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Multinuclear alkylaluminium macrocyclic Schiff base complexes: influence of procatalyst structure on the ring opening polymerisation of ε-caprolactone

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Table S1. Crystallographic data for **3** and **4**.

Compound	**3**	**4**
Formula	$C_{58}H_{70}Al_2N_4O_2$	$C_{66}H_{86}Al_4N_6O_2$
Formula weight	909.1	1103.3
Crystal system	Triclinic	Monoclinic
Space group	P1	$P2_1/n$ (equiv to no 14)
Unit cell dimensions		
a (Å)	10.8444(9)	20.7137(6)
b (Å)	12.1356(11)	13.6334(3)
c (Å)	12.3556(11)	23.6742(7)
α (º)	113.895(9)	90
β (º)	109.772(8)	107.436(3)
γ (º)	99.385(7)	90
V (Å^3)	1311.2(2)	6378.4(3)
Z	1	4
Temperature (K)	140(1)	140(1)
Wavelength (Å)	0.71073	0.71073
Calculated density (g.cm^{-3})	1.151	1.149
Absorption coefficient (mm^{-1})	0.100	0.120
Transmission factors	0.991-1.008	0.983-1.014
Crystal size (mm)	0.63 × 0.38 × 0.18	0.39 × 0.26 × 0.16
θ(max) (°)	27.5	25.0
Reflexions measured	17941	65005
Unique reflexions	11514	11208
Reflexions with $F^2 > 2\sigma(F^2)$	9879	6299
R_{int}	0.019	0.114
Number of parameters	630	705
R_1 [$F^2 > 2\sigma(F^2)$]	0.035	0.053
R_1 (all data)	0.044	0.128
wR_2 (all data)	0.082	0.106
GOOF	0.968	0.909
Largest difference peak and hole (e Å^{-3})	0.25 and -0.18	0.30 and -0.26

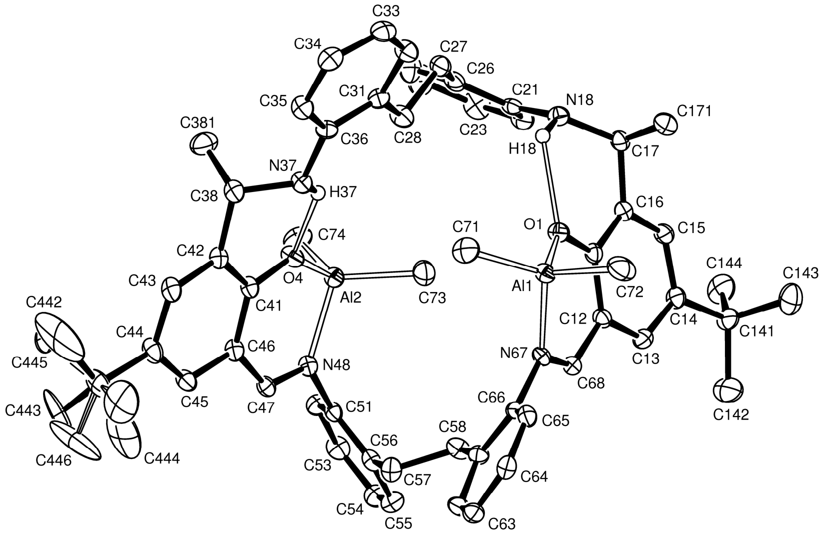

Figure S1. X-ray crystal structure of **3**; thermal ellipsoids are represented at the 50 % level and hydrogen atoms (other than those involved in hydrogen bonds) have been omitted for clarity.

Table S2. Bond lengths (Å) and angles (°) for compound **3**

Al(1)-O(1)	1.7766(13)	Al(2)-O(4)	1.7858(13)
Al(1)-N(67)	1.9723(15)	Al(2)-N(48)	1.9727(14)
Al(1)-C(71)	1.941(2)	Al(2)-C(73)	1.9499(19)
Al(1)-C(72)	1.959(2)	Al(2)-C(74)	1.950(2)
O(1)-Al(1)-N(67)	94.24(6)	O(4)-Al(2)-N(48)	93.79(6)
O(1)-Al(1)-C(71)	112.12(8)	O(4)-Al(2)-C(73)	111.32(8)
O(1)-Al(1)-C(72)	107.87(8)	O(4)-Al(2)-C(74)	111.76(7)
C(71)-Al(1)-N(67)	111.90(7)	C(73)-Al(2)-N(48)	108.78(7)
C(72)-Al(1)-N(67)	108.33(8)	C(74)-Al(2)-N(48)	108.78(8)
C(71)-Al(1)-C(72)	119.42(10)	C(73)-Al(2)-C(74)	119.32(9)
H(18)···O(1)	2.16(3)	H(37)···O(4)	2.11(2)
N(18)-H(18)···O(1)	126(2)	N(37)-H(37)···O(4)	134(2)

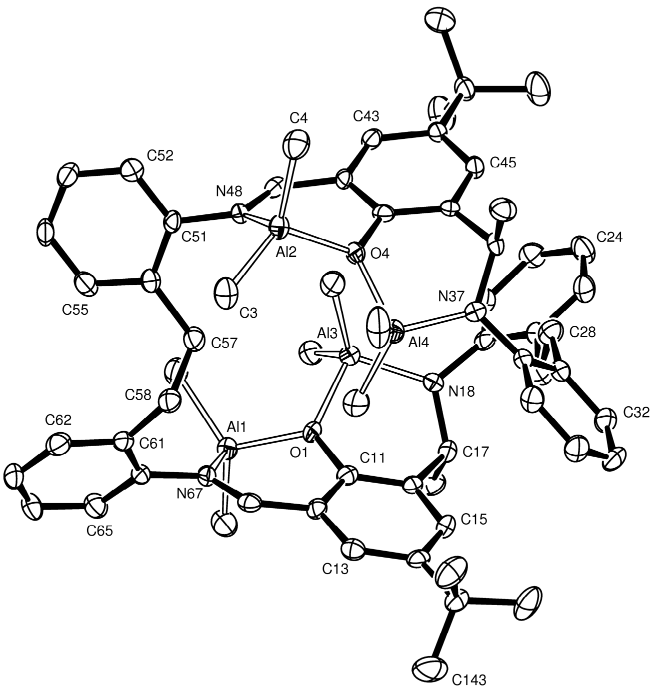

Figure S2. X-ray crystal structure of **4**; thermal ellipsoids are represented at the 50 % level and hydrogen atoms have been omitted for clarity.

Table S3. Bond lengths (Å) and angles (°) for compound **4**

Al(1)-C(1)	1.937(3)	Al(3)-C(7)	1.949(3)
Al(1)-C(2)	1.942(3)	Al(3)-C(8)	1.976(3)
Al(1)-O(1)	1.8473(19)	Al(3)-O(1)	1.9149(19)
Al(1)-N(67)	1.959(2)	Al(3)-N(18)	1.832(2)
Al(2)-C(3)	1.949(3)	Al(4)-C(5)	1.945(3)
Al(2)-C(4)	1.945(3)	Al(4)-C(6)	1.967(3)
Al(2)-O(4)	1.842(2)	Al(4)-O(4)	1.9059(19)
Al(2)-N(48)	1.956(2)	Al(4)-N(37)	1.831(2)
C(1)-Al(1)-C(2)	123.49(13)	C(7)-Al(3)-C(8)	118.28(13)
O(1)-Al(1)-C(1)	108.36(12)	O(1)-Al(3)-C(7)	108.67(11)
C(1)-Al(1)-N(67)	108.27(11)	N(18)-Al(3)-C(7)	111.71(12)
O(1)-Al(1)-C(2)	113.87(12)	O(1)-Al(3)-C(8)	101.78(11)
C(2)-Al(1)-N(67)	105.15(12)	N(18)-Al(3)-C(8)	116.81(12)
O(1)-Al(1)-N(67)	93.12(9)	N(18)-Al(3)-O(1)	96.12(9)
C(4)-Al(2)-C(3)	122.63(14)	C(5)-Al(4)-C(6)	117.18(16)
O(4)-Al(2)-C(3)	117.29(12)	O(4)-Al(4)-C(5)	108.58(12)
C(3)-Al(2)-N(48)	104.76(12)	N(37)-Al(4)-C(5)	112.70(14)
O(4)-Al(2)-C(4)	106.12(11)	O(4)-Al(4)-C(6)	102.00(13)
C(4)-Al(2)-N(48)	109.61(12)	N(37)-Al(4)-C(6)	117.14(13)
O(4)-Al(2)-N(48)	91.84(9)	N(37)-Al(4)-O(4)	95.77(10)

Synthesis and analytical data for **L**H_2 **1**, **2**, **3**, **4**, **6**, **7** and **L′**H_4

General

All manipulations, unless otherwise stated, were carried out under an atmosphere of dry nitrogen using conventional Schlenk and cannula techniques or in a conventional nitrogen-filled glove box. All solvents were refluxed over the appropriate drying agent, distilled and degassed prior to use. ε-caprolactone was dried over calcium hydride, vacuum distilled and degassed prior to use. 2,6-dicarboxy-4-tertbutylphenol[1] and 2,6-(2,6-$i$$Pr_2C_6H_3N=CH)_2$-4-$t$$BuC_6H_2OH$[2] were prepared according to reported procedures. All other chemicals were obtained commercially and used as received.

*Synthesis of **LH**$_2$*

2,6-dicarboxy-4-tertbutylphenol (0.81 g, 3.9 mmol) and 2,2'-ethylenedianiline (0.88 g, 4.2 mmol) were refluxed in toluene for 24 h. The mixture was allowed to cool to room temperature and yellow crystals of **L**H_2 slowly formed. The solid was filtered and dried *in vacuo* overnight (yield: 1.23 g, 82 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (br s, 4H, N=C*H*), 7.47-6.47 (m, 20H, Ar-*H*), 3.30 (br s, 8H, C*H*$_2$), 1.43 (s, 18H, C(C*H*$_3$)$_3$) ppm; elemental analysis calculated for $C_{52}H_{52}N_4O_2$: C 81.64, H 6.85, N 7.32; found C 81.79, H 6.76, N 7.16 %; MS (ES+) m/z: 765.4 $[M+H]^+$; IR (ATR): 2961(w), 1629(s), 1588(m), 1573(m), 1471(m), 1447(s), 1395(w), 1352(w), 1312(w), 1288(w), 1262(w), 1202(m), 1176(m), 1122(w), 1089(w), 1036(m), 1008(m), 973(w), 915(w), 858(w, 798(m), 722(m), 738(s), 694(w), 647(w), 633(w), 612(w) cm^{-1}; m.p. 344 °C (dec.).

*Synthesis of **1***

LH_2 (1.00 g, 1.3 mmol) was dissolved in toluene (30 mL). $AlMe_3$ (2M in hexanes) (1.4 mL, 2.8 mmol) was added while stirring. The mixture was stirred at room temperature for 10 min and then refluxed for 12 h. After removal of solvent, the crude material was washed with hot acetonitrile (30 mL) affording **1** as a yellow powder (yield: 0.70 g, 62 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, J = 2.5 Hz, 2H, C_6H_2), 8.14 (s, 2H, CH=N), 7.58 (d, J = 7.7 Hz, 2H, AlN-*o*-C_6H_4), 7.41 (pseudo t, J = 7.7 Hz, 2H, AlN-*m*-C_6H_4), 7.24 (m, 2H, AlN-*p*-C_6H_4), 7.18 (pseudo t, J = 7.5 Hz, 2H, N-*m*-C_6H_4), 7.02 (d, J = 7.5 Hz, 2H, N-*o*-C_6H_4), 6.91 (d, J = 2.5 Hz, 2H, C_6H_2), 6.88 (pseudo t, J = 7.5 Hz, 2H, N-*p*-C_6H_4), 6.76 (d, J = 7.8 Hz, 2H, AlN-*m*-C_6H_4), 6.50 (d, J = 7.5 Hz, 2H, N-*m*-C_6H_4), 6.29 (s, 2H, CH=N), 3.90 (td, J_t = 3.7 Hz, J_d = 12.1 Hz, 2H, CH_2), 3.55 (dt, J_d = 4.0 Hz, J_t = 12.5 Hz, 2H, CH_2), 3.04 (td, J_t = 3.7 Hz, J_d = 13.7 Hz, 2H, CH_2), 2.62 (dt, J_d = 3.7 Hz, J_t = 12.5 Hz, 2H, CH_2), 1.49 (s, 18H, $C(CH_3)_3$), -0.77 (s, 6H, $AlCH_3$), -1.15 ppm (s, 6H, $AlCH_3$); elemental analysis calculated for $C_{56}H_{62}Al_2N_4O_2$: C 76.69, H 7.13, N 6.39; found: C 76.60, H 6.99, N 6.28 %; MS (EI) m/z: 877.4 $[M+H]^+$; IR (nujol mull, KBr): 1624(m), 1606(w), 1594(m), 1561(w), 1546(m), 1295(w), 1261(m), 1178(m), 1086(m), 1037(w), 1017(w), 992(w), 841(m), 809(m), 765(m), 750(w), 702(w), 682(m) cm^{-1}; m.p. >350 °C.

*Synthesis of **2***

LH_2 (0.19 g, 0.25 mmol) was dissolved in toluene (30 mL). $AlEt_3$ (2M in hexanes) (0.29 mL, 0.55 mmol) was added while stirring. The mixture was stirred at room temperature for 30 min and then refluxed for 12 h. After removal of solvent, the crude material was washed with hot acetonitrile (30 mL) affording **2** as a yellow powder (yield: 0.10 g, 44 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.40 (s, 2H, C_6H_2), 8.17 (s, 2H, CH=N), 7.58 (d, J = 7.6 Hz, 2H, AlN-*o*-C_6H_4), 7.41 (pseudo t, J = 7.6 Hz, 2H, AlN-*m*-C_6H_4), 7.24 (m, 2H, AlN-*p*-C_6H_4), 7.19 (pseudo t, J = 7.7 Hz, 2H, N-*m*-C_6H_4), 7.01 (d, J = 7.7 Hz, 2H, N-*o*-C_6H_4), 6.89 (m, 4H, C_6H_2 and N-*p*-C_6H_4), 6.81 (d, J = 7.4 Hz, 2H, AlN-*m*-C_6H_4), 6.51 (d, J = 7.3 Hz, 2H, N-*m*-C_6H_4), 6.31 (s, 2H, CH=N), 3.91 (d, J = 12.4 Hz, 2H, CH_2), 3.55 (t, J = 12.8 Hz, 2H, CH_2), 3.06 (d, J = 13.8 Hz, 2H, CH_2), 2.64 (t, J = 12.1 Hz, 2H, CH_2), 1.48 (s, 18H, $C(CH_3)_3$), 0.76 (t, J = 8.0 Hz, 6H, $AlCH_2CH_3$), 0.67 (t, J = 7.9 Hz, 6H, $AlCH_2CH_3$), -0.13 (m, 4H, $AlCH_2CH_3$), -0.39 ppm (m, 4H, $AlCH_2CH_3$); elemental analysis calculated for $C_{60}H_{70}Al_2N_4O_2$: C 77.22, H 7.56, N 6.00; found: C 77.18, H 7.48, N 5.92 %; MS (EI) m/z: 932.5 $[M]^+$; IR (nujol mull, KBr): 1624(m), 1588(w), 1560(w), 1545(w), 1260(m), 1206(w), 1177(w), 1089(m), 1019(m), 802(m), 750(m), 665(w) cm^{-1}; m.p. >350 °C.

Synthesis of ***3*** *and* ***4***

LH_2 (1.00 g, 1.3 mmol) was dissolved in toluene (30 mL). $AlMe_3$ (2M in hexanes) (2.9 mL, 5.8 mmol) was added while stirring. The orange solution was stirred at room temperature for 30 min and then refluxed for 12 h. After removal of solvent, the resulting solid was washed with hot acetonitrile (3 x 30 mL). Combining the filtrates and standing at room temperature afforded **3** as yellow prisms (yield: 0.36 g, 31 %). The remaining orange powder was identified as **4** (yield: 0.66 g, 50 %). Further recrystallisation from a saturated acetonitrile solution at room temperature afforded **4** as orange prisms.

Analytical data for **3**

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (s, 2H, C*H*=N), 7.47 (d, 2H, J = 2.4 Hz, C_6H_2), 7.37 (d, 2H, J = 7.4 Hz, Al-N-*o*-C_6H_4), 7.29 (pseudo t, J_{obs} = 7.4 Hz, Al-N-*m*-C_6H_4), 7.25-7.22 (m, 2H, HN-*p*-C_6H_4), 7.08 (d, 7.7 Hz, 2H HN-*m*-C_6H_4), 7.04 (d, J = 7.4 Hz, 2H, Al-N-*m*-C_6H_4), 6.90 (m, 2H, HN-*m*-C_6H_4), 6.87 (d, J = 2.4 Hz, C_6H_2), 6.73 (d, J = 8.0 Hz, 2H, HN-*o*-C_6H_4), 6.55 (pseudo t, J = 7.4 Hz, 2H, Al-N-*p*-C_6H_4), 5.50 (d, J = 10.5 Hz, 2H, N*H*), 4.62 (qd, J_q = 6.5Hz, J_d = 10.5 Hz, 2H, C*H*-NH), 3.04-2.72 (m, 8H, CH_2), 1.65 (d, J = 6.5 Hz, 6H, CH_3-CH), 1.27 (s, 18H, $C(CH_3)_3$), -0.85 (s, 6H, Al-CH_3), -1.21 (s, 6H, Al-CH_3) ppm; elemental analysis calculated for $C_{58}H_{70}Al_2N_4O_2$: C 76.62, H 7.76, N 6.16; found: C 76.78, H 7.81, N 6.18 %; MS (CI-) m/z: 909.1 $[M]^+$; IR (nujol mull, KBr): 3390(w), 2196(m), 1619(w), 1596(m), 1558(m), 1313(w), 1262(m), 1168(m), 1099(m), 1021(w), 850(m), 803(m), 780(w), 765(w), 745(w), 700(w), 682(m) cm^{-1}; m.p. 302 °C.

Analytical data for **4**

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.21 (s, 2H, C*H*=N), 7.38-6.89 (m, 20H, Ar-*H*), 3.85(q, 2H, J = 6.3 Hz, N-C*H*-CH_3), 3.22 (d, 2H, J = 13.9 Hz, CH_2), 2.58 (d, 2H, J = 13.9 Hz, CH_2), 2.51 (pseudo t, 4H, J_{obs} = 7.3 Hz, CH_2), 1.30 (d, 6H, J = 6.3 Hz, N-CH-CH_3), 0.94 (s, 18H, $C(CH_3)_3$), -0.53 (s, 6H, Al-CH_3), -0.67 (s, 6H, Al-CH_3), -0.76 (s, 6H, Al-CH_3), -1.79 (s, 6H, Al-CH_3) ppm; elemental analysis calculated for $C_{62}H_{80}Al_4N_4O_2$: C 72.92, H 7.90, N 5.49; found: C 73.01, H 7.96, N 5.39%; MS (EI at 350 °C) m/z: 991.3 $[M - 2CH_3]^+$, 820.3 $[M - 3Al(CH_3)_2 - 2CH_3]^+$; IR (nujol mull, KBr): 3401(w), 2191(m), 1925(w), 1615(s), 1597(m), 1574(s), 1279(m), 1214(s), 1191(s), 1124(m), 1097(s), 1064(m), 1047(m), 10229w), 9979w), 944(w), 934(w), 900(m), 8859w), 877(w), 854(w), 830(m), 792(m), 780(w), 764(m), 7549w0, 7379w), 698(s), 666(w), 649(w), 617(w) cm^{-1}; m.p. 280 °C.

*Synthesis of **6***

To a stirring solution of 2,6-(2,6-*i*Pr$_2$C$_6$H$_3$N=CH)$_2$-4-*t*BuC$_6$H$_2$OH (0.11 g, 0.21 mmol) in toluene (30 mL) were added dropwise 0.21 mL of AlMe$_3$ (2M in hexanes, 0.42 mmol). The bright red solution was then refluxed for 12 h. Removal of solvent afforded a yellow solid which was then extracted into hot acetonitrile. Slow evaporation of the solvent *in vacuo* afforded **6** as yellow prisms (0.11 g, 86 %)

^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.08 (s, 1H, C*H*=N), 7.35 (d, 1H, J = 2.6 Hz, C$_6$*H*$_2$), 7.32 (d, 1H, J = 7.6 Hz, *i*Pr$_2$C$_6$*H*$_3$), 7.26 (m, 1H, *i*Pr$_2$C$_6$*H*$_3$), 7.24 (dd, 1H, J = 1.7 Hz, J = 2.9 Hz, *i*Pr$_2$C$_6$*H*$_3$), 7.08 (d, 1H, J = 1.7 Hz, *i*Pr$_2$C$_6$*H*$_3$), 7.06 (br s, 2H, *i*Pr$_2$C$_6$*H*$_3$), 7.03 (d, 1H, J = 2.6 Hz, C$_6$*H*$_2$), 4.72 (d, 1H, J = 10.9 Hz, N*H*), 4.10 (qd, 1H, J$_\mathrm{q}$ = 6.7 Hz, J$_\mathrm{d}$ = 10.9 Hz, C(CH$_3$)*H*NH), 3.38 (m, 2H, C*H*(CH$_3$)$_2$), 3.08 (m, 2H, C*H*(CH$_3$)$_2$), 1.55 (d, 3H, J = 6.7 Hz, C(C*H*$_3$)HNH), 1.29 (m, 9H, CH(C*H*$_3$)$_2$), 1.25 (br s, 12H, C(C*H*$_3$)$_3$ and CH(C*H*$_3$)$_2$), 1.14 (d, 6H, J = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.11 (d, 3H, J = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.07 (d, 3H, J = 6.8 Hz, CH(C*H*$_3$)$_2$), -0.77 (s, 3H, AlC*H*$_3$), -0.78 ppm (s, 3H, AlC*H*$_3$); elemental analysis calculated for C$_{39}$H$_{57}$AlN$_2$O: C 78.48, H 9.63, N 4.69; found: C 78.60, H 9.70, N 4.67 %; MS (EI) m/z: 596.4 [M]$^+$; IR (nujol mull, KBr): 1612(w), 1593(w), 1326(m), 1275(m), 1254(w), 1235(w), 1222(w), 1171(m), 1120(w), 1073(w), 934(w), 898(w), 887(w), 870(w), 851(s), 804(m), 778(m), 759(m), 748(m), 723(w), 702(w), 608(m), 576(w), 533(m) cm^{-1}; m.p. 174 °C.

Synthesis of 7

To a stirring solution of 2,6-(2,6-*i*Pr$_2$C$_6$H$_3$N=CH)$_2$-4-*t*BuC$_6$H$_2$OH (0.44 g, 0.84 mmol) in toluene (30 mL) were added dropwise 1.4 mL of AlMe$_3$ (2M in hexanes, 2.8 mmol). The bright red solution was then refluxed for 12 h. Removal of solvent afforded a pale orange solid which was then washed with hot acetonitrile and dried *in vacuo* to afford **7** as an orange solid. (0.14 g, 26 %)

^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.28 (s, 1H, C*H*=N), 7.39 (m, 1H, C$_6$*H*$_2$), 7.36 (d, 1H, J = 7.6 Hz, *i*Pr$_2$C$_6$*H*$_3$), 7.28 – 7.32 (m, 3H, C$_6$H$_2$ and *i*Pr$_2$C$_6$*H*$_3$), 7.10 (d, 1H, J = 7.3 Hz,

$i\mathrm{Pr}_2\mathrm{C}_6H_3$), 7.04 (d, 1H, J = 7.5 Hz, $i\mathrm{Pr}_2\mathrm{C}_6H_3$), 7.00 (d, 1H, J = 7.5 Hz, $i\mathrm{Pr}_2\mathrm{C}_6H_3$), 4.10 (m, 1H, $\mathrm{C}H(\mathrm{CH}_3)_2$), 3.83 (q, 1H, J = 7.0 Hz, $\mathrm{C}H(\mathrm{CH}_3)\mathrm{N}$), 2.96 (m, 3H, $\mathrm{C}H(\mathrm{CH}_3)_2$), 1.61 (d, 3H, J = 7.0 Hz, $\mathrm{CH}(\mathrm{C}H_3)\mathrm{N}$), 1.31 (s, 9H, $\mathrm{C}(\mathrm{C}H_3)_3$), 1.28 –1.24 (m, 12 H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 1.15 (d, 3H, J = 6.9 Hz, $\mathrm{CH}(\mathrm{C}H_3)_2$), 1.07 (d, 3H, J = 6.8 Hz, $\mathrm{CH}(\mathrm{C}H_3)_2$), 0.90 (d, 3H, J = 6.8 Hz, $\mathrm{CH}(\mathrm{C}H_3)_2$), 0.84 (d, 3H, J = 6.9 Hz, $\mathrm{CH}(\mathrm{C}H_3)_2$), -0.52 (s, 3H, $\mathrm{AlC}H_3$), -0.68 (s, 3H, $\mathrm{AlC}H_3$), -0.71 (s, 3H, $\mathrm{AlC}H_3$), -1.09 ppm (s, 3H, $\mathrm{AlC}H_3$); elemental analysis calculated for $\mathrm{C_{41}H_{62}Al_2N_2O}$: C 75.42, H 9.57, N 4.29; found: C 75.57, H 9.68, N 4.19 %; MS (EI) m/z: 652.4 $[\mathrm{M}]^+$; IR (nujol mull, KBr): 1605(s), 1569(m), 1319(m), 1269(w), 1254(m), 1197(m), 1168(m), 1115(w), 1099(m), 1078(w), 1054(w), 1042(w), 935(m), 905(m), 880(m), 863(w), 827(m), 801(m), 776(s), 758(m), 704(s), 652(s), 614(w), 590(w) cm^{-1}; m.p. 178 °C.

Synthesis of ***L'***H_4

0.16 g of **3** (0.18 mmol) were dissolved in dichloromethane (20 mL). Degassed water (5 mL) was added dropwise while stirring. The solution was stirred for 1 h. The organic phase was isolated and the aqueous phase extracted with an additional 20 mL of dichloromethane. The organic layers were combined and dried over magnesium sulphate. Removal of solvent yielded a yellow solid. Recrystallisation from acetonitrile afforded **L'**H_4 as clear yellow prisms (0.13 g, 93 %).

^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz) δ 8.56 (s, 2H, $\mathrm{C}H{=}\mathrm{N}$), 7.43 (s, 2H, C_6H_2), 7.27 (s, 2H, C_6H_2), 7.16 (pt, J_{obs} = 7.7 Hz, 2H, CH=Np-C_6H_4), 7.01 (m, 4H, CH=No,m-C_6H_4), 6.93 (d, J = 7.5 Hz, 2H, HNm-C_6H_4), 6.87 (pt, J_{obs} = 7.5 Hz, 2H, HNm-C_6H_4), 6.69 (d, J = 8.1 Hz, 2H, CH=Nm-C_6H_4), 6.52 (pt, J_{obs} = 7.4 Hz, 2H, HNp-C_6H_4), 6.26 (d, J = 7.4 Hz, 2H, HNo-C_6H_4), 5.42 (d, J = 10.3 Hz, 2H, $\mathrm{N}H$), 4.73 (m, 2H, $\mathrm{C}H$-CH_3) 3.20 (d, J = 9.8 Hz, 2H, $\mathrm{C}H_2$), 3.09-2.88 (m, 4H, $\mathrm{C}H_2$), 2.50 (d, J = 9.8 Hz, 2H, $\mathrm{C}H_2$), 1.74 (d, J = 6.7 Hz, 6H, CH-$\mathrm{C}H_3$), 1.37 (s, 18 H, $\mathrm{C}(\mathrm{C}H_3)_3$) ppm; MS (ES+) m/z: 797.6 $[\mathrm{M+H}]^+$; IR (ATR): 2960(w), 2358(w), 1627(m), 1588(w), 1570(w), 1484(w), 1450(m), 1354(w), 1262(m), 1205(m), 1088(w, 1034(w), 1010(m), 970(w), 860(m), 800(m), 770(m), 725(s), 635(w), 613(w) cm^{-1}; m.p. 166 °C.

Polymerisation procedure

ε-caprolactone polymerisation

ε-caprolactone polymerisations were performed in Schlenk tubes previously dried in an oven at 170°C for 12 h and equipped with magnetic stirrer bars. In a typical polymerisation procedure, 40 mL of dry toluene were transferred into a schlenk tube containing the desired amount of catalyst. The solution was stirred and maintained at the polymerisation temperature with the aid of an oil bath. Benzyl alcohol was then added from a 0.97 M solution in toluene. After an additional five minutes, the polymerisation was started by the addition of 5.0 mL (45 mmol) of ε-caprolactone.

The polymerisation was quenched by precipitating the polymer in methanol. After filtration, the polymer was left to dry *in vacuo* for 12 h.

ε-caprolactone polymerisation monitored by in-situ IR

In a typical polymerisation procedure, a two necked Schlenk tube, previously dried in an oven at 170 °C for 12 h, was charged with the desired amount of catalyst, in a glove box. The Schlenk tube was then adapted to the *in-situ* IR probe. 40 mL of dry toluene were added, followed by benzyl alcohol (0.97 M solution in toluene). The data collection was started when ε-caprolactone (5.0 mL, 45 mmol) was added. At the end of the acquisition time, the polymerisation was quenched by precipitating the polymer in methanol. After filtration, the polymer was left to dry *in vacuo* for 12 h.

References:

1 R. S. Drago, M. J. Desmond, B. B. Corden, and K. A. Miller *J. Am. Chem. Soc.*, 1983, **105**, 2295.

2 V. C. Gibson, D. Nienhuis, C. Redshaw, A. J. P. White and D. J. Williams, *Dalton Trans.*, 2004, 1761.

Ring opening polymerisation of ε-caprolactone by complex **4** monitored by *in situ* IR

The ROP of ε-caprolactone by complex **4** was monitored by *in situ* IR using a Mettler Toledo ReactIR IC10.

Figure S3. monomer conversion and polymer formation over time monitored by *in situ* IR. Conditions: 40 mL of toluene, 25 °C, monomer : metal ratio of 500 (5 mL of ε-caprolactone), 1 equivalent of benzyl alcohol per metal.

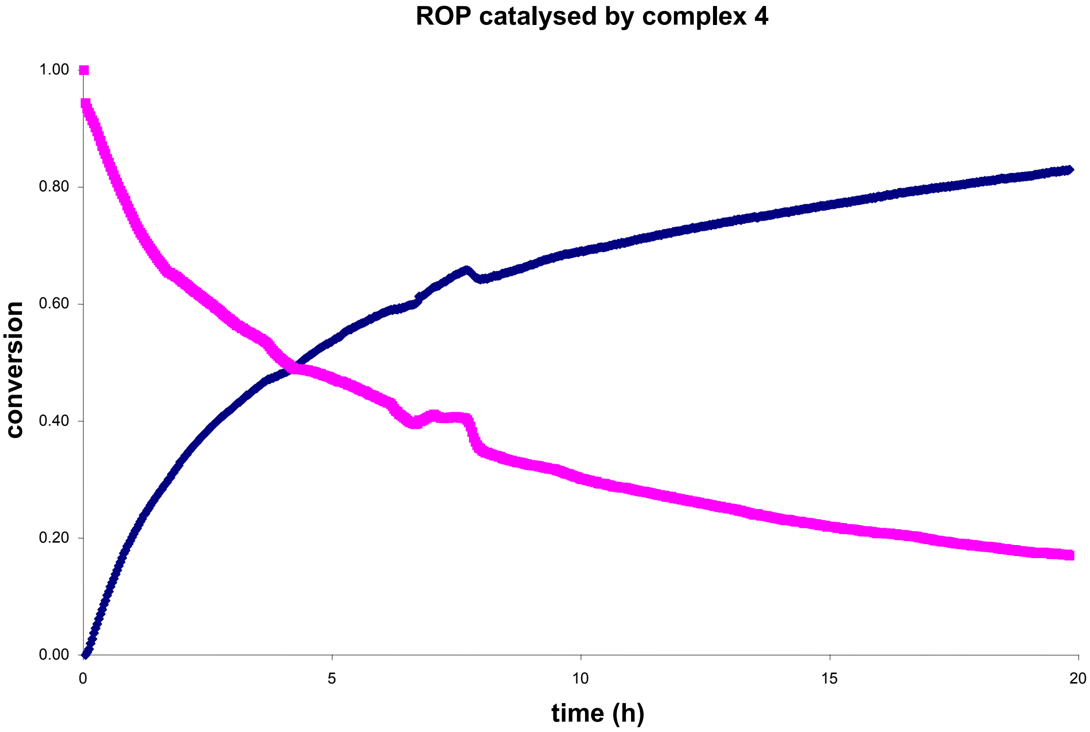

Figure S4. Turnover frequency (h^{-1}) versus monomer conversion for complex **4**

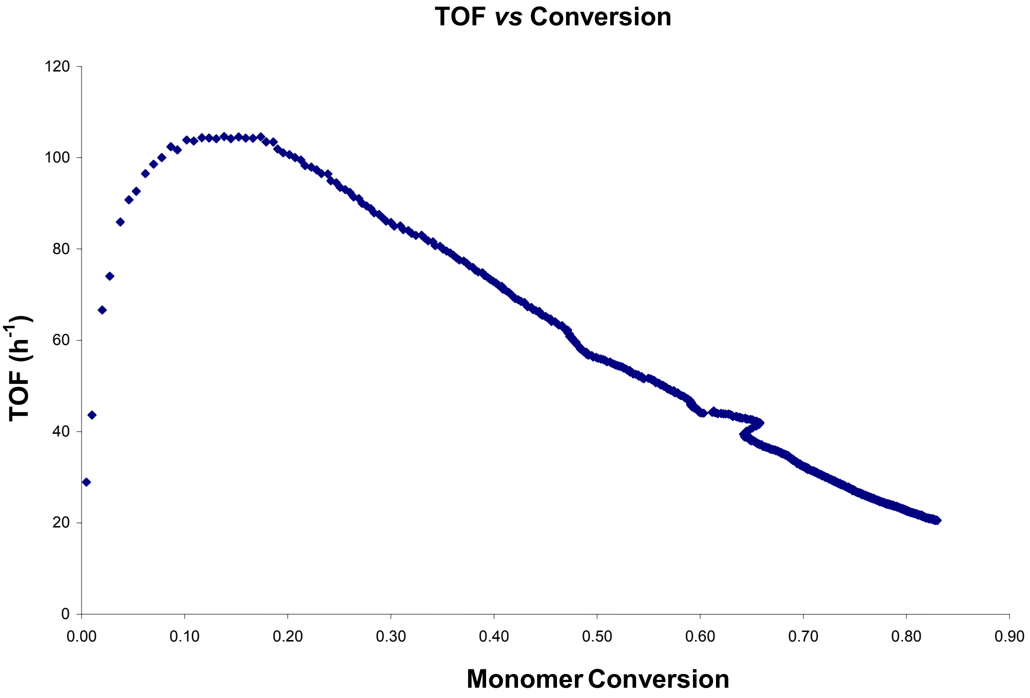

Table S4. Additional polymerisation data for complexes **1** – **3**.[a]

Run	Catalyst	Polymerisation time (h)	Conversion [b]	Mn measured [c] (g/mol)	Mn calculated (g/mol)	IP
1	**1**	6	15 %	11 070	8 550	1.1
2	**1**	11	24 %	14 360	13 730	1.1
3	**1**	72	100 %	42 030	57 320	1.6
4	**2**	11	28 %	10 670	16 020	1.5
5	**2**	72	95 %	36 590	54 320	1.5
6	**3**	1	14 %	7 440	8 010	1.1
7	**3**	3	56 %	14 310	29 990	1.1
8	**3**	12	99 %	49 500	56 650	1.7

[a] Conditions: monomer/metal = 500; 40 mL of toluene; 5 mL of ε-caprolactone; 1 equivalent of benzyl alcohol (from a 0.97 M solution in toluene); 25 °C. [b] calculated by ^{1}H NMR. [c] Mn measured = 0.45 × Mn GPC.