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Synthesis, structures and insertion reactivity of Lewis acidic 9-aluminafluorenes

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Methods and Materials

All manipulations were performed either under an atmosphere of dry argon or in vacuo using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Solvents (both deuterated and non-deuterated) were stored under argon over activated 4 Å molecular sieves. NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer (¹H: 500.1 MHz, ¹³C{¹H}: 125.8 MHz, ²⁷Al: 104.3 MHz, ¹¹B: 160.5 MHz, ³¹P{¹H}: 162.0 MHz). Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei (¹³C{¹H}) or residual protons (¹H) of the solvent. Microanalyses (C, H, N) were performed on an Elementar vario MICRO cube elemental analyzer. High resolution mass spectrometry was performed on a Thermo Scientific Exactive Plus spectrometer using a LIFDI 700 source from Linden CMS. C₁₂H₈Br₂,¹ C₁₂H₈Li₂,² (η^{5} -1,2,4-C₅H₂tBu₃)AlBr₂³, tBuAlCl₂,⁴ Ph₂tBuSiLi,⁵ SC₄H₃Li⁶ were synthesised according to literature procedures.

Synthetic Procedures

Synthesis of 9-bromo-9-aluminafluorene (1)

2,2'-Dibromobiphenyl (1.93 g, 6.17 mmol, 1.00 equiv) was dissolved in diethyl ether (70 mL) and a 1.6 M *n*BuLi solution (7.71 mL, 12.3 mmol, 2.20 equiv) was slowly added at 0 °C. The suspension was stirred at 0 °C for 30 min and then at room temperature for another 60 min. AlBr₃ (1.97 g, 7.37 mmol, 1.20 equiv) was dissolved in hexane (50 mL) and added slowly at 0 °C. After 30 min, the mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo, the residue taken up in benzene (350 mL) and the resulting solution filtered over Celite. Benzene was removed in vacuo and the oily residue taken up in 1,2-difluorobenzene. After two days at -30 °C, the product was obtained in the form of colourless crystals (1.09 g, 3.27 mmol, 53% yield) suitable for single-crystal X-ray diffraction.

¹**H** NMR (500.1 MHz, C₆D₆): δ = 7.91 (d, 2H, ³*J*_{H-H} = 7.84 Hz, Ar*H*), 7.74–7.72 (m, 2H, Ar*H*), 7.33 (ddd, 2H, ³*J*_{H-H} = 7.58 Hz, ³*J*_{H-H} = 7.59 Hz, ⁴*J*_{H-H} = 1.51 Hz, Ar*H*), 7.26–7.23 (m, 2H, Ar*H*), 3.36 (q, 4H, ³*J*_{H-H} = 7.59 Hz, O(C*H*₂C*H*₃)₂), 0.605 (t, 6H, ³*J*_{H-H} = 7.59 Hz, O(C*H*₂C*H*₃)₂) ppm.

¹³C{¹H} NMR (100.6 MHz, C₆D₆): $\delta = 151.0$ (Ar*C*), 142.4 (Ar*C*, detected by HMBC), 136.2 (Ar*C*-H), 130.0 (Ar*C*-H), 127.4 (Ar*C*-H), 121.5 (Ar*C*-H), 69.6 (O(*C*H₂CH₃)₂), 13.5 (O(*C*H₂*C*H₃)₂) ppm.

LIFDI MS (m/z): calculated for $[C_{16}H_{18}AlBrO-H^+] = 333.0384$; found: 333.0378.

Synthesis of 9-Cp^{3t}-9-aluminafluorene (2)

2,2'-Diiodobiphenyl (1.00 g, 2.46 mmol, 1 equiv) was placed in diethyl ether (50 mL). At 0 °C, a 1.6 M *n*BuLi solution (3.08 mL, 4.93 mmol, 2 equiv) was added and the reaction mixture stirred for 50 min at this temperature. The solvent was removed in vacuo and the residue was taken up in hexane (75 mL). $Cp^{3t}AlBr_2$ (1.24 g, 2.96 mmol, 1.2 equiv) was also dissolved in hexane (75 mL) and added dropwise to the 2,2'-dilithiobiphenyl solution at 0 °C. Stirring was continued for 1 h at room temperature. The suspension was concentrated, centrifuged, and the supernatant decanted. Recrystallisation from a toluene solution in the cold (at -30 °C) and evaporation of the solvent *in vacuo* afforded a colourless solid (939 mg, 2.28 mmol, 92% yield), from which crystals were selected for X-ray diffraction analysis.

¹**H** NMR (500.1 MHz, C₆D₆): δ = 7.85–7.84 (m, 2H, Ar*H*), 7.74–7.73 (m, 2H, Ar*H*), 7.29–7.24 (m, 4H, Ar*H*), 6.86 (s, 2H, Cp*H*), 1.42 (s, 18H, C(C*H*₃)₃), 1.16 (s, 9H, C(C*H*₃)₃) ppm.

¹³C{¹H} NMR (100.6 MHz, C₆D₆): $\delta = 151.0$ (ArC), 140.4, (br, ArC), 136.3 (ArC–H), 130.3 (CC(CH₃)₃–Cp), 129.9 (ArC–H), 127.20 (ArC–H), 126.4 (CC(CH₃)₃-Cp), 121.3 (ArC–H), 109.0 (C(Cp)–H), 34.1 (C(CH₃)₃), 33.6 (C(CH₃)₃), 32.1 (C(CH₃)₃), 32.0 (C(CH₃)₃) ppm.

Elemental analysis: calculated for $[C_{29}H_{37}AI] = 412.60$: C 84.42, H 9.04; found: C 84.09, H 9.25.

Synthesis of 9-tert-butyl-9-aluminafluorene (3)

2,2'-Diiodobiphenyl (300 mg, 739 μ mol, 1 equiv) was dissolved in diethyl ether (10 mL). At 0 °C, a 1.6 M *n*BuLi solution (924 μ L, 1.48 mmol, 2 equiv) was added and stirred at 0 °C for 50 min. The solvent was removed in vacuo and the residue taken up in hexane (15 mL). *t*BuAlCl₂ (137 mg, 887 μ mol, 1.2 equiv) was also dissolved in hexane (15 mL) and added dropwise to the 2,2'-dilithiobiphenyl solution at 0 °C. The reaction mixture was stirred for 1 h at room temperature. The suspension was concentrated, centrifuged, and the solution decanted. The solvent was removed to yield the product as a slightly yellowish solid. Recrystallisation from a toluene solution in the cold (at -30 °C) and evaporation of the solvent *in vacuo* afforded the product as a colourless solid (41.0 mg, 739 μ mol, 23% yield).

¹**H NMR** (500.1 MHz, C₆D₆): $\delta = 8.58$ (d, 1H, ${}^{3}J_{H-H} = 7.00$ Hz, Ar*H*), 8.00–7.97 (m, 1H, Ar*H*), 7.80–7.78 (m, 1H, Ar*H*), 7.70 (d, 1H, ${}^{3}J_{H-H} = 7.80$ Hz, Ar*H*), 7.37–7.33 (m, 2H, Ar*H*), 7.31–7.27 (m, 1H, Ar*H*), 7.10 (dd, 1H, ${}^{3}J_{H-H} = 7.21$ Hz, ${}^{3}J_{H-H} = 7.21$ Hz, Ar*H*), 0.57 (s, 9H, C(C*H*₃)₃) ppm.

¹³C{¹H} NMR (100.6 MHz, C₆D₆): δ = 165.0 (Ar*C*), 151.5 (Ar*C*), 149.4 (Ar*C*–H), 138.6 (Ar*C*–H), 136.8 (Ar*C*–H), 129.6 (Ar*C*–H), 128.6 (Ar*C*), 128.2, (Ar*C*–H), 127.1 (Ar*C*–H), 126.5 (Ar*C*–H), 124.9 (Ar*C*), 123.4 (Ar*C*–H), 28.8 (C(*C*H₃)₃), 17.7 (*C*(*C*H₃)₃) ppm.

Elemental analysis: calculated for $[C_{16}H_{17}AI] = C 81.33$, H 7.25; found: C 81.41, H 7.37.

Synthesis of 9-tert-butyldiphenylsilyl-9-aluminafluorene (4)

9-Bromo-9-aluminafluorene as its diethyl ether adduct (1.0 g, 3.0 mmol, 1.00 equiv) was dissolved in THF (4 mL) and cooled to -78 °C. A 0.7 M solution of *tert*-butyldiphenylsilyllithium in THF (0.7 M, 4.2 mL, 3.0 mmol, 1.00 equiv) was added. After 10 min, the brown reaction solution was allowed to thaw to room temperature and stirred for another 16 h at this temperature. The solvent was removed in vacuo and the residue extracted with toluene. The product was obtained as a colourless solid (550 mg, 1.31 mmol, 44% yield) after recrystallisation from toluene.

¹**H** NMR (500.1 MHz, CD₂Cl₂): $\delta = 7.85$ (d, ³*J*_{HH} = 7.8 Hz, 2H, Ar*H*), 7.76–7.74 (m, 4H, C*H*-Ph), 7.74–7.72 (m, 2H, Ar*H*), 7.39–7.34 (m, 6H, C*H*-Ph), 7.31–7.28 (m, 2H, Ar*H*), 7.15 (m, 2H, C*H*-toluene), 7.18–7.14 (m, 2H, Ar*H*), 7.13 (m, 2H, C*H*-toluene), 3.75–3.73 (m, 4H, C*H*₂-thf), 2.34 (s, 3H, C*H*₃-toluene), 1.70–1.67 (m, 4H, C*H*₂-thf), 0.99 (s, 9H, (CH₃)₃) ppm.

¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ = 152.4 (Ar*C*), 148.35 (Ar*C*), 140.8 (*C*-Ph), 138.4 (*C*-toluene), 137.2 (Ar*C*-H), 137.0 (*C*H-Ph), 129.4 (*C*H-toluene), 128.8 (Ar*C*-H), 128.5 (*C*H-toluene), 128.4 (*C*H-Ph), 128.0 (*C*H-Ph), 126.9 (Ar*C*-H), 125.6 (*C*H-toluene), 121.0 (Ar*C*-H), 73.4 (*C*H₂-thf), 29.6 (*C*(CH₃)₃), 25.6 (*C*H₂-thf), 21.5 (*C*H₃-toluene) ppm.

Elemental analysis: calculated for $[C_{32}H_{35}AlOSi + 0.25 C_6H_6CH_3] = C 78.95$, H 7.32; found: C 78.91, H 7.26.

Synthesis of 9-(2-thienyl)-9-aluminafluorene (5)

9-Bromo-9-aluminafluorene as its diethyl ether adduct (214 mg, 643 μ mol, 1.00 equiv) was dissolved in hexane (15 mL). 2-Thienyllithium (57.9 mg, 643 μ mol, 1.00 equiv) was also dissolved in hexane (15 mL) and added to the first solution at 0 °C. After 10 min, the solution was allowed to thaw to room temperature and stirred at this temperature for 1 h. The suspension was concentrated, centrifuged, and the solution decanted. The solvent was removed to yield the product as a white solid. Colourless crystals of the product were obtained from a toluene solution at -30 °C (171 mg, 508 μ mol, 79% yield).

¹**H** NMR (500.1 MHz, CD₂Cl₂): δ = 7.86 (d, 2H, ³*J*_{H-H} = 7.8 Hz, Ar*H*), 7.76 (dd, 2H, ³*J*_{H-H} = 6.8 Hz, ⁴*J*_{H-H} = 0.8 Hz, Ar*H*), 7.71 (dd, 1H, ³*J*_{H-H} = 4.5 Hz, ⁴*J*_{H-H} = 0.6 Hz, C*H*-thiophene), 7.53 (dd, 1H, ³*J*_{H-H} = 3.1 Hz, ⁴*J*_{H-H} = 0.6 Hz, Ar*H*), 7.33–7.29 (m, 3H, C*H*-thiophene, Ar*H*), 7.20–7.17 (m, 2H, Ar*H*), 4.13 (q, 4H, ³*J*_{H-H} = 7.1 Hz, O(CH₂CH₃)₂), 1.30 (t, 6H, ³*J*_{H-H} = 7.1 Hz, O(CH₂CH₃)₂) ppm.

¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): $\delta = 152.3$ (Ar*C*), 145.4 (Ar*C*), 141.4 (*C*-thiophene, detected by HMBC), 137.4 (*C*H-thiophene), 136.7 (Ar*C*-H), 131.3 (*C*H-thiophene), 129.2 (Ar*C*-H), 128.6 (*C*H-thiophene), 127.0 (Ar*C*-H), 121.1 (Ar*C*-H), 69.6 (O(*C*H₂CH₃)₂), 14.1 (O(CH₂CH₃)₂) ppm.

LIFDI MS (m/z): calculated for $[C_{20}H_{21}AIOS] = 336.1123$; found: 336.1119.

Synthesis of the OPEt₃ adduct of 9-bromo-9-aluminafluorene (1-OPEt₃)

9-Bromo-9-aluminafluorene as diethyl ether adduct (23.7 mg, 71.1 μ mol, 1.00 equiv) was dissolved in benzene and triethylphosphine oxide (9.54 mg, 71.1 μ mol, 1.00 equiv) was added. The solid that precipitated from the solution was filtered off and dissolved in dichloromethane. Colourless crystals (20.8 mg, 52.9 μ mol, 74% yield) were obtained by storing the solution at -30 °C.

¹**H** NMR (500.1 MHz, CD₂Cl₂): δ = 7.79 (d, ³*J*_{HH} = 7.8 Hz, 2H, ArH), 7.57 (dd, ³*J*_{HH} = 6.8 Hz, ⁴*J*_{HH} = 0.8 Hz, 2H, ArH), 7.26 (ddt, ³*J*_{HH} = 7.4 Hz, ³*J*_{HH} = 7.4 Hz, ⁴*J*_{HH} = 1.5 Hz, 2H, ArH), 7.13 (ddt, ³*J*_{HH} = 7.0 Hz, ³*J*_{HH} = 7.1 Hz, ⁴*J*_{HH} = 0.9 Hz, 2H, ArH), 2.02–1.94 (m, 6H, CH₂CH₃), 1.23–1.15 (m, 9H, CH₂CH₃).

¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ = 150.9 (ArC), 146.1 (ArC, detected by HMBC), 135.8 (ArC-H), 128.9 (ArC-H), 126.9 (ArC-H), 120.8 (ArC-H), 18.7 (CH₂CH₃), 18.0 (CH₂CH₃), 5.4 (CH₂CH₃), 5.4 (CH₂CH₃) ppm.

²⁷Al NMR (104.3 MHz, CD₂Cl₂): $\delta = 127$ (s, br) ppm.

³¹P{¹H} NMR (162.0 MHz, CD₂Cl₂): 76.6 ppm.

Elemental analysis: calculated for $[C_{18}H_{23}A|BrOP] = C 54.98$, H 5.90; found: C 55.01, H 5.89.

Synthesis of the I^{*i*}Pr adduct of 9-bromo-9-aluminafluorene (6)

9-Bromo-9-aluminafluorene as diethyl ether adduct (15.0 mg, 45.0 μ mol, 1.00 equiv) was dissolved in benzene and mixed with IPr (7.08 mg, 45.9 μ mol, 1.02 equiv). The solid that precipitated was filtered off. Colourless single crystals of the desired product (15.5 mg, 37.8 μ mol, 84% yield) were obtained by diffusing hexane into a saturated benzene solution at room temperature.

¹**H** NMR (400.1 MHz, C₆D₆): δ = 7.88 (d, 2H, ³*J*_{H-H} = 7.9 Hz, Ar*H*), 7.75–7.73 (m, 2H, Ar*H*), 7.33 (ddd, 2H, ³*J*_{H-H} = 7.8 Hz, ³*J*_{H-H} = 7.8 Hz, ⁴*J*_{H-H} = 1.5 Hz, Ar*H*), 7.22 (ddd, 2H, ³*J*_{H-H} = 7.1 Hz, ³*J*_{H-H} = 7.1 Hz, ⁴*J*_{H-H} = 1.0 Hz, Ar*H*), 7.16 (s, 2H, C*H*^{IPr}), 5.36–5.29 (m, 2H, C*H*(CH)₂^{IPr}), 1.47 (d, 12H, ³*J*_{H-H} = 6.7 Hz, C*H*₃^{IPr}) ppm.

¹³C{¹H} NMR (100.6 MHz, C₆D₆): $\delta = 162.9$ (C^{Carbene}), 151.7 (ArC), 147.1 (ArC), 136.2 (ArC–H), 129.0 (ArC–H), 127.0 (ArC–H), 121.2 (ArC–H), 118.6 (N–HC=CH), 52.8 CH(CH₃)₂, 23.9 CH(CH₃)₂ ppm.

Elemental analysis: calculated for $[C_{21}H_{24}AlBrN_2] = C 61.32$, H 5.88, N 6.81; found: C 61.18, H 5.92, N 6.79.

Synthesis of the IMes adduct of 9-bromo-9-aluminafluorene (7)

9-Bromo-9-aluminafluorene as diethyl ether adduct (15.0 mg, 45.0 µmol, 1.00 equiv) was dissolved in benzene and mixed with IMes (17.9 mg, 58.5 µmol, 1.30 equiv). The solid that precipitated was filtered off. Colourless single crystals of the product (14.9 mg, 26.5 µmol, 59% yield) were obtained from a saturated benzene solution at room temperature.

¹**H** NMR (400.1 MHz, CDCl₃): δ = 7.60–7.57 (m, 2H, Ar*H*), 7.11–7.07 (m, 2H, Ar*H*), 7.07 (s, 2H, –*CH*^{IMes}), 6.96–6.92 (m, 4H, –*CH*^{Mes}), 6.76–6.73 (m, 2H, Ar*H*), 6.43–6.26 (m, 2H, Ar*H*), 2.41 (s, 6H, –*CH*₃^{Mes}), 1.91 (s, 12H, –*CH*₃^{Mes}) ppm.

¹³C{¹H}-NMR (100.6 MHz, CDCl₃): $\delta = 167.6$ (C^{Carbene}, detected by HMBC), 151.2 (ArC), 146.2 (ArC, detected by HMBC), 140.4 ($-C(CH_3)^{Mes}$), 136.3 (ArC–H), 135.7 ($-C(CH_3)^{Mes}$), 134.0 (N– C^{Mes}), 129.9 ($-CH^{Mes}$), 127.9 (ArC–H), 125.6 (ArC–H), 124.2 ($-CH^{1Mes}$), 119.8 (ArC–H), 21.3 ($-CH_3^{Mes}$), 17.8 ($-CH_3^{Mes}$) ppm.

²⁷Al NMR (104.3 MHz, C_6D_6): $\delta = 106$ (s, br) ppm.

Elemental analysis: calculated for [C₃₃H₃₂AlBrN₂] = C 70.34, H 5.72, N 4.97; found: C 69.82, H 5.69, N 4.76.

Synthesis of the CAAC^{Me} adduct of 9-bromo-9-aluminafluorene (8)

9-Bromo-9-aluminafluorene as diethyl ether adduct (15.0 mg, 45.0 μ mol, 1.00 equiv) was dissolved in benzene and CAAC^{Me} (12.8 mg, 45.0 μ mol, 1.00 equiv) was added. The solid that precipitated was filtered off. Colourless single crystals of the product (13.9 mg, 25.5 μ mol, 57% yield) were obtained by diffusing hexane into a saturated benzene solution at room temperature.

¹**H** NMR (500.1 MHz, CD₂Cl₂): $\delta = 7.70$ (d, 2H, ³J = 7.8 Hz, ArH), 7.53 (dd, 1H, ³J = 7.8 Hz, p-Ar-H), 7.32 (br s, 2H, m-Ar-H), 7.15 (dd, 3H, ³J = 7.5 Hz, ArH), 6.92 (br s, 3H, ArH), 2.80 (br s, 2H, CH_iPr), 2.13 (s, 2H, CH₂), 1.70 (s, 6H, C(CH₃)₂), 1.44 (s, 6H, NC(CH₃)₂), 1.08 (s, 6H, CH_{3-i}Pr), 1.06 (two d, 6H each, ³J = 6.6 Hz, CH₃^{iPr}) ppm.

¹³C NMR (125.8 MHz, CD₂Cl₂): $\delta = 237.9$ (carbene-*C*, detected by HMBC), 151.2 (Ar*C*^{Fl}), 145.6 (*o*-Dipp-*C*_q), 136.5 (Ar*C*^{Fl}), 134.2 (*i*-Dipp-*C*_q), 130.8 (*p*-Dipp-*C*H), 128.5 (Ar*C*H^{Fl}), 126.5 (Ar*C*H^{Fl}), 126.5 (s, 4C, *m*-Dipp-CH), 84.0 (*C*_q(CH₃)₂), 56.9 (CH₂), 51.0 (*C*_q(CH₃)₂-CH₂), 30.0 (C(*C*H₃)₂), 29.3 (*C*H(CH₃)₂), 24.8 (CH(*C*H₃)₂) ppm.

LIFDI MS (m/z): calculated for $[C_{32}H_{39}AlBr] = 543.2076$; found: 543.2068.

Synthesis of the DMAP adduct of 9-bromo-9-aluminafluorene (9)

9-Bromo-9-aluminafluorene as diethyl ether adduct (15.0 mg, 45.0 μ mol, 1.00 equiv) was dissolved in benzene and mixed with DMAP (5.50 mg, 45.0 μ mol, 1.00 equiv). The solid that precipitated was filtered off and dissolved in dichloromethane. Colourless single crystals of the product (15.9 mg, 41.7 μ mol, 93% yield) were obtained from a saturated dichloromethane solution in the cold (at -30 °C).

¹**H** NMR (500.1 MHz, CDCl₃): $\delta = 8.20-8.13$ (m, 2H, CH^{-DMAP}), 7.77 (d, 2H, ${}^{3}J_{H-H} = 7.90$ Hz, ArH), 7.56–7.54 (m, 2H, ArH), 7.21 (ddd, 2H, ${}^{3}J_{H-H} = 7.70$ Hz, ${}^{3}J_{H-H} = 7.71$ Hz, ${}^{4}J_{H-H} = 1.42$ Hz, ArH), 7.08–7.05 (m, 2H, ArH), 6.43 (d, 2H, ${}^{3}J_{H-H} = 7.33$ Hz, CH^{-DMAP}), 2.97 (s, 6H, N(CH₃)₂) ppm.

¹³C{¹H} NMR (100.6 MHz, CDCl₃): $\delta = 156.4$ (*C*(N(CH₃)₂), 151.5 (Ar*C*), 146.6 (*C*H^{-DMAP}), 144.9 (Ar*C*), 136.2 (Ar*C*–H), 129.1 (Ar*C*–H), 126.8 (Ar*C*–H), 120.9 (Ar*C*–H), 107.1 (*C*H^{-DMAP}), 39.7 (N(*C*H₃)₂) ppm.

Elemental analysis: calculated for [C₁₉H₁₈AlBrN₂] = C 59.86; H 4.76; N, 7.35, found: C₁₉H₁₈AlBrN₂: C 59.49; H 5.07; N, 6.93.

Reaction of 9-bromo-9-aluminafluorene with (tert-butylimino)mesitylborane (10)

9-Bromo-9-aluminafluorene as diethyl ether adduct (905 mg, 2.72 mmol, 1.00 equiv) was dissolved in toluene and cooled to -70 °C. A solution of (*tert*-butylimino)mesitylborane in heptane (0.840 M, 3.23 mL, 2.72 mmol, 1.00 equiv) was added dropwise. The solution was allowed to thaw to room temperature and the solvent removed under reduced pressure. The product was obtained after recrystallisation from difluorobenzene at -30 °C as colourless crystals (1.23 g, 2.30 mmol, 85% yield).

¹**H** NMR (500.1 MHz, CDCl₃): δ = 7.95 (ddd, ³*J*_{HH} = 7.5 Hz, ⁴*J*_{HH} = 1.5 Hz, ⁵*J*_{HH} = 0.7 Hz, 1H, Ar*H*), 7.41–7.48 (m, 3H, Ar*H*), 7.35 (ddd, ³*J*_{HH} = 7.1 Hz, ³*J*_{HH} = 7.1 Hz, ⁵*J*_{HH} = 1.3 Hz, 1H, Ar*H*), 7.26 (dd, ³*J*_{HH} = 7.8 Hz, ⁴*J*_{HH} = 1.0 Hz, 1H, Ar*H*), 7.12–7.15 (m, 1H, Ar*H*), 7.04–7.07 (m, 1H, Ar*H*), 6.75 (s, 1H, –*CH*^{Mes}), 6.46 (s, 1H, –*CH*^{Mes}), 3.84–3.92 (m, 2H, *CH*₂CH₃), 3.70–3.76 (m, 2H, *CH*₂CH₃), 2.64 (s, 3H, –*CH*³^{Mes}), 2.17 (s, 3H, –*CH*³^{Mes}), 1.55 (s, 3H, –*CH*³^{Mes}), 1.29 (s, 9H, NC(*CH*₃)₃), 1.12 (t, ³*J*_{HH} = 7.1 Hz, 6H, *CH*₂*CH*₃) ppm.

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ = 151.1 (ArC), 148.85 (ArC), 148.1 (BC^{Mes}), 148.0 (ArC), 142.9 (ArC), 137.7 (-*C*(CH₃)^{Mes}), 136.3 (ArC–H), 135.7 (ArC–H), 135.0 (-*C*(CH₃)^{Mes}), 134.4 (-*C*(CH₃)^{Mes}), 130.4 (ArC–H), 129.2 (ArC–H), 127.1 (ArC–H), 127.1 (ArC–H), 127.0 (-*C*H^{Mes}), 126.9 (-*C*H^{Mes}), 125.7 (ArC–H), 125.5 (ArC–H), 66.9 (*C*H₂CH₃), 56.5 (*C*(CH₃)₃), 34.0 ((*C*H₃)₃), 24.6 (-*C*(*C*H₃)^{Mes}), 22.2 (-*C*(*C*H₃)^{Mes}), 21.2 (-*C*(*C*H₃)^{Mes}), 12.7 (CH₂*C*H₃) ppm.

¹¹**B** NMR (160.5 MHz, C_6D_6): $\delta = 43.7$ ppm.

LIFDI MS (m/z): calculated for $[C_{29}H_{38}AlBBrNO] = 533.2036$; found: 533.2040.

NMR Spectra



Figure S1. ¹H NMR spectrum of 1 in d_6 -benzene.



Figure S2. ¹³C{¹H} NMR spectrum of **1** in d_6 -benzene.



Figure S3. ¹H NMR spectrum of **2** in d_6 -benzene.



Figure S4. ¹³C{¹H} NMR spectrum of **2** in d_6 -benzene.

Diffusion coefficient of **3**, as determined by ¹H DOSY NMR: $D = 8.623 \cdot 10^{-10} \frac{m^2}{s}$

According to the relation $= \frac{k_B \cdot T}{6\pi \cdot \eta \cdot r_o}$, the calculated hydrodynamic radius at 25 °C is 4.1 Å.

The experimental hydrodynamic radius of the dimer, estimated from its solid-state structure, is 5.4 Å.



Figure S5. ¹H NMR spectrum of **3** in d_6 -benzene.



Figure 6. ¹³C $\{^{1}H\}$ NMR spectrum of **3** d_{6} -benzene.



Figure S8. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectrum of 4 in CD₂Cl₂.





40

30

20

ppm



Figure S12. ¹³C $\{^{1}H\}$ NMR spectrum of **1-OPEt**₃ in CD₂Cl₂.



Figure S13. ³¹P{¹H} NMR spectrum of 1-OPEt₃ in CD_2Cl_2 .



Figure S13. ³¹P{¹H} NMR spectrum of **2-OPEt**₃ in CD_2Cl_2 .



Figure S15. ³¹P{¹H} NMR spectrum of 4-OPEt₃ in CD_2Cl_2 .



Figure S16. ³¹P{¹H} NMR spectrum of **5-OPEt**₃ in CD_2Cl_2 .



Figure S17. ¹H NMR spectrum of **6** in d_6 -benzene.



Figure S18. ¹³C $\{^{1}H\}$ NMR spectrum of 6 in d_{6} -benzene.



Figure S19. ¹H NMR spectrum of 7 in CDCl₃.









Figure S22. ¹³C $\{^{1}H\}$ NMR spectrum of 8 in CD₂Cl₂.



Figure S23. ¹H NMR spectrum of 9 in CDCl₃.





Figure S25. ¹H NMR spectrum of **10** in CDCl₃.



Figure S26. $^{13}C{^{1}H}$ NMR spectrum of 10 in CDCl₃.



Figure S27. ¹¹B NMR spectrum of 10 in CDCl₃.

Crystallographic Details

The crystal data of **1-10** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,⁷ refined with the *SHELXL* program⁸ and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

The crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC-2088754 (1), CCDC-2088756 (1-OPEt₃), CCDC-2088758 (2), CCDC-2088757 (3), CCDC-2088751 (4), CCDC-2088750 (5), CCDC-2088759 (6), CCDC-2088752 (7), CCDC-2088753 (8), CCDC-2088755 (9), and CCDC-2088760 (10). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data request/cif.

Crystal data for 1: The molecule is disordered, therefore the displacement restraints SIMU, RIGU, and ISOR were applied. The displacement parameters of atoms C1 > C4 and C1 > C12 of the residues 2, 12 and 1 were restrained to the same value with the similarity restraint SIMU. The Uii displacement parameters of atoms C1 > C4 and C1 > C12 of the residues 2, 12 and 1 were restrained with the ISOR keyword to approximate isotropic behaviour. The atomic displacement parameters of atoms C1 > C4and C1 > C12 of the residues 2,12 and 1 were restrained with the RIGU keyword in the ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.004 for both parameters s1 and s2 were used). $C_{16}H_{18}AlBrO$, $M_r = 333.19$, colourless needle, $0.268 \times 0.116 \times 0.07 \text{ mm}^3$, monoclinic space group C2/c, a = 25.3861(8) Å, b = 7.1604(3) Å, c = 18.1719(6) Å, $\beta = 108.6420(10)^{\circ}$, V = 3129.89(19) Å³, Z = 8, $\rho_{calcd} = 1.414$ g·cm⁻³, $\mu = 2.673$ mm⁻¹ ¹, F(000) = 1360, T = 105(2) K, $R_I = 0.0653$, $wR^2 = 0.1382$, 3194 independent reflections [20 \leq 52.742°] and 202 parameters.

Crystal data for **2**: C₂₉H₃₇Al, $M_r = 412.56$, colourless block, $0.428 \times 0.28 \times 0.279 \text{ mm}^3$, triclinic space group P $\overline{1}$, a = 11.460(3) Å, b = 13.928(4) Å, c = 17.400(4) Å, $\alpha = 105.12(2)^\circ$, $\beta = 93.95(2)^\circ$, $\gamma = 111.893(12)^\circ$, V = 2444.4(11) Å³, Z = 4, $\rho_{calcd} = 1.121 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 0.096 \text{ mm}^{-1}$, F(000) = 896, T = 100(2) K, $R_I = 0.0665$, $wR^2 = 0.1257$, 10092 independent reflections $[2\theta \le 53.004^\circ]$ and 569 parameters.

Crystal data for **3**: C₃₂H₃₄Al₂, $M_r = 472.55$, colourless block, $0.866 \times 0.576 \times 0.382$ mm³, triclinic space group P $\overline{1}$, a = 8.6539(19) Å, b = 8.928(2) Å, c = 8.996(4) Å, $\alpha = 81.732(8)^\circ$, $\beta = 72.45(3)^\circ$,

 $\gamma = 83.028(9)^{\circ}$, V = 653.5(4) Å³, Z = 1, $\rho_{calcd} = 1.201$ g·cm⁻³, $\mu = 0.130$ mm⁻¹, F(000) = 252, T = 95(2) K, $R_I = 0.0320$, $wR^2 = 0.0817$, 2641 independent reflections $[20 \le 52.738^{\circ}]$ and 157 parameters.

Crystal data for 4: $C_{70}H_{75}Al_2O_2Si_2$, $M_r = 1058.44$, colourless block, $0.477 \times 0.377 \times 0.248$ mm³, triclinic space group P $\overline{1}$, a = 10.039(2) Å, b = 13.899(2) Å, c = 22.275(6) Å, $\alpha = 104.494(13)^\circ$, $\beta = 94.867(17)^\circ$, $\gamma = 98.565(13)^\circ$, V = 2951.4(11) Å³, Z = 2, $\rho_{calcd} = 1.191$ g·cm⁻³, $\mu = 0.135$ mm⁻¹, F(000) = 1130, T = 100(2) K, $R_I = 0.0431$, $wR^2 = 0.1146$, 11953 independent reflections $[20 \le 52.744^\circ]$ and 691 parameters.

Crystal data for **5**: C₂₀H₂₁AlOS, $M_r = 336.41$, colourless block, $0.659 \times 0.152 \times 0.116 \text{ mm}^3$, orthorhombic space group $P2_12_12_1$, a = 7.1151(11) Å, b = 15.212(3) Å, c = 16.066(3) Å, V = 1739.0(5) Å³, Z = 4, $\rho_{calcd} = 1.285 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 0.238 \text{ mm}^{-1}$, F(000) = 712, T = 103(2) K, $R_l = 0.0658$, $wR^2 = 0.1023$, 3531 independent reflections [2 $\theta \le 52.738^\circ$] and 210 parameters.

Crystal data for **1-OPEt**₃: C₁₈H₂₃AlBrOP, $M_r = 393.22$, colourless plate, $0.42 \times 0.154 \times 0.148 \text{ mm}^3$, monoclinic space group $P2_1/n$, a = 8.254(2) Å, b = 23.994(7) Å, c = 19.369(6) Å, $\beta = 102.014(8)^\circ$, V = 3752.1(19) Å³, Z = 8, $\rho_{calcd} = 1.392 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 2.323 \text{ mm}^{-1}$, F(000) = 1616, T = 103(2) K, $R_l = 0.1380$, $wR^2 = 0.1603$, 7620 independent reflections $[2\theta \le 52.736^\circ]$ and 403 parameters.

Crystal data for **6**: C₂₁H₂₄AlBrN₂, $M_r = 411.31$, colourless block, $0.311 \times 0.219 \times 0.216 \text{ mm}^3$, monoclinic space group $P2_1/c$, a = 8.3702(2) Å, b = 23.2949(6) Å, c = 20.4550(5) Å, $\beta = 98.1890(10)^\circ$, V = 3947.71(17) Å³, Z = 8, $\rho_{calcd} = 1.384 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 2.133 \text{ mm}^{-1}$, F(000) = 1696, T = 103(2) K, $R_I = 0.0392$, $wR^2 = 0.0853$, 8050 independent reflections $[2\theta \le 52.742^\circ]$ and 459 parameters.

Crystal data for 7: C₃₃H₃₂AlBrN₂, $M_r = 563.49$, colourless block, $0.372 \times 0.27 \times 0.241$ mm³, monoclinic space group $P2_1/m$, a = 8.523(3) Å, b = 19.290(7) Å, c = 8.998(3) Å, $\beta = 105.63(2)^\circ$, V = 1424.6(9) Å³, Z = 2, $\rho_{calcd} = 1.314$ g·cm⁻³, $\mu = 1.498$ mm⁻¹, F(000) = 584, T = 100(2) K, $R_I = 0.0376$, $wR^2 = 0.1018$, 2888 independent reflections [$2\theta \le 52.038^\circ$] and 175 parameters.

Crystal data for 8: C₃₂H₃₉AlBrN, $M_r = 544.53$, colourless block, $0.391 \times 0.227 \times 0.132 \text{ mm}^3$, monoclinic space group $P2_1/c$, a = 10.4798(12) Å, b = 15.3785(17) Å, c = 17.510(2) Å, $\beta = 90.889(2)^\circ$, V = 2821.7(6) Å³, Z = 4, $\rho_{calcd} = 1.282 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 1.508 \text{ mm}^{-1}$, F(000) = 1144, T = 296(2) K, $R_I = 0.0651$, $wR^2 = 0.1187$, 5761 independent reflections $[2\theta \le 52.74^\circ]$ and 324 parameters. Crystal data for **9:** C₁₉H₁₈AlBrN₂, $M_r = 381.24$, colourless block, $0.256 \times 0.189 \times 0.117 \text{ mm}^3$, monoclinic space group $P2_1/n$, a = 8.4472(3) Å, b = 14.5331(5) Å, c = 14.8704(6) Å, $\beta = 105.110(2)^\circ$, V = 1762.43(11) Å³, Z = 4, $\rho_{calcd} = 1.437 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 2.383 \text{ mm}^{-1}$, F(000) = 776, T = 103(2) K, $R_I = 0.0488$, $wR^2 = 0.0819$, 3600 independent reflections $[2\theta \le 52.744^\circ]$ and 210 parameters.

Crystal data for **10**: The solvent and three of the ethyl groups are disordered. For this reason, the atomic displacement parameters of atoms C1 and C2 of the residues 3, 13, 6, 16, 7 and 17 as well as C1 > C6 of the residue 110, were restrained with the RIGU keyword in the ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.004 for both parameters s1 and s2 were used). The displacement parameters of atoms C1 and C2 of the residues 3, 13, 6, 16, 7 and 17 as well as C1 > C6 of the residue 110 were restrained to the same value with the similarity restraint SIMU. $C_{61}H_{79}Al_2B_2Br_2N_2O_2$, $M_r = 1107.66$, colourless block, $0.331 \times 0.178 \times 0.176$ mm³, monoclinic space group $P2_1/c$, a = 15.9465(6) Å, b = 17.2519(7) Å, c = 21.7463(9) Å, $\beta = 102.646(2)^\circ$, V = 5837.4(4) Å³, Z = 4, $\rho_{calcd} = 1.260$ g·cm⁻³, $\mu = 1.461$ mm⁻¹, F(000) = 2324, T = 103(2) K, $R_I = 0.0816$, $wR^2 = 0.1549$, 11918 independent reflections $[20 \le 52.744^\circ]$ and 686 parameters.



Figure S28. Solid-state structure of **1**. Ellipsoids are set at 50% probability. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1–C1 1.959(5), C1–C2 1.420(6), C2–C3 1.506(5), C3–C4 1.416(6), C4–Al 1.953(5), C4–C5 1.399(6), C5–C6 1.386(7), C6–C7 1.391(7), C7–C8 1.387(6), C8–C3 1.396(6), C2–C9 1.397(6), C9–C10 1.394(6), C10–C11 1.382(7), C11–C12 1.396(7), C12–C1 1.397(6); Al-C1-C2 106.3(3), C1-C2-C3 117.5(4), C2-C3-C4 117.5(4), C3-C4-Al 106.7(3), C4-Al-C1 92.0(2).



Figure S29. Solid-state structure of **2**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1–C1 1.969(2), C1–C2 1.411(3), C2–C3 1.497(3), C3–C4 1.417(3), C4–Al1 1.9716(19), C4–C5 1.394(3), C5–C6 1.394(3), C6–C7 1.382(3), C7–C8 1.382(3), C8–C3 1.397(3), C2–C9 1.402(3), C9–C10 1.382(3), C10–C11 1.387(3), C11–C12 1.389(3), C12–C1 1.392(3); Al1-C1-C2 107.6(1), C1-C2-C3 117.5(2), C2-C3-C4 116.9(2), C3-C4-Al1 107.4(1), C4-Al1-C1 90.19(8); C1-Al1-C4-C3 6.9.



Figure S30. Solid-state structure of **3**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1–C1 2.107(1), C1–C2 1.433(2), C2–C3 1.491(2), C3–C4 1.411(2), C4–Al1 1.966(1), C4–C5 1.400(2), C5–C6 1.391(2), C6–C7 1.391(2), C7–C8 1.387(2), C8–C3 1.399(2), C2–C9 1.396(2), C9–C10 1.376(2), C10–C11 1.387(2), C11–C12 1.387(2), C12–C1 1.415(2), Al1–Al1* 2.6285(8), Al1–C1* 2.147(1); Al1-C1-C2 103.63(8), C1-C2-C3 118.6(1), C2-C3-C4 116.5(1), C3-C4-Al1 110.41(9), C4-Al1-C1 88.05(5); C1-C2-C3-C4 17.7.



Figure S31. Solid-state structure of 4. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1–C1 1.973(2), C1–C2 1.418(2), C2–C3 1.497(2), C3–C4 1.423(2), C4–Al1 1.985(2), C4–C5 1.396(2), C5–C6 1.396(2), C6–C7 1.384(3), C7–C8 1.387(3), C8–C3 1.401(6), C2–C9 1.404(2), C9–C10 1.382(3), C10–C11 1.388(3), C11–C12 1.394(2), C12–C1 1.399(2); Al-C1-C2 107.6(1), C1-C2-C3 117.3(1), C2-C3-C4 117.3(1), C3-C4-Al1 107.4(1), C4-Al1-C1 90.29(7).



Figure S32. Solid-state structure of **5**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al–C1 1.963(4), C1–C2 1.413(5), C2–C3 1.506(5), C3–C4 1.420(5), C4–A1 1.975(4), C4–C5 1.396(5), C5–C6 1.389(5), C6–C7 1.376(6), C7–C8 1.395(5), C8–C3 1.398(5), C2–C9 1.403(5), C9–C10 1.393(5), C10–C11 1.381(6), C11–C12 1.388(5), C12–C1 1.406(5); Al-C1-C2 108.0(3), C1-C2-C3 116.9(3), C2-C3-C4 117.2(3), C3-C4-A1 107.2(3), C4-Al-C1 90.5(2).



Figure S33. Solid-state structure of 1-OPEt₃. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al–C1 1.961(6), C1–C2 1.408(8), C2–C3 1.509(7), C3–C4 1.402(8), C4–Al 1.960(5), C4–C5 1.401(7), C5–C6 1.389(8), C6–C7 1.376(9), C7–C8 1.376(8), C8–C3 1.400(8), C2–C9 1.400(8), C9–C10 1.395(8), C10–C11 1.366(9), C11–C12 1.399(9), C12–C1 1.398(7); Al-C1-C2 107.2(4), C1-C2-C3 117.3(5), C2-C3-C4 116.9(5), C3-C4-Al 107.7(2), C4-Al-C1 90.7(2).



Figure S34. Solid-state structure of **6**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1–C1 1.977(3), C1–C2 1.419(3), C2–C3 1.506(3), C3–C4 1.416(3), C4–Al1 1.980(2), C4–C5 1.398(3), C5–C6 1.389(4), C6–C7 1.385(4), C7–C8 1.383(4), C8–C3 1.395(4), C2–C9 1.396(4), C9–C10 1.391(4), C10–C11 1.390(4), C11–C12 1.384(4), C12–C1 1.404(3); Al1-C1-C2 107.40(17), C1-C2-C3 117.4(2), C2-C3-C4 117.2(2), C3-C4-Al1 107.5(2), C4-Al1-C1 90.3(1).



Figure S35. Solid-state structure of 7. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1–C1 1.971(3), C1–C2 1.420(3), C2–C3 1.505(5), C3–C4 1.420(3), C4–Al1 1.971(3), C4–C5 1.390(4), C5–C6 1.395(4), C6–C7 1.381(4), C7–C8 1.388(4), C8–C3 1.399(4), C2–C9 1.399(4), C9–C10 1.388(4), C10–C11 1.381(4), C11–C12 1.395(4), C12–C1 1.390(4); Al1-C1-C2 107.7(2), C1-C2-C3 117.0(2), C2-C3-C4 117.0(2), C3-C4-Al1 107.7(2), C4-Al1-C1 90.2(2).



Figure S36. Solid-state structure of **8**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1–C1 1.973(3), C1–C2 1.414(4), C2–C3 1.497(4), C3–C4 1.419(4), C4–Al1 1.970(3), C4–C5 1.394(4), C5–C6 1.393(5), C6–C7 1.387(5), C7–C8 1.386(5), C8–C3 1.396(4), C2–C9 1.397(5), C9–C10 1.394(5), C10–C11 1.380(5), C11–C12 1.387(5), C12–C1 1.401(4); Al1-C1-C2 107.1(2), C1-C2-C3 117.7(3), C2-C3-C4 117.2(3), C3-C4-Al1 107.3(2), C4-Al1-C1 90.6(1).



Figure S37. Solid-state structure of **9**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1–C1 1.966(3), C1–C2 1.418(4), C2–C3 1.502(4), C3–C4 1.419(4), C4–Al1 1.953(2), C4–C5 1.394(4), C5–C6 1.393(5), C6–C7 1.387(5), C7–C8 1.394(5), C8–C3 1.394(4), C2–C9 1.409(4), C9–C10 1.383(5), C10–C11 1.382(5), C11–C12 1.402(4), C12–C1 1.400(4); Al1-C1-C2 106.3(2), C1-C2-C3 117.6(3), C2-C3-C4 116.7(3), C3-C4-Al1 107.2(2), C4-Al1-C1 91.1(1).



Figure S38. Solid-state structure of **10**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1–C1 1.945(3), C1–C2 1.414(5), C2–C3 1.490(5), C3–C4 1.415(5), C4–B1 1.642(5), B1–N1 1.403(5), N1–Al1 1.853(3), C4–C5 1.416(5), C5–C6 1.388(5), C6–C7 1.385(6), C7–C8 1.377(5), C8–C3 1.419(5), C2–C9 1.396(5), C9–C10 1.387(5), C10–C11 1.386(5), C11–C12 1.383(5), C12–C1 1.405(5); Al1-C1-C2 121.5(3), C1-C2-C3 120.4(3), C2-C3-C4 124.5(3), C3-C4-B1 130.3(3), C4-B1-N1 122.8(3), B1-N1-Al1 111.7(2), N1-Al1-C1 109.3(1).

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