Synthesis and catalytic application of aluminium anilido-pyrazolate complexes†

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A series of aluminium complexes containing anilido-pyrazolate ligands is described. Reactions of four anilido-pyrazolate ligand precursors, HNPhPz, $HNPh^{TriMe}Pz$, $HNPh^{OMe}Pz$, or $HNPh^{SMe}Pz$ [HNPhPz = *ortho*-C_6H_4(NH-phenyl)(1-pyrazole); $HNPh^{TriMe}Pz$ = *ortho*-C_6H_4(NH-2,4,6-trimethylphenyl)-(1-pyrazole); $HNPh^{OMe}Pz$ = *ortho*-C_6H_4(NH-2-methoxyphenyl)(1-pyrazole); $HNPh^{SMe}Pz$ = *ortho*-C_6H_4(NH-2-methylthiophenyl)(1-pyrazole)], with one molar equivalent of $AlMe_3$ in toluene give the aluminium dimethyl complexes, (NArPz)$AlMe_2$ [Ar = phenyl, (NPhPz)$AlMe_2$ (**1**); Ar = 2,4,6-trimethylphenyl, $(NPh^{TriMe}Pz)AlMe_2$ (**2**); Ar = 2-methoxyphenyl, $(NPh^{OMe}Pz)AlMe_2$ (**3**); Ar = 2-methylthiophenyl, $(NPh^{SMe}Pz)AlMe_2$ (**4**)], respectively. The molecular structures are reported for compounds **1** and **3**. Their catalytic activities toward the ring opening polymerisation reaction of ε-caprolactone in the presence of BnOH are also under investigation.

Introduction

Poly(ε-caprolactone) (PCL), poly(lactide) (PLA) as well as their co-polymers have been proved to be both biocompatible and biodegradable polymers, which have found attractive biomedical applications, such as artificial tissue engineering, drug delivery and environmentally friendly packaging materials.[1] Ring opening polymerisation employing the metal-based initiator/catalysts seems to be an efficient way to produce well-controlled polymers. Indeed, a range of main group and transition metal complexes have been reported and these have been reviewed recently.[2] Among those studied, metal complexes bearing nitrogen-based ligands seem to be the focus of interest mainly due to the successful application of metal β-diketiminate complexes in the ring opening polymerisation reaction. Therefore some metal complexes bearing modified β-diketiminate backbones with similar chelating systems and isoelectronic features were synthesised and some of them have been examined for their catalytic activities in the ring opening polymerisation.[3]

Pyrazole-containing metal complexes have been reported for several decades[4] and some of them showed catalytic activity in the ring opening polymerisation of cyclic esters.[5] Following our previous reports on the anilido-oxazolinate system,[3k] the pyrazole group which is similar to the oxazoline group as a five-membered heterocycle should be a suitable candidate for the replacement of the oxazoline group to form anilido-pyrazolate ligand precursors which are expected to work with a similar coordination mode and isoelectronic features as the β-diketiminate ligand. According to our previous work on zinc[3k] and aluminium[3o] anilido-oxazolinate complexes and the catalytic activities demonstrated by some aluminium complexes bearing β-diketiminate[3n] or anilido-imino ligands[3l-m] in ring opening polymerisations, aluminium anilido-pyrazolate complexes are expected to be efficient initiators/catalysts in ring opening polymerisations. In this paper, several ligand precursors and their aluminium dimethyl complexes have been synthesised. Their catalytic activities in the ring opening polymerisation of ε-caprolactone were also investigated.

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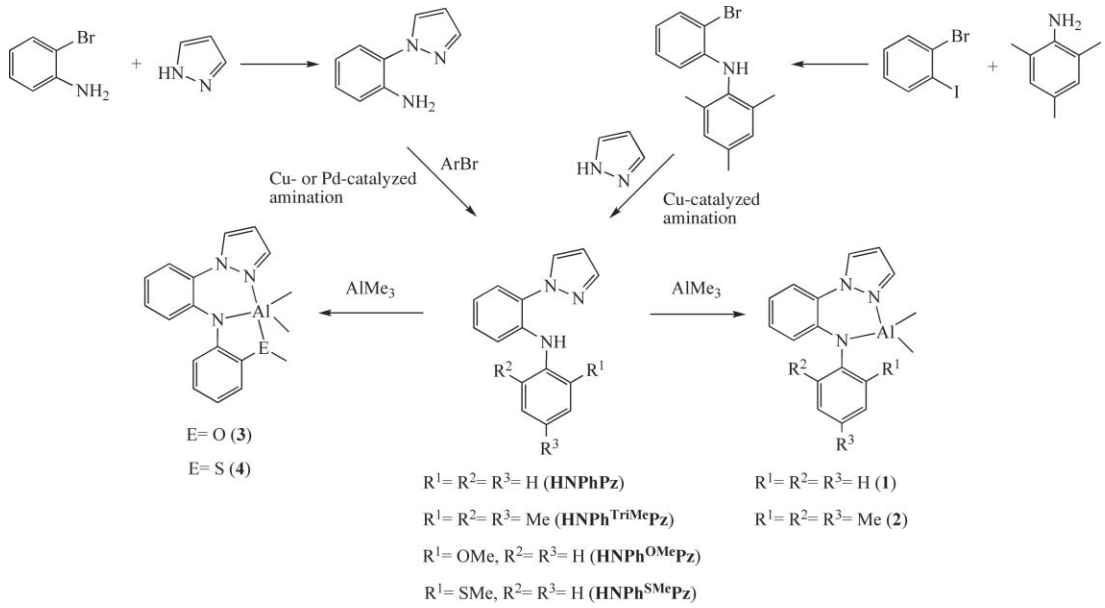
Results and discussion

Synthesis and characterisation

The preparation of the ligand precursors, HNPhPz and $HNPh^{OMe}Pz$, was straightforward using palladium-catalysed amination[6] of 1-(2-aminophenyl)pyrazole[7] with iodobenzene (for HNPhPz) or 2-bromoanisole (for $HNPh^{OMe}Pz$) in the presence of $Pd(OAc)_2$, bis[2-(diphenylphosphanyl)phenyl]ether (DPEPhos) and sodium *tert*-butoxide in refluxing toluene to afford the target compounds in high yield.[8] Ligand precursors, $HNPh^{TriMe}Pz$ and $HNPh^{SMe}Pz$, were prepared by using copper-catalysed amination[9] of *N*-(2-bromophenyl)-2,4,6-trimethylbenzenamine[10] with 1*H*-pyrazole (for $HNPh^{TriMe}Pz$) or 1-(2-aminophenyl)pyrazole with 2-iodothioanisole (for $HNPh^{SMe}Pz$) in the presence of copper reagents (Cu_2O for $HNPh^{TriMe}Pz$; CuI for $HNPh^{SMe}Pz$), supplementary copper-chelating groups (*rac*-*N*,*N*′-*bis*(2-pyridylmethylene)cyclohexane-1,2-diamine[9a] for $HNPh^{TriMe}Pz$; L-proline for $HNPh^{SMe}Pz$) and bases (Cs_2CO_3 for $HNPh^{TriMe}Pz$; K_3PO_4 for $HNPh^{SMe}Pz$) in refluxing solvents (DMF for $HNPh^{TriMe}Pz$; toluene for $HNPh^{SMe}Pz$) to afford the target compounds in moderate to high yields. The compounds, HNPhPz, $HNPh^{TriMe}Pz$, $HNPh^{OMe}Pz$, and $HNPh^{SMe}Pz$, were characterised by NMR spectroscopy as well as elemental analyses.

Treatment of the ligand precursors, HNPhPz, $HNPh^{TriMe}Pz$, $HNPh^{OMe}Pz$, or $HNPh^{SMe}Pz$, with 1.1 molar equivalent $AlMe_3$ in toluene by alkane elimination reaction affords the desired anilido-pyrazolate aluminium dimethyl complexes **1–4** in moderate to high yield. Complexes **1–4** were all characterised by NMR spectroscopy and elemental analyses. The disappearance of the N–H signal of



Scheme 1

the ligand precursors and the appearance of the resonance for protons of methyl groups in the high field region are consistent with the structures proposed in Scheme 1. Due to the symmetric environment around the metal centre, one singlet corresponding to two methyl groups on the metal centre was observed for **1** and **2**. Splitting peaks were found for the methyl groups on the metal centre due to the lower symmetry resulting from the substituents on the anilido groups of the ligands for **3** and **4**. Benzene-d_6 was chosen as the solvent for taking ^{27}Al NMR spectra because the coordination number may vary considerably from non-coordinating to coordinating solvents. The ^{27}Al chemical shifts for the dialkyl complexes without dative functionalities appearing around 145 ppm (145.2 ppm for **1**; 145.5 ppm for **2**) are within the expected region for a four-coordinate aluminium species,[11a-b] whereas the ^{27}Al chemical shifts for the dialkyl complexes with dative functionalities appearing around 120 ppm (119.1 ppm for **3**; 126.3 ppm for **4**) are consistent with five-coordinate aluminium ones in solution.[11a,c]

Suitable crystals for the structural determination of **1** were obtained from concentrated hexane solution. The molecular structure is depicted in Fig. 1. The structure of **1** reveals that the Al centre adopts a distorted tetrahedral geometry with the metal centre chelated by two nitrogen donor atoms of the anilido-pyrazolate ligand and two methyl groups. The difference between Al–N_{amido} (1.8814(16) Å) and Al–$N_{pyrazole}$ (1.9590(17) Å) bond distances might result from the π-donation ability of the anionic amido nitrogen,[12] which is also found in aluminium anilido-aldimino,[3m] anilido-oxazolinate[3o] and amido-pyrazolate complexes.[13] The bond distances of Al–N_{amido} and Al–$N_{pyrazole}$ are comparable with those (1.814(2)–1.890(3) Å for Al–N_{amido}; 1.890(2)–1.994(2)Å for Al–N_{imine}, Al–$N_{oxazoline}$ or Al–$N_{pyrazole}$) found in aluminium anilido-imino,[3m,12] anilido-oxazolinate,[3o] and amido-pyrazolate complexes.[13] The N–Al–N angle (91.65(7)°) is smaller than those (92.65(8)–98.43(10)°) found in aluminium anilido-imine,[3m,12] anilido-oxazolinate,[3o] and amido-pyrazolate complexes.[13]

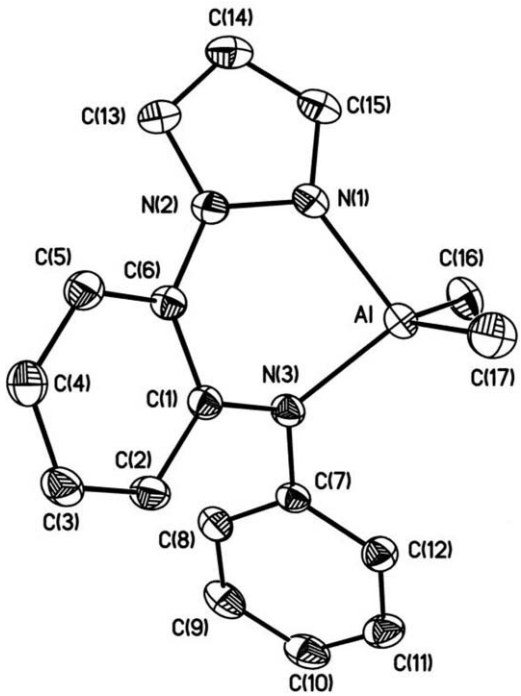


Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and bond angles (°): Al–N(1), 1.9590(17); Al–N(3), 1.8814(16); Al–C(16), 1.948(2); Al–C(17), 1.960(2); N(1)–Al–N(3), 91.65(7); N(3)–Al–C(17), 112.60(9); N(1)–Al–C(16), 105.73(9); C(16)–Al–C(17), 118.86(11). Hydrogen atoms on carbon atoms omitted for clarity.

Suitable crystals for structural determination of **3** were obtained from toluene/hexane solution. The molecular structure is depicted in Fig. 2. The structure of **3** reveals that the metal centre is coordinated by two nitrogen donor atoms and one oxygen donor atom of the anilido-pyrazolate ligand and two methyl groups. The central Al atom adopts a distorted trigonal bipyramidal geometry with a distorted-axis $N_{pyrazole}$–Al–O_{OMe} (164.49(10)°).

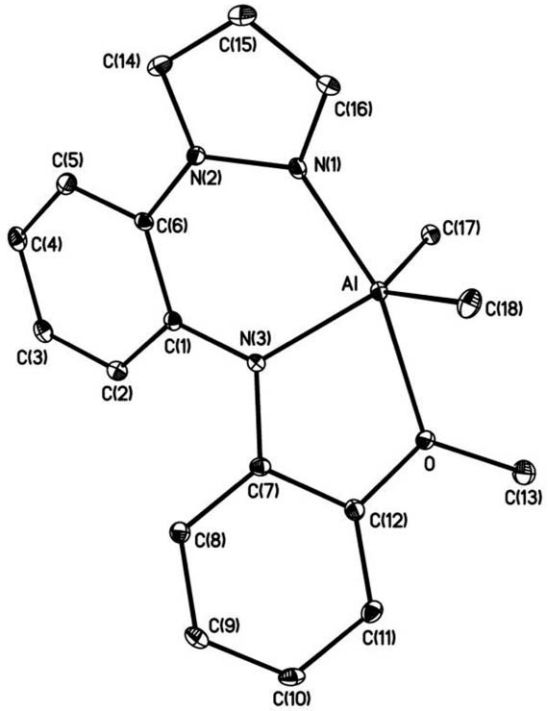


Fig. 2 Molecular structure of **3**. Selected bond lengths (Å) and bond angles (°): Al–O, 2.200(2); Al–N(1), 2.012(3); Al–N(3), 1.900(2); Al–C(17), 1.964(3); Al–C(18), 1.983(3); N(1)–Al–O, 164.49(10); N(3)–Al–C(17), 117.91(12); N(3)–Al–C(18), 120.12(13); N(1)–Al–N(3), 88.23(11); C(17)–Al–C(18), 120.53(15). Hydrogen atoms on carbon atoms omitted for clarity.

The N(3), C(17), and C(18) atoms reside equatorially, forming angles subtended by aluminium of 120° (117.91(12), 120.12(13) and 120.53(15)°). The bond distances of Al–N_{amido} (1.900(2) Å) and Al–$N_{pyrazole}$ (2.012(3) Å) are at the higher end of those discussed above. This elongation might result from the coordination of the dative functionality. The bond distance of Al–O_{OMe} (2.200(2) Å) is close to Al–O_{OMe} (2.2243(17) Å) of the aluminium pendant oxalamidinate complex,[14] however, it is shorter than the bond distance of Al–O_{OMe} (2.675(2) Å) found in the aluminium pendant amido-pyrazolate complex.[13] Comparing the structure of **3** with the aluminium anilido-oxazolinate complex, the pyrazolate group can donate less electrons to the metal centre than the oxazolinate group resulting in a coordination of pendant functionality.

Polymerisation studies

Following our previous studies on aluminium anilido-oxazolinate[3o] complexes in ring opening polymerisation (ROP), the structurally-related aluminium complexes **1–4** were expected to work as catalyst precursors towards the ROP of cyclic esters. Similar conditions were applied to examine the catalytic activities of ring opening polymerisation of ε-caprolactone employing **1–4** as catalyst precursors under a dry nitrogen atmosphere. Representative results are collected in Table 1. Optimised conditions were found to be 15 mL toluene at 50 °C in the presence of benzyl alcohol after several trials on running the polymerisation with CH_2Cl_2, THF and toluene at 25 °C or 50 °C using **1** as catalyst precursors (entries 1–4). The same conditions were applied to examine the catalytic activities of **2**, **3**, and **4** (entries 5–7). Experimental results show compound **1** demonstrates efficient activity, whereas **2–4** exhibit poor conversions within 12 min at 50 °C. Compounds **3** and **4** can reach similar conversions, however with times up to 90 min (entries 8–9). These poor conversions demonstrated by **2–4** might result from the steric effect caused by the bulkier anilido group (for **2**) and the interaction between the pendant functionality and the metal centre (for **3** and **4**), which hindered the coordination of benzyl alcohol or monomer to the metal centre, leading to a decrease in propagation. The linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) demonstrated in Fig. 3 (at 50 °C; entries 4, 10–12) and Fig. 4 (at 25 °C; entries 2, 13–15) implies the "living" character of the polymerisation process. The 'immortal' character was examined using four equiv. ratios (on $[M]_o/[Al]_o$) of benzyl alcohol as the chain transfer agent (entry 16). The M_ns of the polymer created from this polymerisation reaction became half of those found in the reactions with the addition of two equiv. ratios of benzyl alcohol

Table 1 Polymerisation of ε-caprolactone using compounds **1–4** as catalysts in toluene if not otherwise stated[a]

Entry	Catalyst	$[M]_0$:$[Al]_0$:[BnOH]	T (°C)	t (min)	Mn (obsd)[b]	Mn (calcd)[c]	Conv. (%)[d]	Yield (%)[e]	M_w/M_n[b]
1[f]	**1**	100:1:2	25	60	—	—	12	—	—
2	**1**	100:1:2	25	60	9100	5200	91	89	1.12
3[g]	**1**	100:1:2	50	12	2700	2300	38	20	1.15
4	**1**	100:1:2	50	12	8900	5400	92	86	1.11
5	**2**	100:1:2	50	12	—	—	<1	—	—
6	**3**	100:1:2	50	12	—	—	13	—	—
7	**4**	100:1:2	50	12	—	—	11	—	—
8	**3**	100:1:2	50	90	7200	5400	93	90	1.13
9	**4**	100:1:2	50	90	5900	5400	92	85	1.15
10	**1**	200:1:2	50	20	18300	10900	95	83	1.10
11	**1**	300:1:2	50	30	28200	16500	96	90	1.13
12	**1**	400:1:2	50	40	31500	20900	91	86	1.15
13	**1**	200:1:2	25	150	18600	11300	98	95	1.13
14	**1**	300:1:2	25	300	26600	16700	97	90	1.12
15	**1**	400:1:2	25	540	28800	20600	90	82	1.10
16	**1**	200:1:4	25	180	7700	5400	93	85	1.08

[a] in 15 mL. [b] Obtained from GPC analysis times 0.56. [c] Calculated from [M(monomer) × $[M]_0/[Al]_0$ × conversion yield/($[BnOH]_{eq}$)] + M(BnOH). [d] Obtained from ^{1}H NMR analysis. [e] Isolated yield. [f] in 15 mL CH_2Cl_2. [g] in 15 mL THF.

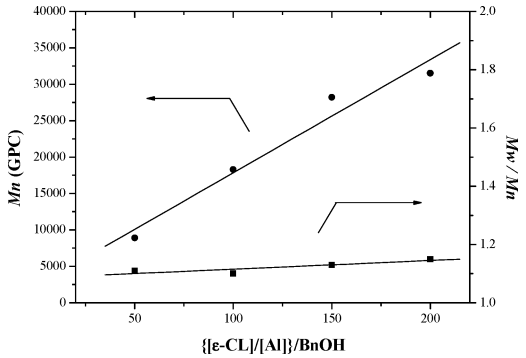


Fig. 3 Polymerisation of ε-caprolactone initiated by **1** in toluene at 50 °C.

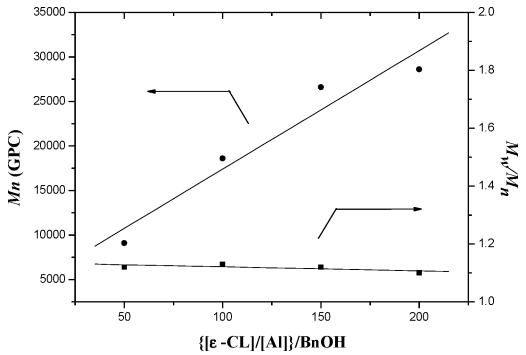


Fig. 4 Polymerisation of ε-caprolactone initiated by **1** in toluene at 25 °C.

(entries 10 and 13). The end group analysis is demonstrated by the ^{1}H NMR spectrum of the polymer produced from ε-caprolactone and **1** ($[M]_o/[BnOH] = 50$; Table 1, entry 1), as shown in Fig. 5. Peaks are assignable to the corresponding protons in the proposed structure. Based on the results discussed above, compound **1** exhibits comparable activity with aluminium anilido-iminate complexes in ROP of ε-caprolactone.[3l-m] Under similar conditions, compound **1** demonstrates better catalytic activity

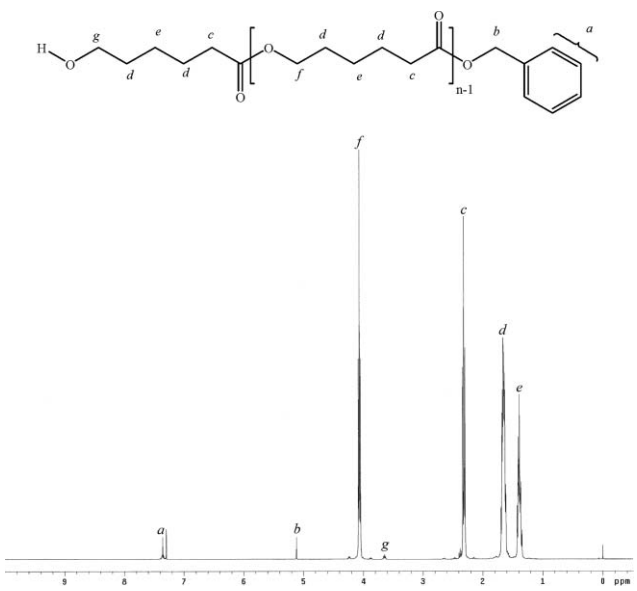


Fig. 5 ^{1}H NMR spectrum of PCL-50 initiated by **1** in toluene at 25 °C (Table 1, Entry 1).

than those complexes with the oxazolinate group instead of the pyrazolate group in ROP of ε-caprolactone at 50 °C.[3o]

Based on the ^{1}H NMR spectrum for end group analysis of the polymer, polymerisation could be initiated by the benzyl alkoxide group in this system. Therefore spectra for the reactions of complexes **1–4** with two equivalents of benzyl alcohol in toluene at room temperature for 5 minutes have been taken in C_6D_6, as shown in Fig. S1.† In the ^{1}H NMR spectra, the protonation process might occur with the release of ligand precursors instead of the substitution of methyl groups with benzyl alkoxide groups upon the formation of the active species when complexes **1**, **3** or **4** reacted with two equivalents of benzyl alcohol, as indicated in (a), (c), (d) of Fig. S1.† A similar observation was recently reported by Roesky.[15] However, only a tiny amount of active species was observed in the reaction of **2** with two equivalents of benzyl alcohol, as indicated in (b) of Fig. S1.† This could explain the poor catalytic activity demonstrated by **2** in the presence of benzyl alcohol. Reactions of $AlMe_3$ with one equiv., two equiv. or three equiv. of BnOH in toluene have been peformed. Based on the ratio of integral intensities between Al–O–CH_2Ph and Al–CH_3 in the NMR spectra, the active species could be formulated as a $[(BnO)_2AlMe]_n$ derivative. According to the catalytic activities and the NMR spectroscopic studies exhibited by **1–4**, substituents on the ligand might strongly affect the formation of the active species and the propagation of polymerisation. Therefore the activity of ROP might be assessed by the determination of the mixed compounds from the protonation of the aluminium anilido-pyrazolate complex and benzyl alcohol.[15] Attempts to isolate the active species have proved unsuccessful. Peaks corresponding to the active species disappeared gradually within 150 minutes.

In conclusion, a family of aluminium dimethyl complexes containing anilido-pyrazolate ligands have been prepared and fully characterised. All of these aluminium complexes show catalytic activities for the ring opening polymerisation of ε-caprolactone in the presence of benzyl alcohol. Under optimised conditions, complex **1** demonstrates efficient activity for the controlled polymerisation of ε-caprolactone with both living and immortal characters. However, the poor performance of complexes **2–4** indicates the bulkier substituents and pendant dative functionalities on the anilido group might strongly affect the catalytic activities of ring opening polymerisation in this system. The activity of ROP might be assessed by the determination of the mixed compounds from the protonation of the aluminium anilido-pyrazolate complex and benzyl alcohol resulting in the formation of the ligand and the $[(BnO)_2AlMe]_n$ derivative. Compounds with the pyrazolate group seem to be more active than those with the oxazolinate group in catalysing the ring opening polymerisation of ε-caprolactone. Preliminary studies on fine-tuning of the ligand precursors and further application of metal complexes to the catalytic reactions are currently underway.

Experimental

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or dry box techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried over molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz)

spectrometers in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. ^{27}Al NMR spectra were taken in C_6D_6 and referenced externally using $AlCl_3$ in D_2O at δ 0 (peak widths at half-height in Hz). Elemental analyses were performed with an Elementar Vario ELIV instrument. The GPC measurements were performed in THF at 35 °C with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and a Waters styragel column (HR4E). Molecular weights and molecular weight distributions were calculated using polystyrene as standard. High-resolution mass spectra (EI-HRMS) were recorded with a Finnigan/Thermo Quest MAT 95XL spectrometer.

$AlMe_3$ (2.0M in toluene, Aldrich), $Pd(OAc)_2$ (Aldrich), 1*H*-pyrazole (Acros), Cu_2O (Acros), iodobenzene (Acros), DPEPhos (*bis*[2-(diphenylphosphanyl)phenyl]ether, Strem), NaO^{t}Bu (TCI), CuI (Strem), Cs_2CO_3 (Aldrich), 2-bromoanisole (Acros), 2-iodothioanisole (Alfa), K_3PO_4 (Alfa), *L*-proline (Lancaster) were used as supplied. 1-(2-Aminophenyl)pyrazole,[7] *N*-(2-bromophenyl)-2,4,6-trimethylbenzenamine[10] and *rac*-*N*,*N*′-*bis*(2-pyridylmethylene)cyclohexane-1,2-diamine[9a] were prepared according to the reported procedures. Benzyl alcohol was dried over magnesium sulfate and distilled before use. ε-Caprolactone was dried over magnesium sulfate and distilled under reduced pressure.

Preparations

HNPhPz. To a flask containing 1-(2-aminophenyl)pyrazole (1.59 g, 10.0 mmol), iodobenzene (1.23 mL, 11.0 mmol), $Pd(OAc)_2$ (0.045 g, 0.20 mmol), *bis*[2-(diphenylphosphanyl)phenyl]ether (DPEPhos, 0.162 g, 0.30 mmol) and NaO^{t}Bu (1.35 g, 14.0 mmol), 12 mL dry toluene were added at room temperature under nitrogen. The reaction mixture was heated at 110 °C for 3.5 days. The solid species were removed by passing the solution through a short column of silica gel. All the volatiles were pumped off, and the crude product was purified by column chromatography (hexane:ethyl acetate = 20:1). This yielded the product as an orange solid. Yield, 1.86 g, 79%. ^{1}H NMR (400 MHz): δ 6.44 (m, 1H), 6.92 (overlap, 2H), 7.12 (m, 2H), 7.19–7.29 (overlap, 4H), 7.46 (d, J = 8.4 Hz, 1H), 7.75–7.77 (overlap, 2H), 8.14 (br, N*H*, 1H). ^{13}C{^{1}H} NMR (100 MHz): δ 106.4, 117.1, 119.2, 119.5, 121.5, 124.1, 128.0, 129.2, 129.8, 140.5 (s, *C*H–Ph or *C*H–Pz), 128.4, 137.6, 141.9 (*tert*-*C*). Anal. Calc. for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.09; H, 5.66; N, 17.70%.

HNPh^{TriMe}Pz. To a flask containing *N*-(2-bromophenyl)-2,4,6-trimethylbenzenamine (2.03 g, 7.0 mmol), 1*H*-pyrazole (0.57 g, 8.4 mmol), Cu_2O (0.05 g, 0.35 mmol), Cs_2CO_3 (2.97 g, 9.1 mmol) and *rac*-*N*,*N*′-*bis*(2-pyridylmethylene)cyclohexane-1,2-diamine (0.41 g, 1.40 mmol), 10 mL DMF were added at room temperature under nitrogen. The reaction mixture was heated at 110 °C for 5 days. The solid species were removed by passing the solution through a short column of silica gel. All the volatiles were pumped off, and the crude product was purified by column chromatography (hexane:ethyl acetate = 40:1). This yielded the product as a yellow powder. Yield, 1.20 g, 62%. ^{1}H NMR (400 MHz): δ 2.17 (s, Ph–C*H*$_3$, 6H), 2.29 (s, Ph–C*H*$_3$, 3H), 6.31 (m, 1H), 6.47 (t, J = 2.0 Hz, 1H), 6.73 (m, 1H), 6.93 (s, 2H), 7.06 (m, 1H), 7.24 (m, 1H), 7.46 (br, N*H*, 1H), 7.77 (m, 1H), 7.80 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz): δ 18.2 (s, Ph–*C*H$_3$), 20.9 (s, Ph–*C*H$_3$), 106.3, 113.4, 116.8, 123.8, 128.4, 129.1, 129.9, 140.4 (s, *C*H–Ph or *C*H–Pz), 126.1, 135.1, 135.3, 135.9, 140.8 (*tert*-*C*). Anal. Calc. for $C_{18}H_{19}N_3$: C, 77.95; H, 6.90; N, 15.15. Found: C, 77.65; H, 6.65; N, 15.48%.

HNPh^{OMe}Pz. To a flask containing 1-(2-aminophenyl)-pyrazole (1.33 g, 8.35 mmol), 2-bromoanisole (1.46 g, 7.80 mmol), $Pd(OAc)_2$ (0.035 g, 0.16 mmol), DPEPhos (0.126 g, 0.24 mmol) and NaO^{t}Bu (1.05 g, 10.92 mmol), 8 mL dry toluene were added at room temperature under nitrogen. The reaction mixture was heated at 110 °C for 3.5 days. The solid species were removed by passing the solution through a short column of silica gel. All the volatiles were pumped off, and the crude product was purified by column chromatography (hexane:ethyl acetate = 5:1). This yielded the product as an orange solid. Yield, 1.80 g, 87%. ^{1}H NMR (400 MHz): δ 3.85 (s, OC*H*$_3$, 3H), 6.43 (m, 1H), 6.84–6.88 (overlap, 3H), 6.92 (m, 1H), 7.24 (m, 1H), 7.29–7.32 (overlap, 2H), 7.51 (m, 1H), 7.73 (d, J = 2.4 Hz, 1H), 7.78 (d, J = 1.6 Hz, 1H), 8.09 (br, N*H*, 1H). ^{13}C{^{1}H} NMR (100 MHz): δ 55.5 (s, O*C*H$_3$), 106.3, 110.9, 116.2, 117.5, 119.7, 120.4, 120.9, 124.5, 127.9, 129.8, 140.4 (s, *C*H–Ph or *C*H–Pz), 129.2, 131.7, 137.3, 149.6 (*tert*-*C*). Anal. Calc. for $C_{16}H_{15}N_3O$: C, 72.43; H, 5.70; N, 15.84. Found: C, 72.28; H, 5.89; N, 15.63%.

HNPh^{SMe}Pz. To a flask containing 1-(2-aminophenyl)-pyrazole (0.58 g, 3.65 mmol), 2-iodothioanisole (0.83 g, 3.32 mmol), K_3PO_4 (1.06 g, 5.00 mmol), L-proline (0.08 g, 0.66 mmol) and CuI (0.06 g, 0.33 mmol), 3 mL dry toluene were added at room temperature under nitrogen. The reaction mixture was heated at 110 °C for 3 days. The solid species were removed by passing the solution through a short column of silica gel. All the volatiles were pumped off, and the crude product was purified by column chromatography (hexane:ethyl acetate = 20:1). This yielded the product as a purple oil. Yield, 0.80 g, 86%. ^{1}H NMR (400 MHz): δ 2.37 (s, SC*H*$_3$, 3H), 6.45 (m, 1H), 6.90 (m, 1H), 6.96 (m, 1H), 7.12 (m, 1H), 7.24 (m, 1H), 7.28–7.43 (overlap, 4H), 7.76 (m, 1H), 7.80 (m, 1H), 8.37 (br, N*H*, 1H).^{13}C{^{1}H} NMR (100 MHz): δ 17.0 (s, S*C*H$_3$), 106.4, 117.2, 118.0, 120.2, 121.5, 124.4, 127.2, 127.9, 129.7, 131.2, 140.5 (s, *C*H–Ph or *C*H–Pz), 129.3, 137.1, 141.7 (*tert*-*C*). Anal. Calc. for $C_{16}H_{15}N_3S$: C, 68.30; H, 5.37; N, 14.93. Found: C, 68.41; H, 5.36; N, 14.85%.

(NPhPz)AlMe$_2$ (1). To a flask containing HNPhPz (0.47 g, 2.0 mmol) and 30 mL dry toluene, 1.10 mL $AlMe_3$ (2 M in toluene, 2.20 mmol) were added at 0 °C under nitrogen. The reaction mixture was allowed to warm to room temperature and reacted for 0.5 h. The volatiles were removed under reduced pressure. The residue was washed with 10 mL hexane to afford an off-white solid. Yield, 0.42 g, 72%. Suitable crystals of **1** for structural determination were recrystallised from concentrated hexane solution. ^{1}H NMR (600 MHz, C_6D_6): δ –0.29 (s, Al–C*H*$_3$, 6H), 5.61 (t, J = 2.4 Hz, 1H), 6.47 (m, 1H), 6.64 (m, 1H), 6.86–6.93 (overlap, 3H), 7.03 (m, 1H), 7.19 (m, 2H), 7.28 (overlap, 3H). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ –9.5 (s, Al–*C*H$_3$), 107.8, 117.3, 121.4, 122.0, 122.5, 124.9, 129.5, 129.6, 129.8, 130.4, 138.1 (s, *C*H–Ph or *C*H–Pz), 126.2, 145.7, 150.2 (*tert*-*C*). ^{27}Al NMR (156 MHz, C_6D_6): δ 145.2 ($\Delta\nu_{1/2}$ = 4869.4). Anal. Calc. for $C_{17}H_{18}AlN_3$: C, 70.09; H, 6.23; N, 14.42. Found: C, 70.14; H, 6.62; N, 14.66%. EI-HRMS: m/z Calc. for $C_{17}H_{18}AlN_3$: 291.1316 [M]$^+$; found: 291.1319.

(NPh^{TriMe}Pz)AlMe$_2$ (2). To a flask containing HNPh^{TriMe}Pz (0.28 g, 1.0 mmol) and 30 mL dry toluene, 0.55 mL AlMe$_3$ (2 M in toluene, 1.10 mmol) were added at 0 °C under nitrogen. The reaction mixture was allowed to warm to room temperature and reacted for 18 h. The volatiles were removed under reduced pressure. The residue was washed with 10 mL hexane to afford an off-white solid. Yield, 0.15 g, 44%. ^{1}H NMR (600 MHz, C_6D_6): δ –0.37 (s, Al–CH_3, 6H), 2.21 (overlap, Ph–*o*-CH_3 and Ph–*p*-CH_3, 9H), 5.70 (t, J = 2.4 Hz, 1H), 6.43 (m, 1H), 6.66 (dd, J = 8.4 Hz and 1.2 Hz, 1H), 6.76 (dd, J = 8.1 Hz and 1.5 Hz, 1H), 6.88 (m, 1H), 6.91 (s, 2H), 6.98 (m, 1H), 7.07 (d, J = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ –9.4 (s, Al–*C*H$_3$), 19.0 (s, Ph–*C*H$_3$), 21.0 (s, Ph–*C*H$_3$), 107.5, 115.2, 119.6, 120.3, 129.6, 129.9, 130.0, 137.3 (s, *C*H–Ph or *C*H–Pz), 124.5, 128.3, 133.9, 136.2, 142.7, 145.4 (*tert-C*). ^{27}Al NMR (156 MHz, C_6D_6): δ 145.5 ($\Delta\nu_{1/2}$ = 4508.5). Anal. Calc. for $C_{20}H_{24}AlN_3$: C, 72.05; H, 7.26; N, 12.60. Found: C, 71.08; H, 7.25; N, 12.20%. EI-HRMS: *m*/*z* Calc. for $C_{20}H_{24}AlN_3$: 333.1786 [M]$^+$; found: 333.1776.

(NPh^{OMe}Pz)AlMe$_2$ (3). To a flask containing HNPh^{OMe}Pz (0.40 g, 1.50 mmol) and 20 mL dry toluene, 0.83 mL AlMe$_3$ (2 M in toluene, 1.65 mmol) were added at 0 °C under nitrogen. The reaction mixture was allowed to warm to room temperature and reacted for 3 h. The volatiles were removed under reduced pressure. The residue was washed with 10 mL hexane to afford an off-white solid. Yield, 0.44 g, 91%. Suitable crystals of **3** for structural determination were recrystallised from toluene/hexane solution. ^{1}H NMR (600 MHz, C_6D_6): δ –0.42 (s, Al–CH_3, 3H), –0.33 (s, Al–CH_3, 3H), 3.39 (s, OCH_3, 3H), 5.72 (t, J = 2.4 Hz, 1H), 6.51(m, 1H), 6.53(m, 1H), 6.73–6.75 (overlap, 2H), 6,83(m, 1H), 6.88(m, 1H), 6.95(m, 1H), 7.32(m, 1H), 7.44(m, 1H), 7.62(m, 1H). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ –9.5 (br, Al–*C*H$_3$), –8.9 (s, Al–*C*H$_3$), 53.9 (s, O*C*H$_3$), 106.9, 110.3, 117.5, 120.0, 121.3, 121.4, 121.5, 122.6, 128.8, 129.0, 138.4 (s, *C*H–Ph or *C*H–Pz), 127.3, 140.3, 144.8, 150.6 (*tert-C*). ^{27}Al NMR (156 MHz, C_6D_6): δ 119.1 ($\Delta\nu_{1/2}$ = 6385.0). Anal. Calc. for $C_{18}H_{20}AlN_3O$: C, 67.28; H, 6.27; N, 13.08. Found: C, 66.92; H, 6.52; N, 13.12%. EI-HRMS: *m*/*z* Calc. for $C_{18}H_{20}AlN_3O$: 321.1422 [M]$^+$; found: 321.1427.

(NPh^{SMe}Pz)AlMe$_2$ (4). To a flask containing HNPh^{SMe}Pz (0.28 g, 1.02 mmol) and 20 mL dry toluene, 0.56 mL AlMe$_3$ (2 M in toluene, 1.12 mmol) were added at 0 °C under nitrogen. The reaction mixture was allowed to warm to room temperature and reacted for 3 h. The volatiles were removed under reduced pressure. The residue was washed with 10 mL hexane to afford an off-white solid. Yield, 0.36 g, 72%. ^{1}H NMR (600 MHz, C_6D_6): δ –0.32 (s, Al–CH_3, 3H), –0.18 (s, Al–CH_3, 3H), 1.997 (s, SCH_3, 3H), 5.70 (t, J = 2.4 Hz, 1H), 6.54 (m, 1H), 6.70 (m, 1H), 6.75 (m, 1H), 6.89 (m, 1H), 6.93 (m, 1H), 6.96 (d, J = 3.0 Hz, 1H), 7.02 (m, 1H), 7.11 (m, 1H), 7.29 (d, J = 2.4 Hz, 1H), 7.52 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ –9.1 (s, Al–*C*H$_3$), –7.4 (s, Al–*C*H$_3$), 19.9 (s, S*C*H$_3$), 107.3, 118.2, 121.0, 121.5, 123.3, 125.0, 129.1, 129.2, 130.1, 134.6, 137.9 (s, *C*H–Ph or *C*H–Pz), 129.6, 146.3, 154.1 (*tert-C*). ^{27}Al NMR (156 MHz, C_6D_6): δ 126.3 ($\Delta\nu_{1/2}$ = 6240.16). Anal. Calc. for $C_{18}H_{20}AlN_3S$: C, 64.07; H, 5.97; N, 12.45. Found: C, 63.68; H, 6.42; N, 12.70%. EI-HRMS: *m*/*z* Calc. for $C_{18}H_{20}AlN_3S$: 337.1193 [M]$^+$; found: 337.1185.

Polymerisation procedure of ε-caprolactone. Typically, to a flask containing the prescribed amount of monomers (ε-caprolactone) and catalyst precursors (0.125 mmol) were added 15 mL (containing 0.25 mmol benzyl alcohol) toluene. The reaction mixture was stirred at the prescribed temperature for the prescribed time. After the reaction was quenched by the addition of 10 mL acetic acid solution (0.35 N), the resulting mixture was poured into 50 mL n-heptane to precipitate the polymers. Crude products were recrystallised from THF–hexane and dried *in vacuo* up to a constant weight.

Crystal structure data

Crystals were grown from concentrated hexane solution (**1**) or toluene/hexane solution (**3**), and isolated by filtration. Suitable crystals of **1** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker CCD Smart-1000 diffractometer. Suitable crystals of **3** were mounted onto glass fiber using perfluoropolyether oil and cooled rapidly in a stream of cold nitrogen gas using an Oxford Cryosystems Cryostream unit. Diffraction data were collected at 100 K using an Oxford Gemini S diffractometer. For **1**, the absorption correction was based on the symmetry equivalent reflections using the SADABS program.[16] For **3**, empirical absorption correction was based on spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm from CrysAlis RED, Oxford Diffraction Ltd. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.[17] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Table 2.

Table 2 Summary of crystal data for compounds **1** and **3**

	1	**3**
Formula	$AlC_{17}H_{18}N_3$	$AlC_{18}H_{20}N_3O$
Fw	291.32	321.35
T, K	293(2)	100(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a, Å	10.380(2)	10.4157(6)
b, Å	10.366(2)	10.5978(6)
c, Å	15.271(3)	15.1969(7)
α, °	90	90
β, °	102.726(4)	90
γ, °	90	90
V, Å^3	1602.7(6)	1677.49(16)
Z	4	4
ρ_{calc}, Mg/m^3	1.207	1.272
μ(Mo K$_\alpha$), mm^{-1}	0.123	0.129
Reflections collected	8830	6118
No. of parameters	190	208
Indep. reflns (R_{int})	3144(0.0387)	2184(0.0276)
Final R indices R_1[a], wR_2[a]	0.0445, 0.1211	0.0435, 0.1175
R indices (all data)	0.0637, 0.1335	0.0525, 0.1207
GoF[b]	0.999	1.000

[a] $R1 = [\Sigma\,|F_o| - |F_c|]/\Sigma\,|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ $w = 0.10$. [b] GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

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