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Synthesis and characterisation of aluminium (III) imine bis(phenolate) complexes with application for the Polymerisation of *rac*-LA

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1. Experimental

1.1. General Procedures

Trimethylaluminium (2M in hexane, Aldrich) was used as supplied. All other starting materials were used as received from either Sigma Aldrich or TCI, Ltd. *rac*-lactide (Aldrich) was recrystallized from dry toluene and sublimed twice prior to use in polymerisation reactions.

Preparation of all metal complexes and subsequent ROP of *rac*-lactide were performed under an inert atmosphere of argon using standard Schlenk or glove-box techniques. All solvents used in the preparation of metal complexes were dry and obtained *via* an SPS (Solvent Purification System).

1.2. NMR Spectroscopy

Solution ^{1}H and $^{13}C\{^{1}H\}$ NMR experiments were performed at ambient temperature unless otherwise stated using a Bruker Avance-300, Bruker DRX400 or Bruker DRX500 MHz FT-NMR spectrometer with samples dissolved in $CDCl_3$, DMSO-d_6, $C_6D_5CD_3$ or C_6D_6. $CDCl_3$ for analysis of complexes was distilled from calcium hydride prior to use. C_6D_6 for complex analysis was distilled and stored over sodium. Wilmad 5 mm NMR tubes were used for ligand and polymer characterisation, while NMR tubes fitted with Young's taps were used for complexes and kinetic experiments. All chemical shifts are quoted as δ values in ppm relative to residual protio solvent resonances and all coupling constants are given in Hertz.

Homonuclear decoupled ^{1}H NMR spectra were recorded on a Bruker DRX400 or Bruker DRX500 MHz FT-NMR spectrometer and the methine region of the spectra analysed for the determination of the P_r value using equations given in the literature.[1]

1.3. Gel Permeation Chromatography (GPC)

GPC analyses were performed on a Polymer Laboratories PL-GPC 50 integrated system using PLgel 5µm MIXED-D 300 x 7.5 mm column at 35°C, using THF as the solvent at a flow rate of 1.0 ml/min. The polydispersity index (PDI) was determined from M_n/M_w where M_n is the number average molecular weight and M_w is the weight average molecular weight. The polymers were referenced to 11 narrow molecular weight polystyrene standards with a range of M_w 615 – 568000Da.

1.4. Mass Spectrometry

High-resolution mass spectrometry of ligands, and intermediates thereof, were recorded on a micrOTOFQ electrospray quadrupole time-of-flight (ESI-TOF) spectrometer. The samples were dissolved in methanol and the spectra recorded in positive mode.

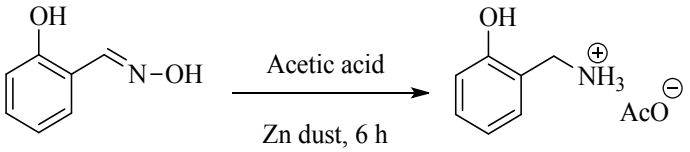
1.5. Elemental Analysis

Elemental analysis was performed by Mr. A. Carver at the University of Bath, on an Exeter Analytical CE440 Elemental Analyzer, or by Mr Stephen Boyer (London Metropolitan University).

1.6. Synthetic Procedures

1.6.1. Starting Materials

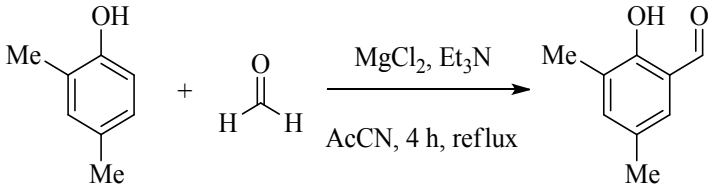
Salicylammonium acetate [2] and 3,5-dimethyl-2-hydroxybenzyaldehyde[3] were synthesised according to literature procedures.



Salicylaldoxime (5.8g, 42.3 mmol) was dissolved in Acetic acid (200ml, 3.47mmol) before the addition of zinc dust (17.0g) at a slow rate and with vigorous stirring to minimise the exotherm. (Figure 5.1) The reaction mixture was left to stir at room temperature for 6 hours before removing the zinc dust via filtration and most of the acetic acid by rotary evaporation. The resulting yellow oil was allowed to cool to room temperature before adding diethyl ether to cause a white solid to form. The white solid salicylammonium acetate (5.53g, 30.2 mmol, 71%) was isolated via filtration, washed with diethyl ether and dried under high vacuum.

^{1}H NMR (d_6-DMSO) 1.80 (3H, s, CH_3(C=O)), 3.86 (2H, s, PhCH_2N), 6.72 (1H, td J = 7.5, 0.9 Hz, Ar-H), 6.84 (1H, dd J = 7.5, 0.9 Hz, Ar-H), 7.11 (1H, td J = 7.5, 0.9 Hz, Ar-H), 7.18 (1H, dd J = 7.5, 0.9 Hz, Ar-H).

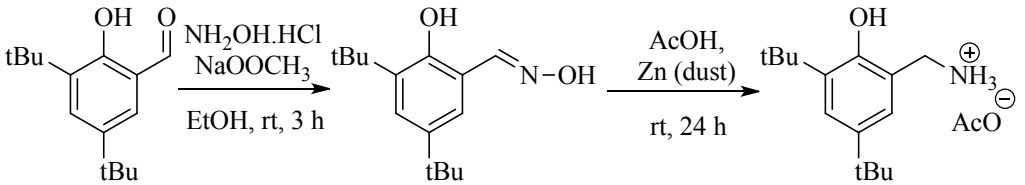
^{13}C{^{1}H} NMR (d_6-DMSO) 22.9 (H_3C(C=O)), 41.3 (PhCH$_2$N), 116.2, 118.2, 124.6, 129.0, 129.5 (Ar-CH), 158.0 (Ar-O), 174.1 (C=O).



2,4-dimethylphenol (10.0 g, 81.9 mmol), magnesium chloride (11.7 g, 123.0 mmol) and triethylamine (31.1 g, 307.0 mmol) were charged to a round-bottom flask and stirred with acetonitrile (400ml). Paraformaldehyde (16.6 g, 552.0 mmol) was added and the reaction mixture refluxed for 4 hours. (Figure 5.3) The solution was cooled before the addition of 5% aqueous hydrochloric acid (250ml). The product was extracted using diethyl ether (2x 200ml, 2x 150ml). Removal of the solvent by rotary evaporation yielded a yellow oil that was further purified via flash chromatography (9.0 g, 59.9 mmol, 73% yield)

^{1}H NMR ($CDCl_3$) 2.21 (3H, s, Me-Ph), 2.27 (3H, s, Me-Ph), 7.08 (1H, s, Ar-H), 7.15 (1H, s, Ar-H), 9.74 (1H, s, CHO), 11.08 (1H, s, OH)

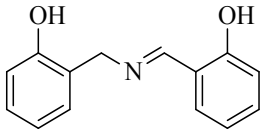
^{13}C{^{1}H} NMR ($CDCl_3$) 14.6 (H_3C-Ph), 20.1 (H_3C-Ph), 119.7 (Ar-CH), 126.4 (Ar-C), 128.8 (Ar-C), 131.8 (Ar-C), 139.0 (Ar-CH), 157.9 (Ar-OH), 157.9 (*C*HO).



3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (7.00g, 29.9 mmol) was dissolved in ethanol (75ml) before the addition of a 10% molar excess of hydroxylamine hydrochloride

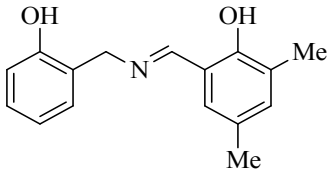
(2.28g, 32.9 mmol) and sodium acetate (2.70g, 32.9 mmol). The reaction mixture was stirred at room temperature for 4 hours before the solvent was removed by rotary evaporation. Further drying under high vacuum yielded a white solid that was washed with water to remove all salts. The remaining solid was dried under vacuum to yield 3,5-di-*tert*-butyl-2-hydroxybenzyaldoxime (7.40g, 29.7 mmol, 99% yield).
^{1}H NMR ($CDCl_3$) 1.31 (9H, s, $C(CH_3)_3$), 1.45 (9H, s, $C(CH_3)_3$), 7.02 (1H, d (J = 2.4 Hz), Ar-H), 7.37 (1H, d (J = 2.4 Hz), Ar-H), 8.25 (1H, s, CH=N), 10.1 (1H, bs, Ar-OH).
^{13}C{^{1}H} NMR ($CDCl_3$) 29.8 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 116.0 (Ar-*C*), 125.9 (Ar-*C*), 126.6 (Ar-*C*), 136.9 (Ar-*C*H), 141.6 (Ar-*C*H), 154.5 (*C*H=N), 154.7 (Ar-O).
3,5-di-*tert*-butyl-2-hydroxybenzaldoxime (7.40g, 29.7 mmol) was dissolved in acetic acid (250 ml) and cooled in a water bath (15 °C). Zinc dust (12.0g) was added gradually to the solution and the reaction mixture stirred for 24 hours. The suspension was filtered to remove the zinc metal and acetic acid removed via rotary evaporation to give an orange oil. Further drying under high vacuum yielded a white solid (8.60g, 29.1 mmol, 98% yield)
^{1}H NMR ($(CD_3)_2SO$) 1.24 (9H, s, $C(CH_3)_3$), 1.35 (9H, s, $C(CH_3)_3$), 1.84 (3H, s, CH_3C=O), 3.89 (2H, s, N=CH_2), 7.03 (1H, d (J = 2.2 Hz), Ar-H), 7.12 (1H, d (J = 2.2 Hz), Ar-H).

1.6.2. Imine bis(phenolate) ligands



H_2**1**

Salicylammonium acetate (2.00g, 10.9 mmol) and sodium bicarbonate (3.67g, 43.7 mmol) were mixed with Ethanol (100ml) and heated to 60°C. Salicylaldehyde (1.33g, 10.9 mmol) was added drop-wise to the reaction mixture and left to stir for 2 hours. The reaction mixture was then hot filtered and washed with hot ethanol to remove insoluble salts. Solvent was removed by rotary evaporation and the resulting yellow solid washed with distilled water to remove any soluble sodium salts. The disalicylaldimine, a yellow solid, was washed with hexane to remove unreacted aldehyde and dried under high vacuum (1.68g, 7.39 mmol, 68%).
^{1}H NMR (d_6-DMSO) 4.73 (2H, s, $PhCH_2N$), 6.85 (4H, m, Ar-H), 7.15 (2H, m, Ar-H), 7.32 (1H, td J = 7.5, 0.9 Hz, Ar-H), 7.45 (1H, dd J = 0.9, 7.5 Hz, Ar-H), 8.63 (1H, s, CH=N), 9.65 (1H, bs, OH), 13.72 (1H, bs, OH).
^{13}C{^{1}H} NMR (d_6-DMSO) 57.03 (CH_2N=C), 115.1, 116.5, 118.4, 118.6, 119.0, 124.4, 128.5, 129.3, 131.6, 132.3 (Ar-CH), 155.2 (Ar-O), 160.89 (*C*H=N), 166.1 (Ar-O).
m/z calc. $[C_{14}H_{13}NO_2+Na]^+$ = 250.0844, found 250.0831.



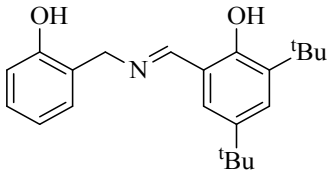
H_2**2**

Salicylammonium acetate (2.00g, 10.9 mmol) and sodium bicarbonate (3.67g, 43.7 mmol) were mixed with ethanol (80 ml) and heated to 60°C. 3,5-dimethyl-2-hydroxybenzyaldehyde (1.64g, 10.9 mmol) in ethanol (20 ml) was added drop-wise to the reaction mixture and left to stir for 2 hours. The reaction mixture was then hot filtered and washed with hot ethanol to remove insoluble $NaHCO_3$. Solvent was removed by rotary evaporation and the resulting yellow solid washed with distilled water to remove any soluble sodium salts. The yellow solid was washed with hexane to remove unreacted aldehyde and dried under high vacuum (1.87g, 7.32 mmol, 67% yield).

^{1}H NMR (DMSO-d_6) 2.11 (3H, s, Me-Ph), 2.21 (3H, s, Me-Ph), 4.72 (2H, s, N-CH_2), 6.76-6.86 (2H, m, ^{H}Ar-H), 7.03 (1H, s, ^{Me}Ar-H), 7.05 (1H, s, ^{Me}Ar-H), 8.55 (1H, s, CH=N).

^{13}C{^{1}H} NMR (DMSO-d_6) 14.8 (H_3C-Ar), 19.7 (H_3C-Ar), 57.1 (CH_2N), 115.5, 117.9, 119.4, 125.0, 125.0, 126.7, 128.7, 129.5, 129.6, 134.3 (Ar-CH), 155.6, 157.2 (Ar-O), 166.6 (CH=N).

m/z calc. $[C_{16}H_{17}NO_2 + H]^+$ = 256.1338, found 256.1328



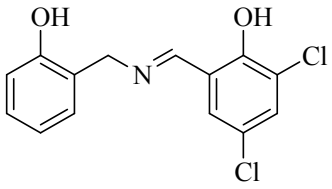
H_2**3**

Salicylammonium acetate (2.00g, 10.9 mmol) and sodium bicarbonate (3.67g, 43.7 mmol) were mixed with ethanol (80 ml) and heated to 60°C. 3,5-di-tert-butyl-2-hydroxybenzyaldehyde (2.56g, 10.9 mmol) in ethanol (20 ml) was added drop-wise to the reaction mixture and left to stir for 2 hours. The reaction mixture was then hot filtered and washed with hot ethanol to remove insoluble $NaHCO_3$. Solvent was removed by rotary evaporation and the resulting yellow solid washed with distilled water to remove any soluble sodium salts. The yellow solid was recrystallized from methanol to remove any unreacted aldehyde (1.31g, 3.86 mmol, 35% yield).

^{1}H NMR (DMSO-d_6) 1.26 (9H, s, ^{t}Bu), 1.35 (9H, s, ^{t}Bu), 4.71 (2H, s, N-CH_2), 6.77-6.86 (2H, m, ^{H}Ar-H), 7.09-7.21 (2H, m, ^{H}Ar-H), 7.28 (1H, s, ^{tBu}Ar-H), 7.29 (1H, s, ^{tBu}Ar-H), 8.63 (1H, s, CH=N).

^{13}C{^{1}H} NMR (DMSO-d_6) 29.6 (C(CH_3)$_3$), 31.7 (C(CH_3)$_3$), 34.2 (C(CH_3)$_3$), 34.9 (C(CH_3)$_3$), 57.3 (CH_2-N), 115.6, 118.1, 119.4, 124.8, 126.6, 128.5, 128.7, 129.9 (Ar-CH), 136.0, 139.7 (Ar-C), 155.7, 158.3 (Ar-O), 167.6 (CH=N).

m/z calc. $[C_{22}H_{29}NO_2 + H]^+$ = 340.2277, found 340.2264.



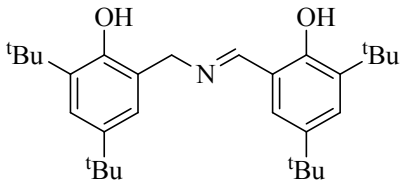
H_2**4**

Salicylammonium acetate (2.00g, 10.9 mmol) and sodium bicarbonate (3.67g, 43.7 mmol) were mixed with ethanol (80 ml) and heated to 60°C. 3,5-di-tert-butyl-2-hydroxybenzyaldehyde (2.56g, 10.9 mmol) in ethanol (20 ml) was added drop-wise to the reaction mixture and left to stir for 2 hours. The reaction mixture was then hot filtered and washed with hot ethanol to remove insoluble $NaHCO_3$. Solvent was removed by rotary evaporation and the resulting yellow solid washed with distilled water to remove any soluble sodium salts. The yellow solid was recrystallized from methanol to remove any unreacted aldehyde (1.31g, 3.86 mmol, 35% yield).

^{1}H NMR (DMSO-d_6) 4.77 (2H, s, CH_2-N), 6.79-6.89 (2H, m, ^{H}Ar-H), 7.15-7.25 (2H, m, ^{H}Ar-H), 7.44 (1H, s, ^{Cl}Ar-H), 7.55 (1H, s, ^{Cl}Ar-H), 8.64 (1H, s, CH=N).

^{13}C {^{1}H} NMR (DMSO-d_6) 53.5 (*C*H_2-N), 115.6, 117.0, 117.1, 119.5, 122.9, 125.1 (Ar-*C*H), 129.8, 130.1 (Ar-Cl), 130.7, 133.3 (Ar-*C*H), 155.9 (*C*H=N), 164.2, 165.6 (Ar-O).

m/z calc. $[C_{14}H_{11}NO_2Cl_2 + Na]^+$ = 318.0065, found 318.0066.



H_2**5**

3,5-di-*tert*-butyl-2-hydroxybenzylammonium acetate (2.00 g, 6.77 mmol) and sodium bicarbonate (2.28 g, 27.1 mmol) were mixed in ethanol (80 ml) and heated (70 °C). 3,5-di-*ter*-butyl-2-hydroxybenzyaldehyde (1.59 g, 6.77 mmol) was dissolved in ethanol (20 ml) and charged slowly to the reaction mixture. The reaction was stirred at temperature (70 °C) under a blanket of argon for 4 hours. The reaction was hot-filtered to remove any insoluble sodium salts before removing the solvent via rotary evaporation. The resulting yellow solid was washed with water and then dried under high vacuum. The crude product was recrystallized in minimal hot methanol and a yellow solid isolated (2.63 g, 5.82 mmol, 86 % yield).

^{1}H NMR ($CDCl_3$) 1.23 (18H, s, ^{t}Bu), 1.36 (9H, s, ^{t}Bu), 1.37 (9H, s, ^{t}Bu), 4.74 (2H, s, N-CH_2), 6.98 (1H, d (J = 2.3 Hz), Ar-H), 7.02 (1H, d (J = 2.6 Hz), Ar-H), 7.22 (1H, d (J = 7.2 Hz), Ar-H), 7.32 (1H, d (J = 2.3 Hz), Ar-H), 8.42 (1H, s, N=CH).

^{13}C{^{1}H} NMR ($CDCl_3$) 29.4, 29.9, 31.5, 31.6 (C(*C*H_3)$_3$), 34.2, 34.3, 34.8, 35.1 (*C*(CH_3)$_3$), 61.3 (N-*C*H_2), 117.9, 123.8, 124.2, 126.4, 127.5, 136.0, 136.8, 140.5, 142.6, 151.0 (Ar-*C*), 157.6, 159.1 (Ar-O), 167.8 (*C*H=N).

m/z $[C_{30}H_{45}NO_2 + Na]^+$ = 474.3348, found 474.3371.

1.6.3. Aluminium imine bis(phenolate) complexes

Imine bis(phenolate) complexation was carried out on a 0.5 g scale. Ligand H_2(**1-5**) was charged to a Schlenk flask and placed under an inert atmosphere using standard air-sensitive techniques. Dry toluene (~10 ml) was added to the flask *via* a cannula before the addition of 1 equivalent of $AlMe_3$ (2 M in hexane) *via* syringe. The reaction was stirred at room temperature for 1 hour before the removal of solvent under reduced pressure to yield a yellow solid. Crude material was recrystallised in minimal hot toluene.

The high dilution method for the coordination of H_2**4** to $AlMe_3$ was carried out through the addition of appropriate amounts of $AlMe_3$ to dry toluene (~10 ml) in a schlenk under an inert atmosphere before the drop-wise addition of a similar solution of ligand (H_2**4**) in ~10 ml of dry toluene. Crude material was isolated by solvent removal under vacuum and recrystallisation attempted from hot toluene.

$Al_2(Me)_2$(**1**)$_1$ (5°-5° geometry)

^{1}H NMR (C_6D_6) -0.03 (6H, s, Al-CH_3), 3.53 (2H, d (J = 14.0 Hz), CH_2-N), 5.30 (2H, d (J = 14.0 Hz), CH_2-N), 6.64 (2H, dd (J = 1.0, 6.9 Hz), Ar-H), 6.74 (2H, dd (J = 1.7, 7.7 Hz), Ar-H), 6.94 (2H, dt (J = 1.6, 7.5 Hz), Ar-H), 6.99-7.05 (4H, m, Ar-H), 7.12 (2H, dd (J = 1.9, 6.9 Hz), Ar-H), 7.29 (2H, s, CH=N), 7.37 (2H, dt (J = 1.7, 7.9 Hz), Ar-H), 8.41 (2H, dd (J = 0.7, 8.5 Hz), Ar-H).

^{13}C {^{1}H} NMR (C_6D_6) -8.10 (Al-*C*H_3), 60.8 (N-*C*H_2), 117.3, 119.9, 121.1, 122.1, 122.8, 126.3, 128.2, 129.0, 133.3, 135.4 (Ar-*C*), 154.4 (*C*H=N), 164.0, 165.2 (Ar-O).

Anal: calc. for $C_{15}H_{14}NO_2Al$: C, 67.4; H, 5.28; N, 5.24. Found: C, 66.7; H, 5.27; N, 4.72.

$Al_2(Me)_2$(**2**)$_2$ (6°-4° geometry)

^{1}H NMR (C_6D_6) -0.49 (6H, s, Al-CH_3), 1.66 (6H, s, CH_3), 2.13 (6H, s, CH_3), 4.43 (2H, d (J = 17.3 Hz), CH_2-N), 5.05 (2H, d (J = 17.3), CH_2-N), 6.48-6.96 (12H, m, Ar-H), 7.70 (2H, s, CH=N).

^{13}C {^{1}H} NMR (C_6D_6) -11.6 (Al-*C*H_3), 14.5, 19.0 (*C*H_3), 61.1 (*C*H_2-N), 117.2, 119.5, 121.1, 122.0, 122.5, 127.1, 129.0, 129.2, 129.3, 135.5 (Ar-*C*), 151.9 (*C*H=N), 160.9, 167.4 (Ar-O).

$Al_2(Me)_2$(**3**)$_2$

^{1}H NMR (C_6D_6) -0.39 (6H, s, Al-CH_3), 0.98 (18H, s, C(CH_3)$_3$), 1.29 (18H, s, C(CH_3)$_3$), 4.24 (2H, d (J = 16.8 Hz), CH_2-N), 5.43 (2H, d (J = 16.8 Hz), CH_2-N), 6.72 (2H, d (J = 2.0 Hz), Ar-H), 6.80-6.87 (4H, m, Ar-H), 6.94 (2H, d (J = 2.6 Hz), Ar-H), 6.96 (2H, d (J = 2.0 Hz), Ar-H), 7.41 (2H, d (J = 2.6 Hz), Ar-H), 7.76 (2H, s, CH=N).

^{13}C{^{1}H} NMR (C_6D_6) 0.0 (Al-*C*H_3), 27.8, 30.2 (C(*C*H_3)$_3$), 32.7 (*C*(CH_3)$_3$), 33.8 (*C*(CH_3), 61.9 (*C*H_2-N), 117.6, 120.6, 121.8, 124.3, 127.1, 127.9, 128.8, 129.8, 136.8, 139.6 (Ar-*C*), 153.2, 161.9 (Ar-O), 170.2 (*C*=N).

Anal: calc for $C_{23}H_{30}AlNO_2$: C, 72.80; H, 7.97; N, 3.69. Found: C, 72.68; H, 8.12; N, 3.55.

$Al_2(Me)_2$(**4**)$_2$ (5°-5° geometry)

^{1}H NMR (C_6D_6) -0.29 (6H, s, Al-CH_3), 3.38 (2H, d (J = 13.5), N-CH_2), 5.09 (2H, d (J = 13.5 Hz), N-CH_2), 6.27 (2H, d (J = 2.5 Hz), Ar-H), 6.63 (2H, s, CH=N), 6.79 (2H, d (J = 7.2

Hz), Ar-H), 6.92 (2H, t (J = 7.2 Hz), Ar-H), 7.14 (2H, d (J = 7.2 Hz), Ar-H), 7.35 (2H, t (J = 7.2 Hz), Ar-H), 8.66 (2H, d (J = 7.2 Hz), Ar-H).
^{13}C{^{1}H} NMR (C_6D_6) 1.71 (Al-*C*H_3), 61.0 (*C*H_2-N), 121.0, 121.6, 122.1, 124.2, 126.1, 127.7, 129.9, 131.2, 134.9, 138.2 (Ar-*C*), 154.1, 158.0 (Ar-O), 164.0 (*C*H=N).

$Al_2(Me)_2$(**5**)$_2$ (6°-4° geometry)

^{1}H NMR (C_6D_6) -0.20 (6H, s, Al-CH_3), 0.89 (18H, s, C(CH_3)$_3$), 1.19 (18H, s, C(CH_3)$_3$), 1.37 (18H, s, C(CH_3)$_3$), 1.371 (18H, s, C(CH_3)$_3$), 4.05 (2H, d (J = 14.7), CH_2-N), 6.14 (2H, d (J = 14.3), CH_2-N), 6.94 (2H, d (J = 2.5 Hz), Ar-H), 7.24 (2H, d (J = 2.5 Hz), Ar-H), 7.35 (2H, d (J = 2.5 Hz), Ar-H), 7.45 (2H, d (J = 2.5 Hz), Ar-H), 7.94 (2H, s, CH=N).
^{13}C{^{1}H} NMR (C_6D_6) -4.44 (Al-CH_3), 29.5, 31.6, 31.7, 31.8 (C(*C*H_3)$_3$), 33.9, 34.5, 34.6, 35.2 (*C*(CH$_3$)$_3$), 66.4 (*C*H_2-N), 119.6, 124.3, 125.3, 125.7, 128.5, 129.3, 130.0, 130.2, 136.9, 139.9, 140.7, 144.8, 150.7, 163.1
Anal: calc. for $C_{31}H_{46}NO_2Al$: C, 75.7; H, 9.43; N, 2.85. Found: C, 75.2; H, 9.13; N, 2.56.

1.7. Polymerisation Trials

1.7.1. Polymerisation Procedure

Solvent-based polymerisations were carried out in toluene at a lactide concentration of 0.8 M. The monomer/initiator/co-initiator ratio used was 100:1:1, with benzyl alcohol acting as the co-initiator. Monomer (1.0 g) was purified through recrystallisation and double sublimation. Reactions were prepared air-sensitively and sealed before being carried out at 80 °C. After the desired reaction time, the reaction was quenched with methanol (1 ml). Solvents were then removed under reduced pressure and the resulting solid analysed by ^{1}H NMR to determine conversion. Quantification was achieved through the integration of the monomer methine quartet (4.9 ppm) and the polymer methine multiplet (5.1 ppm) with conversion calculated using the following equation: $conv. = \frac{[PLA]}{[LA] + [PLA]} \times 100$. The solid was washed with methanol to remove all unreacted monomer. Homonuclear decoupled ^{1}H NMR spectroscopy ($CDCl_3$) was used to determine the polymer tacticity, with quantification as a P_r value (probability of racemic enchainment). GPC (THF, referenced to polystyrene standards) provided relative molecular weights (M_n) and polydispersity index (PDI) of the polymers produced. Theoretical molecular weight was calculated using the following equation: $Mn = \left(\frac{conv.}{100} \times 144 \times 100\right) + 108$, where 108 is the mass of the end groups {H/OCH_2Ph}.

1.7.2. Homonucelar-decoupled ^{1}H {^{1}H} NMR Spectroscopy

^{1}H {^{1}H} NMR spectroscopy of polymeric material was carried out using Bruker DRX400 NMR instrument. Purified material (monomer removed through MeOH wash and subsequent drying under vacuum) was dissolved in $CDCl_3$ at a concentration of 10 mg ml^{-1}. A standard ^{1}H NMR spectrum was acquired with note taken of the chemical shift of the pendant methyl doublet signal of the lactidyl repeat unit (~1.61 ppm). The decoupled spectrum was then acquired with the secondary frequency set to that of the methyl doublet ("o2p=1.61") and the power level ("pl24=40"). Number of scans used ("ns=4") whilst fine tuning of decoupling was achieved before final acquisition of a decoupled spectrum with an increased number of scans ("ns=8"). P_r

values were calculated through integration of [sis] tetrad with respect to remaining tetrads (as identified in section 1.4.3). The following equation was used to calculate probability of racemic enchainment, $P_r = \sqrt{2 \times [sis]}$, where: $[sis] = \frac{\int sis\ tetrad}{\sum\left(\int all\ tetrads\right)}$.

1.7.3. Kinetics-scale solvent polymerisations of *rac*-lactide & L-lactide

Polymerisations were carried out in a Young's NMR tube, prepared under an inert atmosphere using standard glove-box techniques. Monomer/initiator/BnOH ratio was 100:1:1 with a monomer concentration of 0.8 M. 0.5ml of solvent (toluene-d_8) was added to the monomer in the Young's NMR tube. A solution of initiator was prepared containing five times the amount required in 0.50 ml of toluene-d_8. 0.10 ml of this solution was then transferred to the NMR tube. Benzyl alcohol was added to the NMR tube using a micro-syringe. Kinetic experiments were carried out at 80 °C in the NMR spectrometer. ^{1}H NMR spectra were obtained at regular intervals and the conversion calculated based on relative integrals of monomeric and polymeric signals for the lactide methine (4.21 ppm $\rightarrow$ 5.15 ppm). $[M]_t = [M]_0 \times conv.$ The pseudo first-order rate constant (k_{app}) was calculated from the gradient of $\ln\left(\frac{[M]_0}{[M]_t}\right) vs.\ t$.

2. ^{1}H NMR Spectra

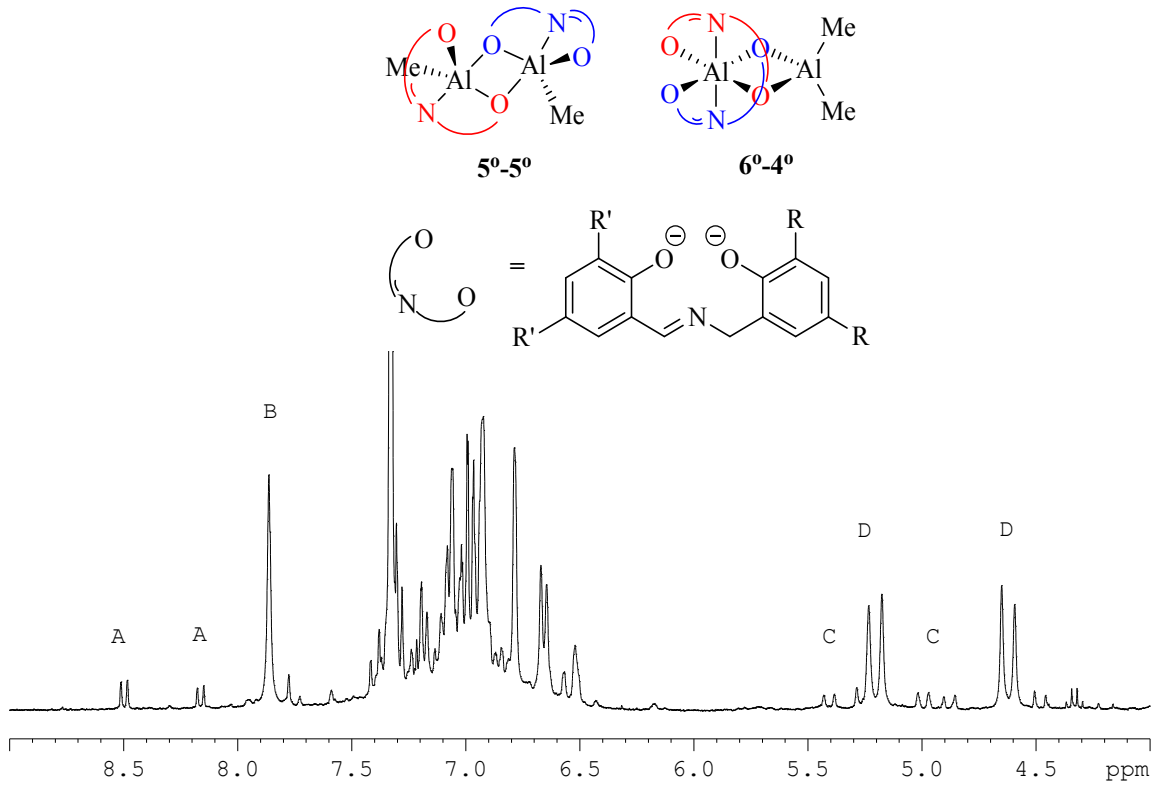


Figure S1 Extract of the ^{1}H NMR spectrum (C_6D_6) for non-recrystallised $Al_2(Me)_2$(**2**)$_2$ exhibiting signals for the 5°-5° structural geometry: A (imine), C (methylene bridge) and the predominant 6°-4° structural geometry: B (imine) and D (methylene bridge).

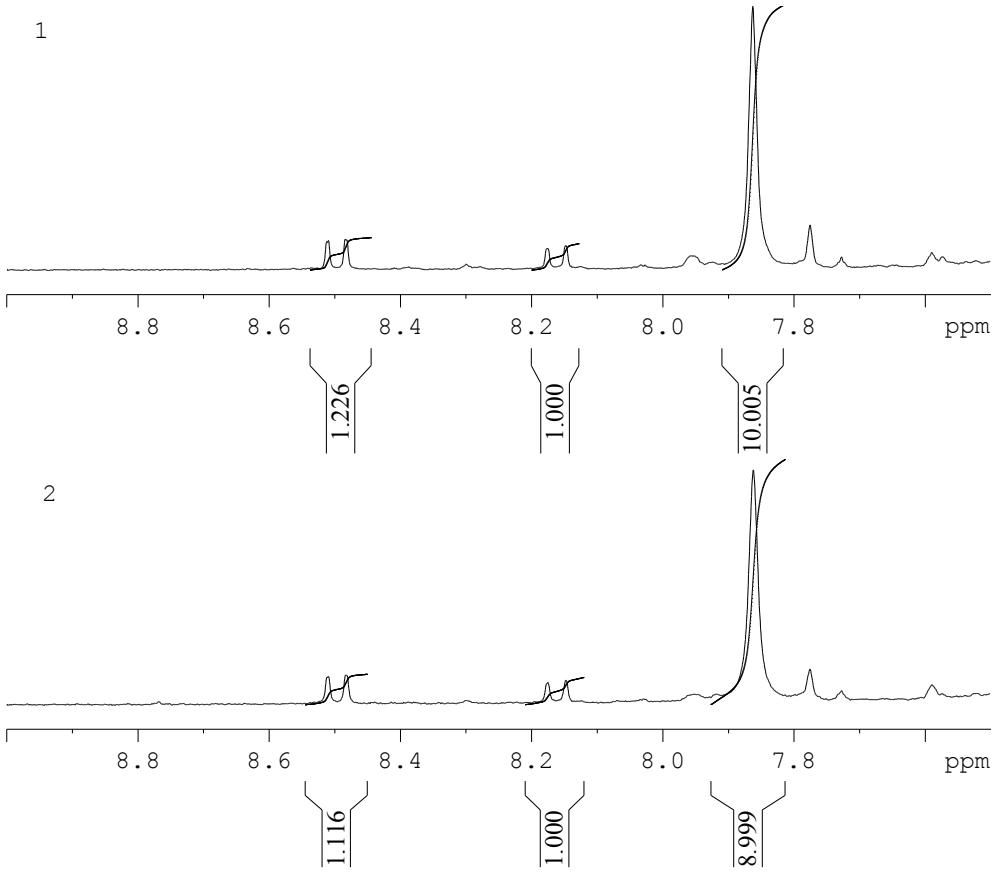


Figure S2 Extracts of the ^{1}H NMR spectra (C_6D_6) for the synthesis of $Al_2(Me)_2(\mathbf{2})_2$ at: 1. 0.2 M ligand concentration and 2. 0.1 M ligand concentration

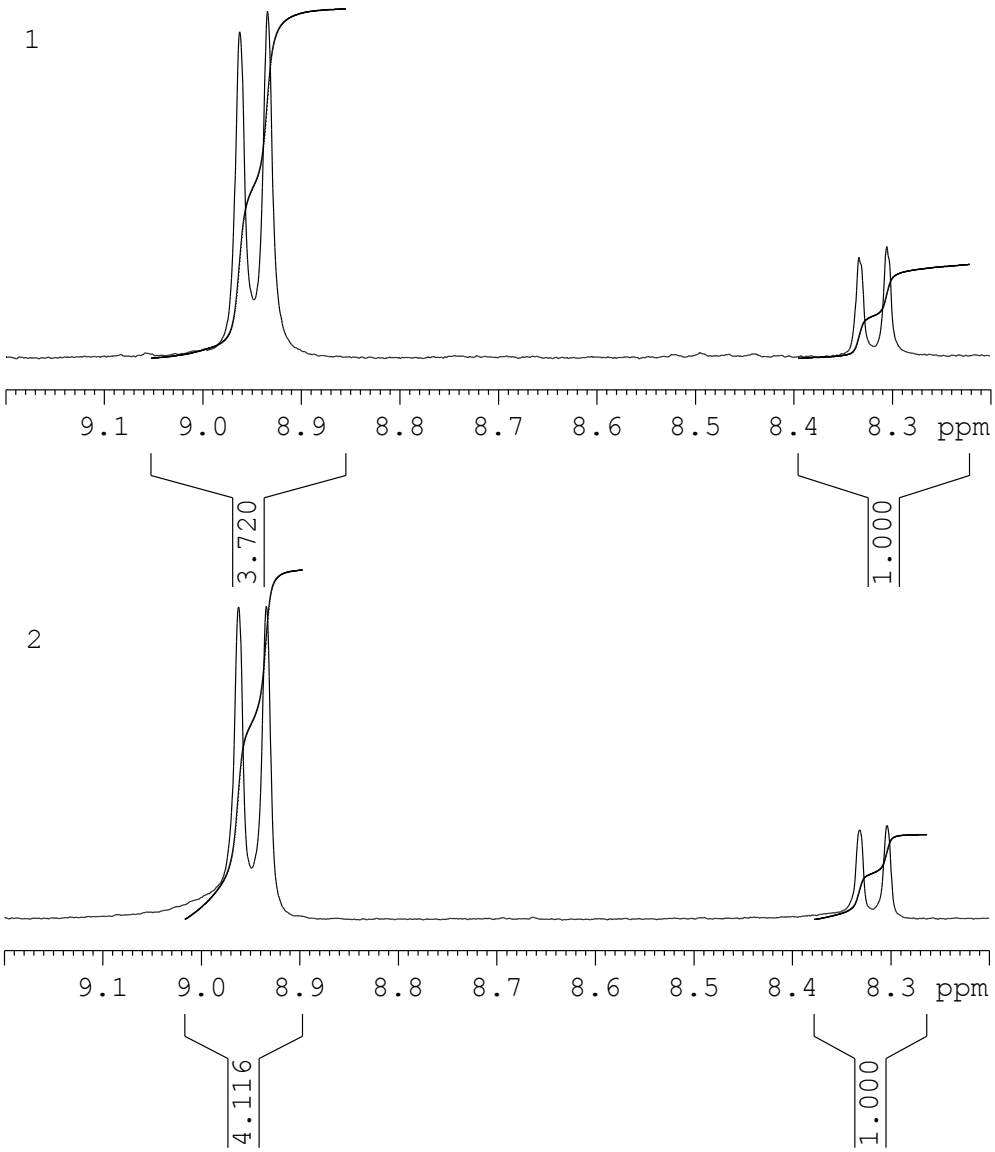


Figure S3 Extracts of the ^{1}H NMR spectra (C_6D_6) of $Al_2(Me)_2(\mathbf{4})_2$ synthesised by: 1. High dilution method and 2. Low dilution method. Showing the imine signals of the proposed major (8.95 ppm) and minor (8.32 ppm) isomers of the 5°-5° structural motif

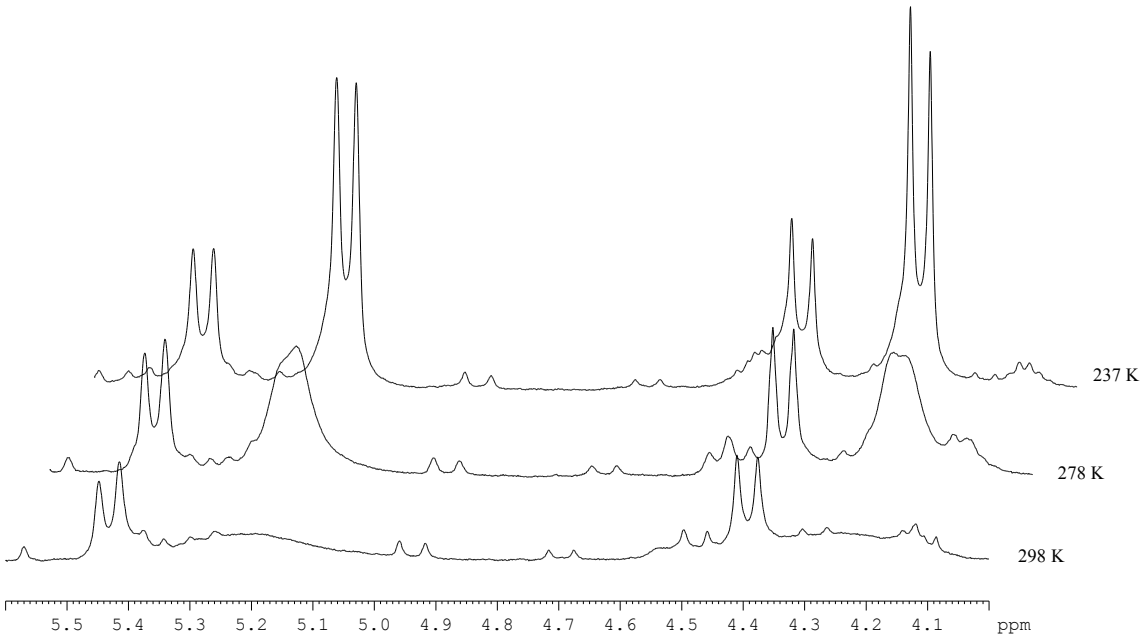
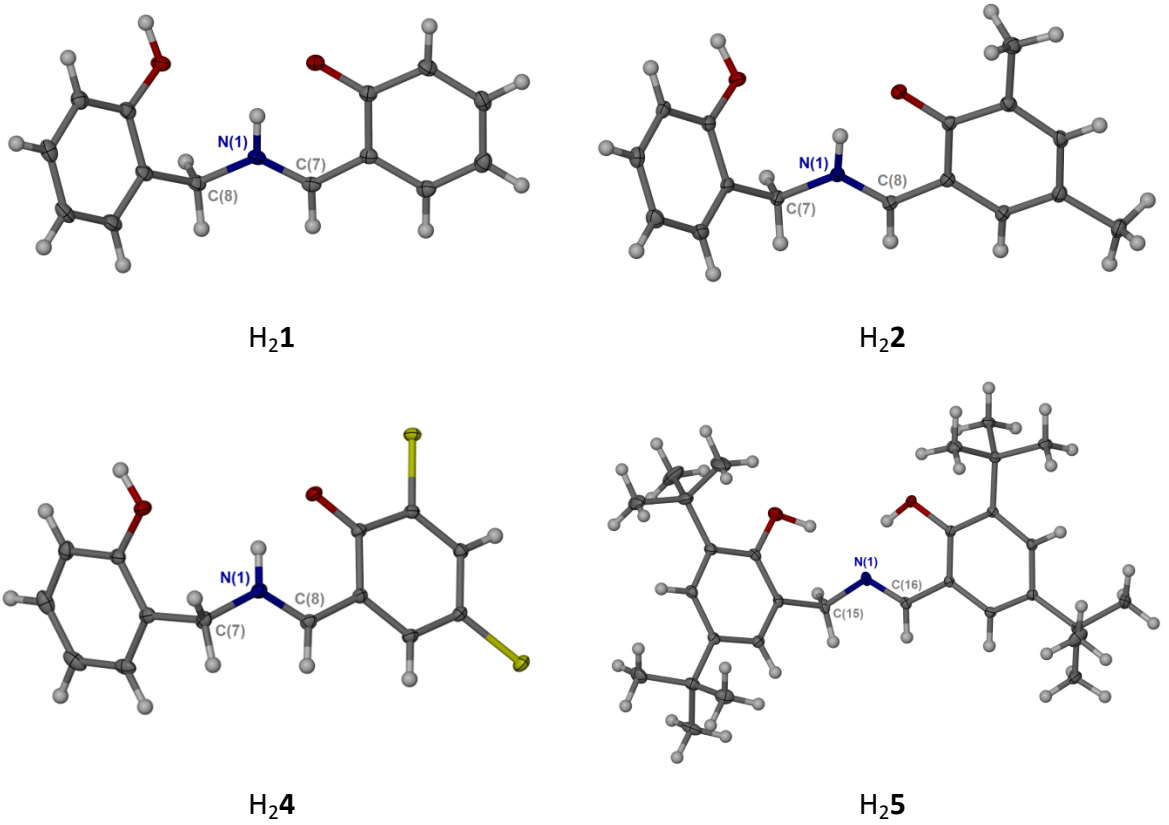


Figure S4 Extracts of the ^{1}H NMR spectra for $Al_2(Me)_2$(**1**)$_2$ acquired *via* VT-NMR spectroscopy in THF-d_8. Comparison of spectra shows that in a coordinative solvent (d_8-THF) one set of doublets, assigned to the diastereotopic CH_2 protons of the methylene bridge, is unchanged. Cooling of the sample slows the reversible coordination of the solvent making the doublet more disernable.

3. Crystal Data and Structure Refinement

All data were collected on a Nonius kappa CCD diffractometer with MoKα radiation (λ = 0.71073 Å). T = 150(2) K throughout and all structures were solved by direct methods and refined on F^2 data using the SHELXL-97 suite of programs. Hydrogen atoms, were included in idealised positions and refined using the riding model, except those involved in H-bonding networks which were located in the final difference Fourier map. All solutions were relatively straightforward expect the following: $Al_2(Me)_2(\mathbf{4})_2$ The asymmetric unit consists of two independent Al complexes and seven solvent molecules of toluene. All solvent molecules have been constrained to form rigid hexagons. Solvent molecules with atoms C100-C106, C200-C206 and C400-C406 have then been refined anisotropically. Solvent molecule C400-C406 shows potential disorder. However, this could not be refined satisfactory. Solvent molecules C300-C306, C500-C506 and C600-C606 show disorder in the ratio 50:50 60:40 and 55:45 respectively. These have been refined isotropically and some of the bond lengths and angles of the methyl groups have been restrained. $Al_2(Me)_2(\mathbf{5})_2$ the methyl moieties of two tert-butyl groups (C10-C12 and C30-C32) are disordered over two positions in a 75:25 ratio the minor component was refined isotropically.



$H_2\mathbf{1}$ $H_2\mathbf{2}$

$H_2\mathbf{4}$ $H_2\mathbf{5}$

Figure S5 Structures of ligands $H_2\mathbf{1}$, $H_2\mathbf{2}$, $H_2\mathbf{4}$ and $H_2\mathbf{5}$ as determined by single-crystal X-ray diffraction

	$H_2\mathbf{1}$	$H_2\mathbf{2}$	$H_2\mathbf{4}$	$H_2\mathbf{5}$
N(1) – C(8)	1.2915(18)	1.2994(18)	1.294(2)	-
N(1) – C(7)	1.4710(16)	1.4685(18)	1.473(2)	-

C(7) – N(1) – C(8)	125.18(12)	124.66(12)	123.46(14)	-
N(1) – C(16)	-	-	-	1.2765(17)
N(1) – C(15)	-	-	-	1.4705(15)
C(15) – N(1) – C(16)	-	-	-	117.54(11)

Table S1 Selected bond length (Å) and bond angles (°) for H_2**1**, H_2**2**, H_2**4** and H_2**5** as determined by single-crystal X-ray diffraction

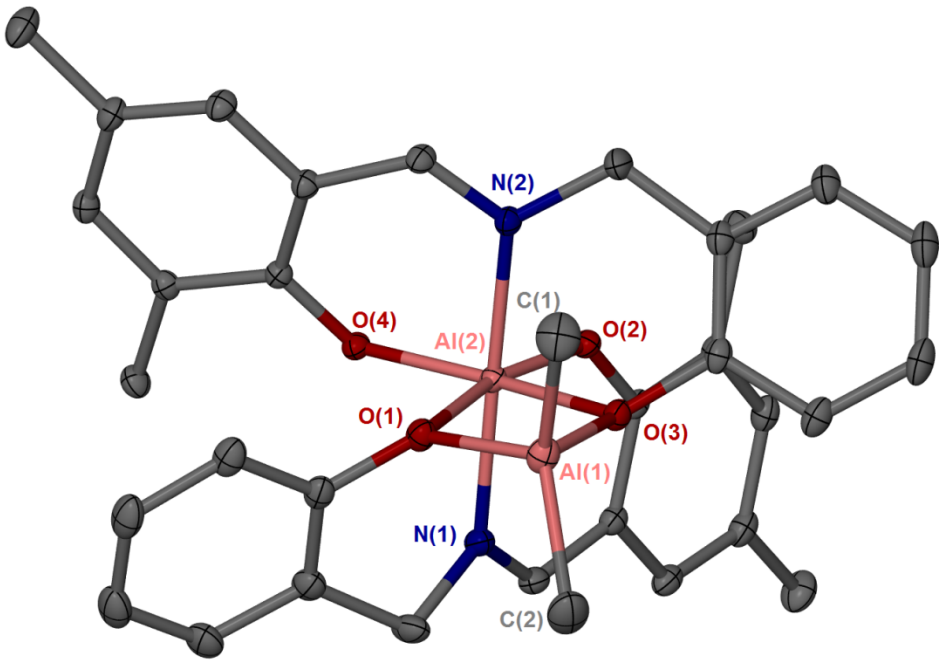


Figure S6 Solid-state structure of $Al_2(Me)_2$(**2**)$_2$ as determined by single-crystal X-ray diffraction. Ellipsoids are shown at the 30% probability level. All disorder and hydrogen atoms have been removed for clarity

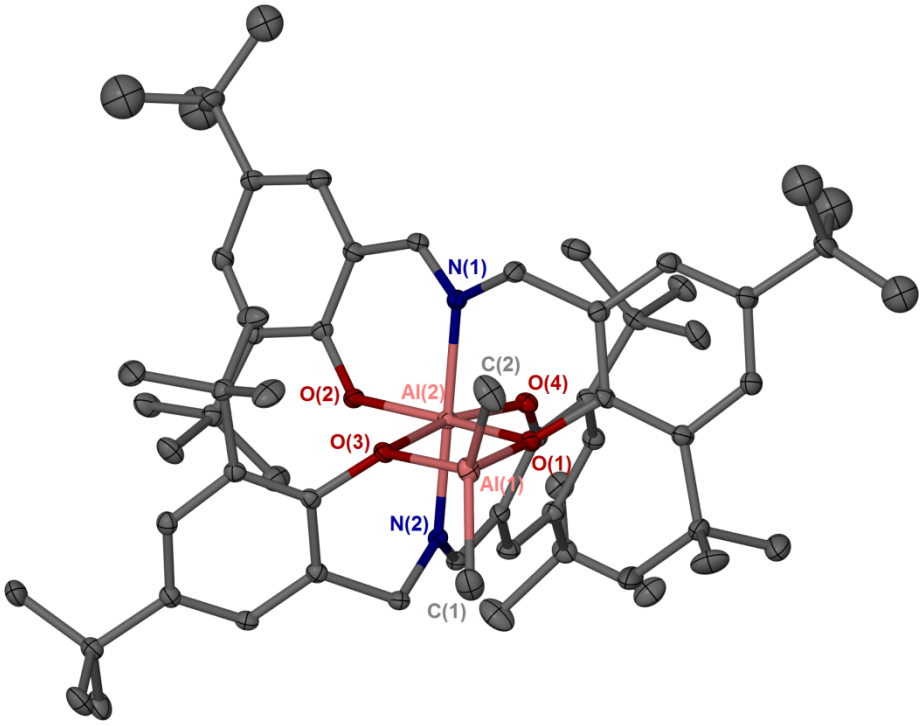


Figure S7 Solid-state structure of $Al_2(Me)_2(\mathbf{5})_2$ as determined by single-crystal X-ray diffraction. Ellipsoids are shown at the 30% probability level. All disorder and hydrogen atoms have been removed for clarity

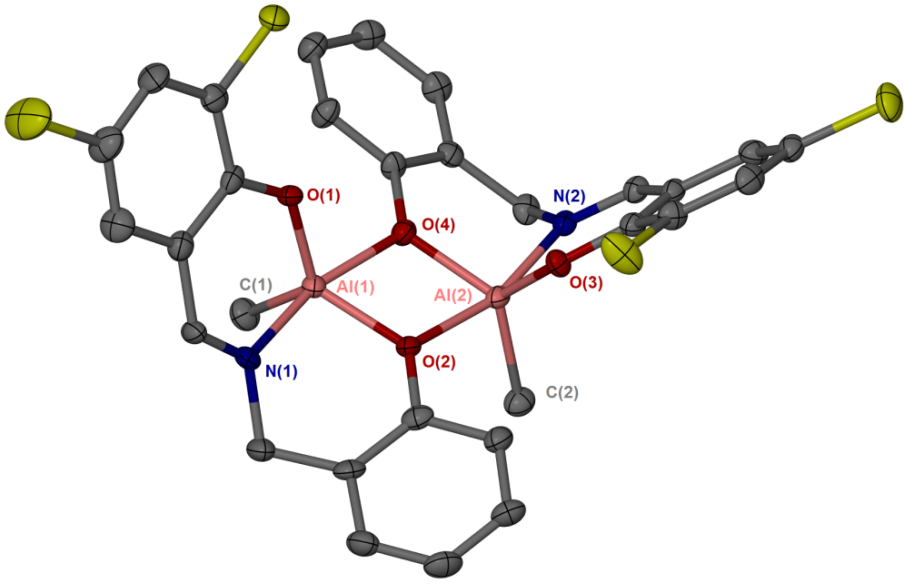


Figure S8 Solid-state structure of $Al_2(Me)_2(\mathbf{4})_2$ as determined by single-crystal X-ray diffraction. Ellipsoids are shown at the 30% probability level. All disorder and hydrogen atoms have been removed for clarity

	$Al_2(Me)_2(\mathbf{2})_2$	$Al_2(Me)_2(\mathbf{5})_2$
Al(1) – O(1)	1.8226(10)	1.842(2)
Al(1) – O(3)	1.8387(10)	1.843(2)
Al(1) – C(1)	1.9560(19)	1.964(4)

Al(1) – C(2)	1.9560(19)	1.964(4)
Al(2) – O(1)	1.9858(10)	1.973(2)
Al(2) – O(3)	1.9480(10)	2.029(2)
Al(2) – O(2)	1.8101(100	1.817(2)
Al(2) – O(4)	1.8011(9)	1.820(2)
Al(2) – N(1)	2.0427(12)	2.008(3)
Al(2) – N(2)	2.0043(11)	2.007(3)
Al(1) – O(1) – Al(2)	101.91(5)	103.74(10)
Al(1) – O(3) – Al(2)	102.77(5)	101.54(10)
C(1) – Al(1) – C(2)	118.40(10)	109.73(19)
O(1) – Al(1) – O(3)	80.81(4)	81.16(10)
O(1) – Al(2) – O(3)	74.21(4)	73.55(9)
O(2) – Al(2) – O(4)	101.97(4)	101.64(10)
O(2) – Al(2) – N(2)	90.05(4)	88.34(10)
O(2) – Al(2) – O(3)	93.55(4)	92.93(10)
O(1) – Al(2) – O(4)	90.55(4)	92.14(10)
N(1) – Al(2) – N(2)	178.00(5)	177.74(11)

Table S2 Selected bond lengths (Å) and bond angles (°) for $Al_2(Me)_2$(**2**)$_2$ and $Al_2(Me)_2$(**5**)$_2$ as determined by single-crystal X-ray diffraction

	$Al_2(Me)_2$(**4**)$_2$
Al(1) – O(1)	1.784(4)
Al(1) – O(2)	1.855(5)
Al(1) – O(4)	1.948(5)
Al(1) – N(1)	2.006(6)
Al(1) – C(1)	1.977(7)
Al(2) – O(2)	1.974(5)
Al(2) – O(3)	1.777(4)
Al(2) – O(4)	1.855(5)
Al(2) – N(2)	1.988(6)
Al(2) – C(2)	1.953(7)
C(1) – Al(1) – O(1)	120.3(3)
C(1) – Al(1) – O(2)	123.6(3)
O(1) – Al(1) – O(2)	116.0(2)
N(1) – Al(1) – O(1)	89.9(2)
N(1) – Al(1) – O(4)	164.3(2)
C(2) – Al(2) – O(3)	123.2(3)
C(2) – Al(2) – O(4)	120.6(3)
O(3) – Al(2) – O(4)	115.8(2)
N(2) – Al(2) – O(3)	90.2(2)
N(2) – Al(2) – O(2)	164.6(2)

Al(1) – O(2) – Al(2)	102.9(2)

Table S3 Selected bond lengths (Å) and bond angles (°) for $Al_2(Me)_2(\mathbf{4})_2$ as determined by single-crystal X-ray diffraction

H_2**1**

Identification code	k10mdj26
Empirical formula	C_{14} H_{13} N O_2
Formula weight	227.25
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/*c*
Unit cell dimensions	a = 22.3830(16) Å alpha = 90°.
	b = 5.7810(5) Å beta = 99.915(4)°.
	c = 17.8440(16) Å gamma = 90°.
Volume	2274.5(3) $Å^3$
Z, Calculated density	8, 1.327 Mg/m^3
Absorption coefficient	0.089 mm^{-1}
F(000)	960
Crystal size	0.1 x 0.2 x 0.2 mm
Theta range for data collection	3.64° to 25.03°.
Limiting indices	-26≤h≤26, -6≤k≤6, -21≤l≤20
Reflections collected / unique	11736 / 2008 [R(int) = 0.0478]
Completeness to theta = 25.03	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2008 / 0 / 166
Goodness-of-fit on F^2	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0855
R indices (all data)	R1 = 0.0470, wR2 = 0.0923
Largest diff. peak and hole	0.129 and -0.237 $e.Å^{-3}$

H_2**2**

Identification code	k11mdj02
Empirical formula	C_{16} H_{17} N O_2
Formula weight	255.31
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/a$
Unit cell dimensions	a = 9.5050(2) Å alpha = 90°.
	B = 11.2580(2) Å beta =109.0580(10)°.
	C = 13.5330(3) Å gamma = 90°.
Volume	1368.76(5) A^3
Z, Calculated density	4, 1.239 Mg/m^3
Absorption coefficient	0.082 mm^{-1}
F(000)	544
Crystal size	0.20 x 0.15 x 0.10 mm
Theta range for data collection	3.62 to 27.49°.
Limiting indices	-12≤h≤12, -14≤k≤14, -17≤l≤17
Reflections collected / unique	25556 / 3133 [R(int) = 0.0666]
Completeness to theta = 27.49	99.6 %
Absorption correction	multi-scan
Max. and min. transmission	0.9919 and 0.9839
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3133 / 0 / 182
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0458, wR2 = 0.1046
R indices (all data)	R1 = 0.0696, wR2 = 0.1182
Largest diff. peak and hole	0.167 and -0.221 e.$Å^{-3}$

H_2**4**

Identification code	h10mdj27
Empirical formula	C_{14} H_{11} Cl2 N O_2
Formula weight	296.14
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	a = 8.0410(5) Å alpha = 90°.
	B = 8.6470(6) Å beta = 95.121(4)°.
	C = 18.7420(10) Å gamma = 90°.
Volume	1297.94(14) A^3
Z, Calculated density	4, 1.515 Mg/m^3
Absorption coefficient	0.496 mm^{-1}
F(000)	608
Crystal size	0.20 x 0.10 x 0.10 mm
Theta range for data collection	3.57 to 27.44°.
Limiting indices	-10≤h≤10, -11≤k≤11, -24≤l≤24
Reflections collected / unique	21524 / 2946 [R(int) = 0.0503]
Completeness to theta = 27.44	99.3 %
Absorption correction	None
Max. and min. transmission	0.9521 and 0.9074
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2946 / 0 / 175
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0357, wR2 = 0.0857
R indices (all data)	R1 = 0.0482, wR2 = 0.0930
Largest diff. peak and hole	0.221 and -0.403 e.$Å^{-3}$

H_2**5**

Identification code	k13mdj01
Empirical formula	C_{30} H_{45} N O_2
Formula weight	451.67
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 9.96000(10) Å alpha = 90°
	b = 24.2760(3) Å beta = 104.9810(10)°
	c = 12.2260(2) Å gamma = 90°
Volume	2855.64(7) A^3
Z, Calculated density	4, 1.051 Mg/m^3
Absorption coefficient	0.064 mm^{-1}
F(000)	992
Crystal size	0.30 x 0.20 x 0.20 mm
Theta range for data collection	3.55 to 27.49°.
Limiting indices	$-12 \le h \le 12$, $-31 \le k \le 31$, $-15 \le l \le 15$
Reflections collected / unique	38743 / 6517 [R(int) = 0.0509]
Completeness to theta = 27.49	99.7 %
Max. and min. transmission	0.9873 and 0.9810
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6517 / 0 / 318
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1286
R indices (all data)	R1 = 0.0651, wR2 = 0.1392
Largest diff. peak and hole	0.622 and -0.282 $e.A^{-3}$

$Al_2(Me)_2(2)_2$

Identification code	k11mdj01
Empirical formula	C_{34} H_{36} Al_2 N_2 O_4
Formula weight	590.6
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 11.55200(10) Å alpha = 90°.
	b = 12.36600(10) Å beta = 97.83°.
	c = 22.1490(2) Å gamma = 90°.
Volume	3134.55(5) $Å^3$
Z, Calculated density	4, 1.252 Mg/m^3
Absorption coefficient	0.133 mm^{-1}
F(000)	1248
Crystal size	0.50 x 0.50 x 0.40 mm
Theta range for data collection	3.56 to 27.49°.
Limiting indices	-15≤h≤14, -16≤k≤16, -28≤l≤28
Reflections collected / unique	60619 / 7141 [R(int) = 0.0474]
Completeness to theta = 27.49	99.6 %
Absorption correction	mult-scan
Max. and min. transmission	0.9488 and 0.9366
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7141 / 0 / 385
Goodness-of-fit on F^2	0.997
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.1011
R indices (all data)	R1 = 0.0475, wR2 = 0.1101
Largest diff. peak and hole	0.291 and -0.286 $e.Å^{-3}$

$Al_2(Me)_2(4)_2$

Identification code	h10mdj30
Empirical formula	C_{102} H_{95} Al_4 Cl_8 N_4 O_8
Formula weight	1896.34
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, *Pbn*2_1
Unit cell dimensions	a = 12.0601(2) Å alpha = 90°.
	b = 22.5938(3) Å beta = 90°.
	c = 35.5013(6) Å gamma = 90°.
Volume	9673.5(3) Å^3
Z, Calculated density	4, 1.302 Mg/m^3
Absorption coefficient	0.327 mm^{-1}
F(000)	3948
Crystal size	0.10 x 0.10 x 0.10 mm
Theta range for data collection	3.54 to 25.02°.
Limiting indices	-14≤h≤14, -26≤k≤26, -42≤l≤42
Reflections collected / unique	77915 / 16713 [R(int) = 0.0963]
Completeness to theta = 25.02	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9680 and 0.9680
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16713 / 8 / 906
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0836, wR2 = 0.1978
R indices (all data)	R1 = 0.1232, wR2 = 0.2241
Absolute structure parameter	0.24(8)
Largest diff. peak and hole	0.762 and -0.392 e.Å^{-3}

$Al_2(Me)_2(5)_2$

Identification code	h11mdj16
Empirical formula	$C_{69}\ H_{100}\ Al_2\ N_2\ O_4$
Formula weight	1075.47
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 13.632(3) Å alpha = 90°
	b = 19.1280(17) Å beta = 99.037(7)°
	c = 25.491(2) Å gamma = 90°
Volume	6564.3(15) A^3
Z, Calculated density	4, 1.088 Mg/m^3
Absorption coefficient	0.090 mm^{-1}
F(000)	2344
Crystal size	0.10 x 0.10 x 0.05 mm
Theta range for data collection	3.52 to 25.03°.
Limiting indices	-16≤h≤16, -22≤k≤22, -30≤l≤30
Reflections collected / unique	73557 / 11493 [R(int) = 0.1273]
Completeness to theta = 25.03	99.1 %
Absorption correction	None
Max. and min. transmission	0.9955 and 0.9910
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11493 / 9 / 746
Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0643, wR2 = 0.1596
R indices (all data)	R1 = 0.1107, wR2 = 0.1954
Largest diff. peak and hole	1.040 and -0.926 e.$Å^{-3}$

4. References

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