (125 MHz, toluene-*d*₈, 100 °C): $\delta = 13.06$ (β-CH₂CH₃), 16.21 (α-CH₂CH₃), 24.56 (α-CH₂CH₃), 25.67 (β-CH₂CH₃), 146.52 (Al-C=C), 178.52 (Al-C=C); ¹H NMR (600 MHz, toluene-*d*₈, -60 °C): $\delta =$ 0.87 (t, *J* = 7.2 Hz, 3H, β-CH₂CH₃), 1.03 (t, *J* = 7.2 Hz, 3H, β-CH₂CH₃), 1.12 (t, *J* = 7.2 Hz, 3H, α-CH₂CH₃), 1.48 (t, *J* = 7.2 Hz, 3H, α-CH₂CH₃), 1.53 (m, 1H, α-CH₂CH₃), 1.87 (m, 1H, β-CH₂CH₃), 1.95 (m, 1H, β-CH₂CH₃), 1.98 (m, 1H, β-CH₂CH₃), 2.10 (m, 1H, α-CH₂CH₃), 2.38 (m, 1H, β-CH₂CH₃), 2.46 (m, 2H, α -CH₂CH₃); ¹³C NMR (151 MHz, C₆D₆): δ = 12.16 (β -CH₂CH₃), 14.03 (β -CH₂CH₃), 16.29 (α -CH₂CH₃), 16.78 (α -CH₂CH₃), 23.15 (β -CH₂CH₃), 24.62 (α -CH₂CH₃), 25.27 (β -CH₂CH₃), 25.40 (α -CH₂CH₃), 124.33 (Al-C=C), 155.15 (Al-C=C), 165.37 (Al-C=C), 201.57 (Al-C=C); No ²⁷Al NMR signal was observed even after long-time measurement for 2 days; Elemental analysis (%): calcd for C₁₂H₂₀AlBr (**2**): C, 53.15; H, 7.43; found: C, 52.97; H, 7.62.



Figure S1. ¹H NMR spectrum of **2** in C_6D_6 (25 °C).



Figure S2. ¹³C NMR spectrum of 2 in C_6D_6 (25 °C).







Figure S4. ¹³C NMR spectrum of **2** in toluene- d_8 (100 °C).



Figure S5. ¹H NMR spectrum of **2** in toluene- d_8 (-60 °C).



Figure S6. ¹³C NMR spectrum of **2** in toluene- d_8 (-60 °C).

Reaction of 1-bromoalumole 2 with THF: In a 5mm ϕ J.Young NMR tube, to a C₆D₆ solution (0.5 mL) of **2** (7.0 mg, 12.9 µmol) was added THF (1 drop, *ca.* 0.1 mL) at room temperature. The reaction was monitored by ¹H NMR spectroscopy at 25 °C, indicating the quantitative formation of THF adduct **4**. After removal of volatiles under reduced pressure, adduct **4** was obtained as colourless oil (6.6 mg, 19 µmol, 74%). ¹H NMR (300 MHz, C₆D₆, 25 °C): $\delta = 0.90$ (t, J = 6.8 Hz, 4H, OCH₂CH₂), 1.10 (t, J = 7.5 Hz, 6H, β -CH₂CH₃), 1.31 (t, J = 7.5 Hz, 6H, α -CH₂CH₃), 2.45 (q, J = 7.5 Hz, 8H, β -CH₂CH₃), 3.61 (t, J = 6.8 Hz, 4H, OCH₂CH₂); ¹³C NMR (75 MHz, C₆D₆, 25 °C): $\delta = 15.39$ (β -CH₂CH₃), 17.48 (α -CH₂CH₃), 22.02 (α -CH₂CH₃), 24.89 (β -CH₂CH₃), 24.99 (OCH₂CH₃), 71.95 (OCH₂CH₃), 140.82 (Al-C=C), 156.16 (Al-C=C).



Figure S7. ¹H NMR spectrum of adduct 4 (C₆D₆, 25 °C).



Figure S8. ¹³C NMR spectrum of adduct **4** (C_6D_6 , 25 °C).

Synthesis of Mes*-substituted alumole 1: In a 5mm ϕ J.Young NMR tube, to a C₆D₆ solution (0.7 mL) of 1-bromoalumole 2 (22.1 mg, 81.2 μ mol) was added Mes*Li (23.1 mg, 91.5 μ mol) at room temperature. The reaction was monitored by ¹H NMR spectroscopy, and the reaction was completed after 48 h at 60 °C. The solvent was removed under reduced pressure, and the residue was dissolved in hexane and filtered. The filtrate was concentrated and stored at -35 °C to afford 1 as a colourless solid (17.1 mg, 39.2 μ mol, 48%).

X-Ray crystallographic analysis: Single crystals of 2 suitable for X-ray crystallographic analysis were obtained by slow recrystallization from hexane at -35 °C. The intensity data were collected at the BL38B1 beamline of the SPring-8 using an ADSC Quantum 315 CCD detector and Si(111)-monochromated X-ray radiation ($\lambda = 0.85000$ Å). The reflection data were integrated, scaled, and averaged by using the HKL-2000 program package.^{S4} Semi-empirical absorption correction was applied using the program of MULABS.^{S5} The structures were solved by a direct method (SIR2004)^{S6} and refined by full-matrix least square method on F^2 for all reflections (SHELXL-97).^{S7} All hydrogen atoms were placed using AFIX instructions, while the other atoms were refined anisotropically.



Figure S9. Molecular structure of **2B** (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): 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* 2.049(4), 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).

Computational details: All calculations were performed with the Gaussian 09 (revision C.01) program package^{S8} at the DFT-B3PW91 level employing the 6-311G(2df) basis set. Frequency calculations confirmed that all the optimized structures are equilibrium structures. NMR chemical shifts were calculated by using the GIAO method at the DFT-B3PW91/6-311+G(2df) level of theory. Computational time was provided by the Super Computer Laboratory, Institute for Chemical Research, Kyoto University.

Br	-2.286641	-1.910021	-1.933498	С	-1.35023	-2.099791	1.828201
Al	-0.919333	-0.354845	-0.920835	Н	-2.37469	-2.41595	1.606544
С	-1.51534	1.487178	-0.654235	Н	-0.711743	-2.829239	1.319494
С	-1.986689	1.541946	0.613068	С	-4.496275	-0.386274	1.124713
С	-1.089064	-0.710319	1.244951	Н	-4.648643	0.364278	0.348102
С	-2.066937	0.253394	1.352809	Н	-5.432909	-0.505717	1.673695
С	-2.468494	2.807817	1.297888	Н	-4.274525	-1.328442	0.621561
Н	-2.390231	2.691646	2.383981	Al	0.919333	-0.354846	0.920834
Н	-1.772287	3.612331	1.043614	Br	2.286641	-1.910021	1.933499
С	-3.367528	0.012001	2.082324	С	1.515341	1.487176	0.654235
Н	-3.253081	-0.75983	2.841129	С	1.986689	1.541946	-0.613068
Н	-3.654966	0.923462	2.614027	С	1.089064	-0.710319	-1.244952
С	-2.295594	2.498657	-2.823519	С	2.066936	0.253394	-1.352809
Н	-2.046516	1.587672	-3.373418	С	2.468496	2.807816	-1.297886
Н	-2.170177	3.345812	-3.502173	Н	2.390232	2.691647	-2.383979
Н	-3.352408	2.434555	-2.555291	Н	1.772289	3.612331	-1.043612
С	-1.415989	2.657503	-1.581405	С	3.367528	0.012001	-2.082325
Н	-0.374175	2.748413	-1.91226	Н	3.253081	-0.75983	-2.84113
Н	-1.65967	3.604293	-1.0864	Н	3.654966	0.923463	-2.614027
С	-3.883061	3.263977	0.938362	С	2.295596	2.498654	2.823519
Н	-3.991063	3.398753	-0.139456	Н	2.04652	1.587669	3.373418
Н	-4.112789	4.217712	1.420335	Н	2.17018	3.345808	3.502174
Н	-4.640314	2.544866	1.254763	Н	3.35241	2.434552	2.55529
С	-1.091874	-2.223222	3.331618	С	1.41599	2.657501	1.581407
Н	-0.046919	-2.024933	3.570933	Н	0.374176	2.74841	1.912263
Н	-1.322006	-3.234899	3.674862	Н	1.65967	3.604291	1.086402
Н	-1.699219	-1.528237	3.915115	С	3.883063	3.263976	-0.93836

Optimized geometry of the dimer of 1-bromoalumole 2 (in Å, C₂ symmetry)

Н	3.991064	3.398751	0.139457	С	1.350228	-2.09979	-1.828204
Н	4.112792	4.21771	-1.420334	Н	2.374689	-2.41595	-1.606548
Н	4.640315	2.544864	-1.254761	Н	0.711742	-2.829238	-1.319496
С	1.091871	-2.22322	-3.331621	С	4.496274	-0.386275	-1.124714
Н	0.046917	-2.024924	-3.570935	Н	4.648643	0.364277	-0.348103
Н	1.321997	-3.234898	-3.674864	Н	5.432909	-0.505718	-1.673696
Н	1.69922	-1.528239	-3.915117	Н	4.274524	-1.328443	-0.621563



Figure S10. Optimized structure of the dimer of **2** (*C*₂ symmetry). Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg): Al1–Al1* 2.602, Al1–Br1 2.305, Al1–Cl 2.201, Cl–C2 1.377, C2–C3 1.488, C3–C4 1.353, Al1–C4 1.954, Al1–C1* 2.065, C1–Al1–C4 89.68, Al1–Cl–C2 91.08, C1–C2–C3 121.92, C2–C3–C4 116.70, C3–C4–Al1 105.79, Al1–C1–Al1* 75.10, C1–Al1–Cl* 101.63, C1–Al1–Br1 106.11, C4–Al1–Br1 120.99.



Figure S11. Calculated NMR chemical shifts (ppm) of the dimer of 2.

Optimized geometry of 1-bromoalur	mole 2 (in Å, <i>C</i> ₂ symmetry)
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Al	0	0	0.919819	Н	0.915368	-3.775881	-0.063371
С	0.475928	1.362976	-0.359165	Н	0.279732	-3.273076	1.50343
С	0.268059	0.72008	-1.530401	С	0.597485	1.346456	-2.865576
С	-0.475928	-1.362976	-0.359165	С	2.017607	1.020987	-3.334162
С	-0.268059	-0.72008	-1.530401	Н	0.488598	2.430604	-2.793812
С	1.000928	2.753552	-0.179017	Н	-0.118615	1.032814	-3.628621
С	0	3.671044	0.524189	Н	2.220276	1.465577	-4.311778
Н	1.300334	3.209732	-1.128686	Н	2.755085	1.406715	-2.627102
Н	1.914852	2.714012	0.427517	Н	2.180892	-0.056237	-3.416153
Н	0.418363	4.668841	0.67824	С	-0.597485	-1.346456	-2.865576
Н	-0.915368	3.775881	-0.063371	С	-2.017607	-1.020987	-3.334162
Н	-0.279732	3.273076	1.50343	Н	-0.488598	-2.430604	-2.793812
С	-1.000928	-2.753552	-0.179017	Н	0.118615	-1.032814	-3.628621
С	0	-3.671044	0.524189	Н	-2.220276	-1.465577	-4.311778
Н	-1.300334	-3.209732	-1.128686	Н	-2.755085	-1.406715	-2.627102
Н	-1.914852	-2.714012	0.427517	Н	-2.180892	0.056237	-3.416153
Н	-0.418363	-4.668841	0.67824	Br	0	0	3.191218



Figure S12. Optimized structure of **2** (*C*₂ symmetry). Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg): Al1–C1 1.929, Al1–Br1 2.271, C1–C2 1.352, C2–C2* 1.537, C1–Al–C1* 96.92, Al1–C1–C2 101.56, C1–C2–C2* 119.95, C1–Al1–Br1 131.54.



Figure S13. Calculated NMR chemical shifts (ppm) of 1-bromoalumole 2.

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