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Synthesis of aluminium complexes bearing a piperazine-based ligand system

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ABSTRACT

Aluminium complexes bearing the *N,N*-chelating ligand 1,4-bis(2-hydroxy-3,5-di-*tert*-butyl)piperazine (**1**) have been synthesised. Both monometallic and bimetallic aluminium methyl complexes (**2** and **3**, respectively) were prepared by treatment of **1** with the appropriate amount of $AlMe_3$. Complex **2** can be converted to **3** by addition of excess $AlMe_3$. Bimetallic aluminium-ethyl complex **4** was also prepared. Treatment of **1** with $AlEt_2Cl$ afforded the monometallic chloride complex **5**. Treatment of this latter complex with potassium alkoxides (KOR, R = Me, Et, ^{i}Pr, ^{t}Bu) or AgOTf afforded the corresponding aluminium alkoxide complexes (**6**, R = Et; **7**, R = Me; **8**, R = ^{i}Pr; **9**, R = ^{t}Bu; **10**, R = OTf) in good yields. Aluminium ethoxide complex **6** was also synthesised by treatment of **1** with $AlEt_2OEt$. All of these complexes were tested as potential catalysts in the ring-opening polymerisation of *rac*-lactide and caprolactone with limited success.

1. Introduction

Aluminium complexes have been shown to be active on the ring-opening polymerisation (ROP) of cyclic esters such as lactides and lactones [1–3]. As such, a variety of aluminium alkoxides as well as aluminium alkyl complexes have been synthesised and have shown to be active catalytic precursors [4–10]. Many of these species employ phenoxy-based ancillary ligands, including bidentate and tetradentate Schiff-based systems [5–7,10,11] as well as phenoxymethyl-bisamine-based ligand systems [8].

N-substituted piperazines are versatile ligands as they can potentially be used to bind either one- or two-metal centres, the former of which results in a conformational strain around the piperazine ring as the 6-membered piperazine ring forms the less stable boat conformation [12]. Generally, the nitrogen atoms of the piperazine ring are further substituted in order in increase the tacticity of the ligand, resulting in a wide variety of binding possibilities to create monometallic and bimetallic species (Fig. 1). For instance, Limberg has generated the neutral ligand 1,4-bis(2-pyridylmethyl)piperazine ligand and has shown that it can coordinate to iron(II) as either a tetradentate or bidentate ligand, the latter of which forms a bimetallic species in which the piperazine bridges two iron metal centres [13]. Other uses of similar piperazine ligands include Wieghardt's 1,4-bis(2-amino-benzyl)piperazine [14], which was used as a neutral ligand on late transition metals, and Mountford's 1,4-bis(2-amino-4-*tert*-butylbenzyl)piperazine for use as a dianionic ligand to stabilise titanium imido complexes [15]. Recently, the groups of Lappert as well as Balakrishna have utilised 1,4-bis(2-hydroxy-3,5-di-*tert*-butyl)piperazine (**1**) as a ligand to stabilise zinc and palladium complexes [16,17]. In most of the above cases, the piperazine-based ligands were not used interchangeably between the monometallic and bimetallic binding modes; only Limberg has been able to take advantage of the diversity of the piperazine-based ligand to ligate both one or two iron centres [13].

We have utilised ligand **1** to generate a series of new aluminium complexes, including aluminium alkyl and aluminium alkoxide species. With regard to the alkyl complexes, we have shown that this ligand can bind either one or two aluminium metal centres; however, the bimetallic species is significantly more stable than the corresponding monometallic complex. All of the aluminium alkoxide complexes were obtained as monometallic complexes; attempts to obtain their corresponding bimetallic species were unsuccessful.

2. Results and discussion

2.1. Aluminium alkyl complexes

Monometallic aluminium methyl complex **2** was obtained in 86% yield through treatment of a toluene solution of ligand **1** with one equivalent of $AlMe_3$ at 50 °C, followed by a five-hour reflux (Eq. (1)). A white solid was isolated which did not contain any measurable amount of impurities. The ^{1}H NMR spectrum of complex **2** revealed a singlet integrating to three hydrogens at δ −0.79 ppm, consistent with an Al–Me resonance. Three sets of piperazine-based resonances with a ratio of 1:1:2, respectively,

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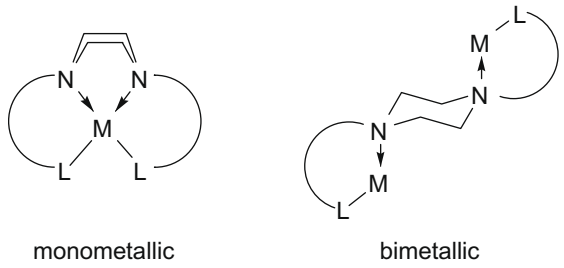
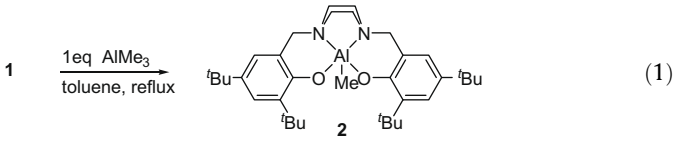


Fig. 1. The two different binding modes of piperazine-based ligands.

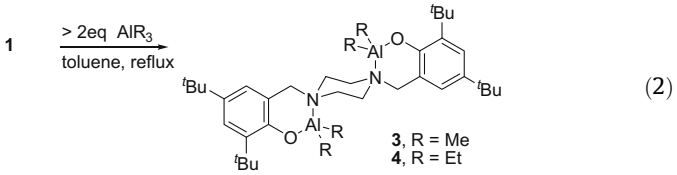
were observed at δ 2.95, 2.61 and 1.21 ppm. In addition, two doublets integrating to two hydrogens each were observed at δ 3.35 and 3.13 ppm, which can be assigned to the benzylic protons. These latter resonances are indicative of the monometallic complexes of ligand **1**.



(1)

Crystals suitable for an X-ray diffraction study were grown by slow diffusion of pentane into a saturated THF solution of **2** at room temperature. An ORTEP diagram is shown in Fig. 2. Selected bond lengths and angles are shown in Table 1. Complex **2** has a distorted square based pyramidal geometry around the aluminium metal centre (τ = 0.34) [11]. There is a tetradentate coordination from the piperazine-based ligand (N_2O_2), occupying the base of the pyramid and the methyl group occupies the axial position. The Al–O, Al–N and Al–C bond lengths are similar to other known dianionic N_2O_2-aluminium complexes [18,19].

Treatment of a toluene solution of ligand **1** with two equivalents of $AlMe_3$ at −20 °C, followed by reflux for 5 h resulted in formation of bimetallic aluminium complex **3** (Eq. (3)). Two sets of doublets corresponding to the piperazine protons are observed in ^{1}H NMR spectrum. The presence of four Al–Me groups is evident from new singlets at δ −0.41 and −0.45 ppm in a 1:3 ratio, suggesting that one of the methyl groups is in a different environment to the other three on the NMR spectroscopic timescale. Only one resonance corresponding to the benzylic protons was observed at δ 3.18 ppm. X-ray analysis of crystals of **3** grown from a wide variety of different solvents was only able to confirm connectivity; and disorder within the molecule did not allow for further refinement of the structure.



(2)

Slightly different reactivity between ligand **1** and $AlEt_3$ was observed. Treatment of a toluene solution of ligand **1** with $AlEt_3$ resulted in formation of bimetallic complex **4**. We were unable to obtain any evidence of the corresponding monometallic species, even when reaction conditions were varied. Reactivity differences between $AlMe_3$ and $AlEt_3$ has also been noted by Gambarotta and co-workers [20]. The X-ray crystallographic analysis of bimetallic **4** was successful. An ORTEP diagram is shown in Fig. 3 and selected bond lengths and angles are given in Table 2. A tetrahedral geometry around the aluminium centres is observed, and the piperazine backbone has adopted a chair conformation.

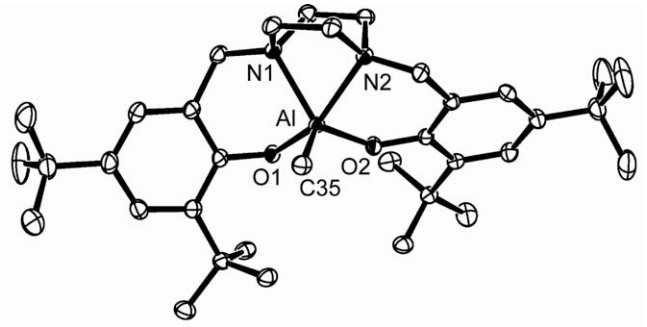
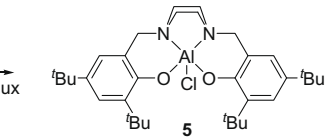


Fig. 2. Thermal ellipsoid plot (30%) of **2**. H atoms omitted for clarity.

The monomeric species **2** was converted to the bimetallic dimethyl-aluminium complex **3** upon addition of excess $AlMe_3$ to a solution of **2**. The converse reaction did not occur; that is, treatment of bimetallic species **3** with excess ligand **1** did not result in formation of monometallic species **2**.

2.2. Aluminium chloride complex

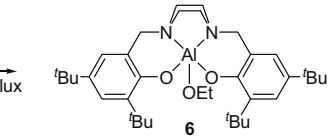
Monometallic aluminium chloride complex **5** was obtained by treatment of ligand **1** with one equivalent of $AlEt_2Cl$ (Eq. (3)). The ^{1}H NMR spectrum of chloride **5** is similar to that of the monometallic aluminium methyl complex in that two doublets corresponding to the benzylic protons are observed at δ 3.52 and 3.07 ppm. X-ray analysis confirmed the connectivity; the ORTEP diagram is shown in Fig. 4, selected bond lengths and angles are given in Table 1. Similar to the monometallic aluminium methyl complex **2**, a distorted square based pyramidal geometry is observed (τ = 0.47). Attempts to generate the analogous bimetallic complex were unsuccessful.



(3)

2.3. Aluminium alkoxide complexes

A variety of aluminium alkoxide complexes were generated utilising two different methodologies. The first and less general route involved treatment of ligand **1** with one equivalent of $AlMe_2OEt$ to generate an aluminium ethoxide complex (**6**) (Eq. (4)). As with other monometallic systems, the benzylic protons appear as two doublets integrating to two hydrogens each at δ 3.56 and 2.97 ppm. Crystals suitable for and X-ray diffraction study were grown from a saturated diethyl ether solution of **6** at −30 °C. Similar to the other monometallic complexes, a distorted square based pyramidal geometry around the aluminium centre is observed (τ = 0.31), with the ethoxide functionality occupies the apical site (Fig. 5, see Table 1 for selected bond lengths and angles). The Al–OEt bond lengths is 1.729(2) Å is shorter than that of Al–OAr bond lengths within the molecule (1.795(2) and 1.766(2) Å), but similar to other known Al–OEt complexes such as Atwood's salen(*t*Bu)AlO-Et 1.737(2) Å (salen(*t*Bu) = *N,N′*-ethylenebis(3,5-di-*tert*-buthylsalicylideneimine) [21].



(4)

Table 1
Selected bond lengths and angles for **2**, **5**, **6**, **8**, **9** and **10**. (**2**, X = C35; **5**, X = Cl; **6**, **8**, **9** and **10**, X = O3).

	didi-AlMe **2**	didi-AlCl **5**	didi-AlOEt **6**	didi-AlO^{i}Pr **8**	didi-AlO^{t}Bu **9**	didi-AlOTf **10**
Al–O1	1.804(2)	1.781(3)	1.766(2)	1.7644(12)	1.7937(16)	1.769(3)
Al–O2	1.759(2)	1.737(3)	1.795(2)	1.7827(11)	1.7812(16)	1.731(3)
Al–N1	2.091(3)	2.072(3)	1.729(2)	2.0803(13)	1.7191(17)	1.819(3)
Al–N2	2.127(3)	2.104(3)	2.085(2)	2.0932(14)	2.105(2)	2.046(4)
Al–X	1.974(3)	2.1610(16)	2.105(2)	1.7166(11)	2.182(2)	2.074(4)
O1–Al–O2	92.90(10)	95.95(13)	94.45(10)	92.22(5)	99.00(7)	97.30(14)
N1–Al–N2	69.51(10)	70.18(13)	69.48(9)	70.43(5)	68.65(7)	70.97(15)
O1–Al–N1	88.65(10)	90.23(13)	88.81(9)	88.30(5)	89.34(8)	91.30(15)
O1–Al–N2	150.49(11)	157.29(14)	133.24(10)	133.17(6)	154.42(8)	159.37(16)
O2–Al–N1	129.71(12)	128.85(14)	151.84(10)	151.37(6)	130.52(8)	138.77(16)
O2–Al–N2	86.75(10)	88.14(13)	88.44(10)	88.86(5)	86.64(7)	89.87(14)
O1–Al–X	107.11(12)	104.32(10)	114.70(11)	116.76(6)	109.29(8)	100.84(15)
O2–Al–X	116.72(14)	104.32(10)	111.01(11)	112.38(5)	115.73(9)	112.98(16)
N1–Al–X	110.62(13)	112.46(11)	92.71(10)	92.67(5)	106.81(8)	104.71(15)
N2–Al–X	99.26(13)	94.03(10)	107.47(11)	105.78(6)	90.12(8)	94.02(15)

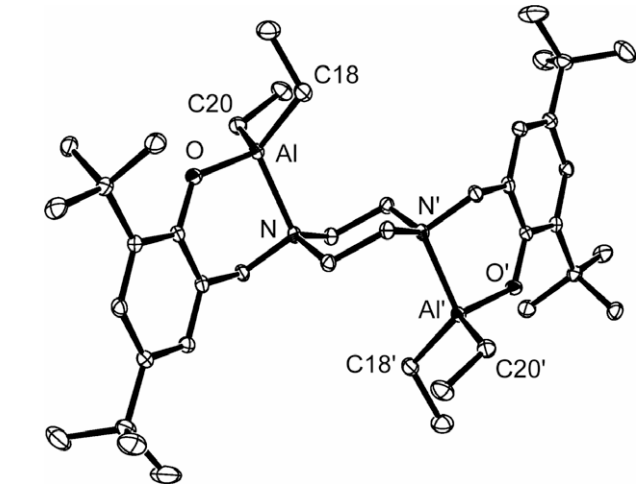


Fig. 3. Thermal ellipsoid plot (30%) of **4**. H atoms omitted for clarity.

Table 2
Selected bond lengths and angles for **4**.

	didi-(AlEt$_2$)$_2$ **4**
Al–O	1.7586(12)
Al–N	2.0631(14)
Al–C18	1.9687(18)
Al–C20	1.9632(18)
O–Al–N	96.51(5)
O–Al–C18	110.36(7)
O–Al–C20	112.62(7)
N–Al–C18	115.08(7)
N–Al–C20	105.49(7)
C18–Al–C20	115.30(8)

Attempts to generate the corresponding bimetallic species were unsuccessful. However, ethoxide **6** was also generated by treatment of aluminium chloride **5** with KOEt, in similar yields (Eq. (5)). This latter method was used to create a series of other aluminium alkoxide complexes, including an aluminium methoxide (**7**), aluminium isopropoxide (**8**) and aluminium *tert*-butoxide (**9**). Although we were unable to grow crystals suitable for and X-ray diffraction study of methoxide **7**, the spectroscopic data of **7** was consistent with a monomeric species; that is, two benzylic resonances at δ 4.03 and 3.41 ppm were observed in the ^{1}H NMR spectrum, and the methoxide resonance was found as a singlet at δ 3.46 ppm.

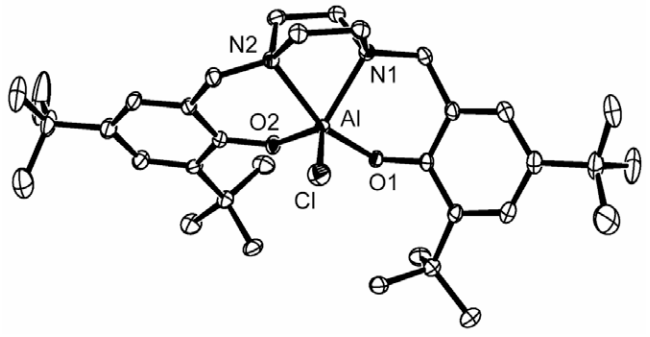


Fig. 4. Thermal ellipsoid plot (30%) of **5**. H atoms omitted for clarity.

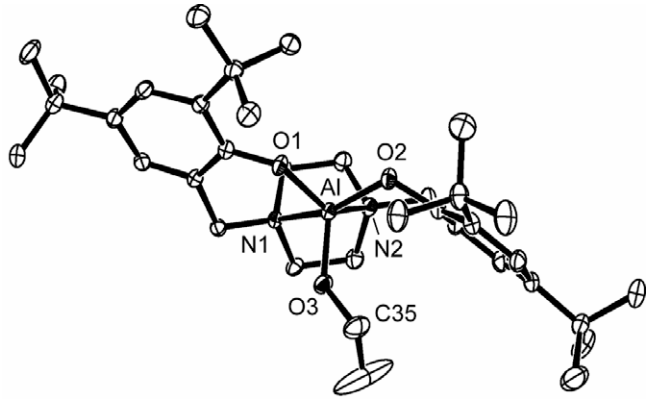
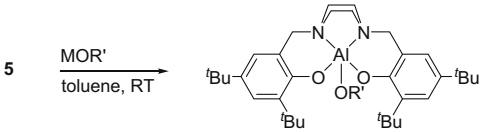


Fig. 5. Thermal ellipsoid plot (30%) of **6**. H atoms omitted for clarity.



MOR' = KOMe, KO^{i}Pr, KO^{t}Bu, AgOTf

6, R = Et
7, R = Me
8, R = ^{i}Pr
9, R = ^{t}Bu
10, R = OTf

(5)

The X-ray crystal structure of isopropoxide **8** is shown in Fig. 6. As with the other monometallic species, complex **8** has a distorted square-based pyramidal geometry around the aluminium centre (τ = 0.31), with the isopropoxide group occupying the apical site.

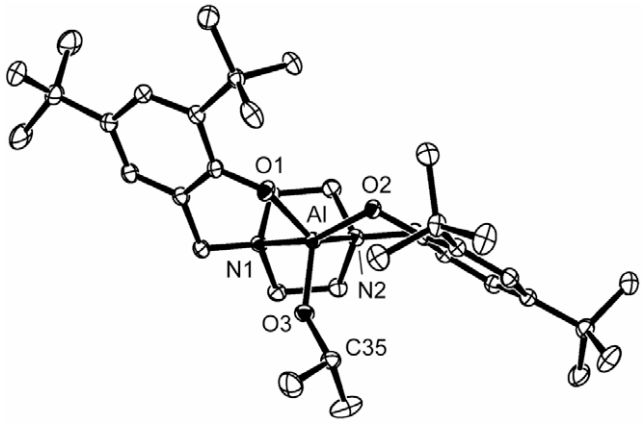


Fig. 6. Thermal ellipsoid plot (30%) of **8**. H atoms omitted for clarity.

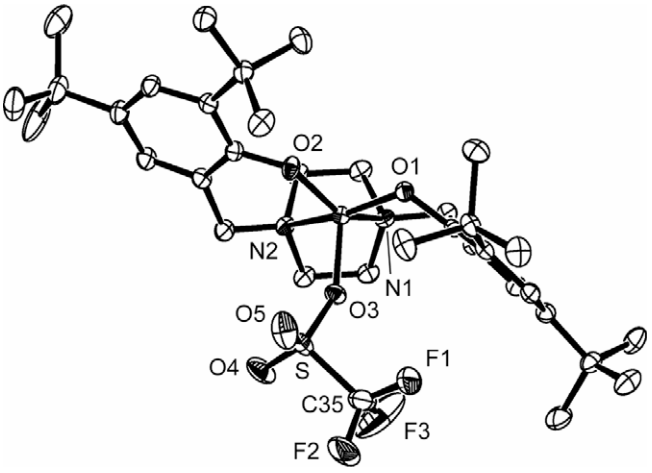


Fig. 8. Thermal ellipsoid plot (30%) of **10**. H atoms omitted for clarity.

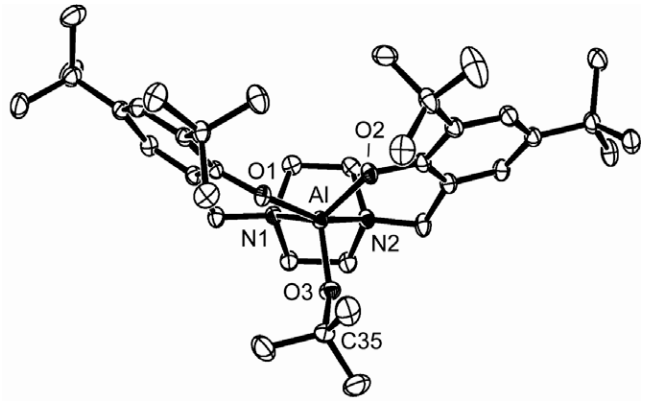


Fig. 7. Thermal ellipsoid plot (30%) of **9**. H atoms omitted for clarity.

The Al–O bond length of 1.7166(11) Å is shorter than Tolman's $^{t\mathrm{Bu},}$ $^{t\mathrm{Bu}}$BPBA-aluminium isopropoxide complex ($^{t\mathrm{Bu},}$ $^{t\mathrm{Bu}}$BPBA = bis-3,5-*tert*-butyl-phenoxymethyl-bisamine) of 1.7359(10) Å [8]. However, in contrast to our system, the isopropoxide ligand of this distorted square pyramidal complex occupies one of the equatorial sites.

The X-ray crystal structure was also determined for the larger congener **9** (Fig. 7). As with the other monomeric complexes, a distorted square pyramidal geometry around the aluminium centre is observed **9** ($\tau = 0.40$), with the *tert*-butoxide ligand at the apical site. To our knowledge, this is the first structurally characterised is penta-coordinate aluminium metal centre bearing a *tert*-butoxide ligand. The Al–O^{t}Bu bond length of 1.7191(17) Å is similar to the isopropoxide congener (**8**).

Monometallic aluminium triflate (**10**) was obtained in 43% yield through treatment of chloride complex **5** with one equivalent of AgOTf in toluene overnight at room temperature. X-ray analysis of crystals of **10** revealed the expected distorted square pyramidal ($\tau = 0.34$) around the aluminium centre, with the triflate ligand in the apical position (Fig. 8). Complex **10** is a rare example of a terminal aluminium-triflate complex, and the only penta-coordinate aluminium complex bearing a triflate ligand. The Al–OTf bond length of 1.819(3) Å is slightly shorter than Smith's β-diketiminate aluminium methyl triflate complex (1.841 Å) [22], and significantly shorter than Cowley's diketiminate-bipyridine aluminium bis(triflate) complex, although the latter is hexacoordinate [23].

2.4. Polymerisation studies

Preliminary studies on the ring opening polymerisation (ROP) of *rac*-lactide were carried out using both the methyl complexes (**2** and **3**) as well as the alkoxide complexes (**6**–**10**) [24]. Unfortunately, initial results showed limited to no activity for all catalysts. However, we were able to obtain limited success in the ROP of caprolactone. That is, after 24 h at 60 °C with 100 equivalents of monomer, the monometallic methyl complex **2** achieved a 12% conversion of monomer. The monometallic ethoxide **6**, isopropoxide **8** and triflate **10** showed a slightly better activity with 27%, 29% and 24% conversion, respectively. Monometallic methoxide complex **7** proved to be the most active catalysts, with 47% monomer conversion observed. The bulky *tert*-butoxide complex **9** showed no activity. The most active catalyst was the dimetallic methyl complex **3** with 68% conversion. Note that $AlMe_3$ showed a monomer conversion of 72% under the same conditions. We were unable to obtain evidence for a living process as nonlinearity was observed when the molecular weight was monitored over time.

3. Conclusions

In conclusion, 10 new aluminium complexes have been synthesised, eight of which have been fully characterised. With regards to the aluminium alkyl species **2**, **3** and **4**, the bimetallic complexes **3** and **4** appear to be more stable than the corresponding monometallic species **2**. A series of aluminium alkoxide complexes were also synthesised (**6**, **7**, **8**, **9** and **10**) from the corresponding aluminium chloride complex **5**. We were unsuccessful in our attempts to synthesise the corresponding bimetallic complexes. All of our compounds were tested as catalysts in the ROP of *rac*-lactide and caprolactone to which limited success was observed.

4. Experimental

All manipulations were carried out in an atmosphere of dry nitrogen or argon using standard Schlenk techniques or in an inert-atmosphere glovebox. Solvents were dried from the appropriate drying agent, distilled, degassed and stored over 4 Å sieves. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer, a Varian 400 MHz spectrometer, or a Varian 500 MHz spectrometer. The ^{1}H and ^{13}C NMR spectroscopy chemical shifts are given relative to residual solvent peaks.

4.1. Synthesis of N,N-bis(benzyl-3,5-di-tert-butyl-phenol)piperazine (**1**)

Ligand **1** was prepared with modifications to the literature procedures [16,17]. Piperazine (8.00 g, 92.9 mmol) was dissolved in methanol (100 mL) and combined with formaldehyde (16.2 mL of 37% by weight solution in water, 0.200 mol) in methanol (100 mL). To this was added 2,4-di-*tert*-butyl-phenol (38.3 g, 186 mmol). The mixture was refluxed at 75 °C overnight. The resulting solid was redissolved in diethyl ether (500 mL) and was washed with 3 M NaOH (200 mL) followed by water (200 mL). The ether layer was collected, and the solvent was removed *in vacuo*. The white product was then recrystallized from a minimum of hot THF three times and dried by *in vacuo*. (Yield: 31.6 g, 66%). ^{1}H NMR (C_6D_6): δ 10.79 (s, OH, 2H) 7.57 (s, Ar-*H*, 2H) 6.94 (s, Ar-*H*, 2H) 3.27 (s, CH_2, 4H) 1.90–2.40 (broad s, pip-C*H*, 8H) 1.79 (s, ^{t}Bu, 18H) 1.46 (s, ^{t}Bu, 18H).

4.2. Synthesis of methyl aluminium-N,N-bis(benzyl-3,5-di-tert-butyl-phenol)piperazine (**2**)

$AlMe_3$ (1.00 mL of a 2 M solution in hexanes, 2.00 mmol) was added dropwise to a solution of 1 (1.00 g, 1.93 mmol) in toluene (50 mL) at 50 °C. The reaction was stirred at 50 °C until the evolution of gas had ceased (approx. 30 min). The mixture was refluxed at 110 °C for 5 h. The solvent was removed *in vacuo* and the resulting solid was washed with pentane (10 mL) three times. The product was pumped dry to give a white solid. (Yield: 86%). ^{1}H NMR (C_6D_6): δ 7.70 (d, Ar-*H*, 2H) 6.89 (d, Ar-*H*, 2H) 3.35 (d, CH_2, 2H) 3.13 (d, CH_2, 2H) 1.33, 2.61 and 2.95 (t, d, d pip-C*H*, 8H) 1.94 (s, ^{t}Bu, 18H) 1.48 (s, ^{t}Bu, 18H) −0.80 (s, Al-CH_3, 3H). ^{13}C NMR (C_6D_6): δ 158.75 (q, Ar-O) 139.94 (q, Ar-*C*) 138.28 (q, Ar-*C*) 124.27 (Ar-*C*H) 122.96 (Ar-*C*H) 120.42 (q, Ar-*C*) 58.48 (benzyl CH_2) 49.47 (pip-CH_2) 48.54 (pip-CH_2) 36.00 (q, ^{t}Bu) 34.35 (q, ^{t}Bu) 32.22 (CH_3, ^{t}Bu) 30.57 (CH_3, ^{t}Bu). *Anal.* Calc. for $C_{35}H_{55}AlN_2O_2$: C, 74.69; H, 9.85; N, 4.98. Found: C, 74.70; H, 9.91; N, 4.93%.

4.3. Synthesis of bis-dimethyl aluminium-N,N-bis(benzyl-3,5-di-tert-butyl-phenol)piperazine (**3**)

$AlMe_3$ (2.00 mL of a 2 M solution in hexanes, 4.00 mmol) was added rapidly to a solution of 1 (1.00 g, 1.93 mmol) in toluene (15 mL) at 0 °C. The reaction was stirred at 0 °C until the evolution of gas had ceased (approx. 30 min). The mixture was refluxed at 110 °C for 5 h. The solvent was removed *in vacuo* and the resulting solid was washed with pentane (10 mL) three times. The product was dried under reduced pressure to give a white solid. (Yield: 93%). ^{1}H NMR (C_6D_6): δ 7.66 (d, Ar-*H*, 2H) 6.76 (d, Ar-*H*, 2H) 3.23 (s, CH_2, 4H) 2.46 (d, pip-C*H*, 4H) 2.02 (d, pip-C*H*, 4H) 1.73 (s, ^{t}Bu, 18H) 1.39 (s, ^{t}Bu, 18H) −0.45 (s, Al-CH_3, 4H). ^{13}C NMR (C_6D_6): δ 152.62 (q, Ar-*C*) 143.23 (Ar-*C*H) 140.14 (Ar-*C*H) 129.36 (q, Ar-*C*) 125.72 (q, Ar-*C*) 121.90 (Ar-*C*H) 63.99 (CH_2) 52.45 (pip-CH_2) 36.08 (q, ^{t}Bu) 34.37 (q, ^{t}Bu) 31.85 (CH_3, ^{t}Bu) 31.74 (CH_3, ^{t}Bu) 31.74 (CH_3, ^{t}Bu) −7.46 (Al–Me). Repeated attempts at obtaining elemental analysis for compound **3** were unsuccessful.

4.4. Synthesis of bis-diethyl aluminium-N,N-bis(benzyl-3,5-di-tert-butyl-phenol)piperazine (**4**)

$AlEt_3$ (0.265 mL neat, 1.94 mmol) was added rapidly to a solution of 1 (0.503 g, 0.969 mmol) in toluene (15 mL) at 0 °C. The reaction was stirred at 0 °C until the evolution of gas had ceased (approx. 30 min). The mixture was refluxed at 110 °C for 5 h. The solvent was removed *in vacuo* and the resulting solid was washed with pentane (10 mL) three times. The product was dried under reduced pressure to give a white solid. (Yield: 90%). ^{1}H NMR (C_6D_6): δ 7.61–7.59 (d, Ar-*H*, 2H) 6.72 (d, Ar-*H*, 2H) 3.21–3.12 (s, CH_2, 4H) 2.30 (d, pip-C*H*, 4H) 1.85 (d, pip-C*H*, 4H) 1.68 (s, ^{t}Bu, 18H) 1.41 (s, ^{t}Bu, 18H) 0.20–0.01 (m, Al-CH_2, 8H). *Anal.* Calc. for $C_{42}H_{72}Al_2N_2O_2$: C, 73.00; H, 10.50; N, 4.05. Found: C, 72.92; H, 10.42; N, 3.96%.

4.5. Synthesis of aluminium monochloride-N,N-bis(benzyl-3,5-di-tert-butyl-phenol)piperazine (**5**)

$AlEt_2Cl$ (1.00 mL of a 1 M solution in hexanes, 1.00 mmol) was added dropwise to a solution of 1 (0.501 g, 0.964 mmol) in toluene (50 mL) at 50 °C. The reaction was stirred at 50 °C until the evolution of gas had ceased (approx. 15 min). The mixture was refluxed at 115 °C for 5 h. The solvent was removed *in vacuo* and the resulting solid was washed with pentane (10 mL) three times. The product was pumped dry to a white solid. (Crude yield: >99%). ^{1}H NMR (C_6D_6): δ 7.67 (d, Ar-*H*, 2H) 6.82 (d, Ar-*H*, 2H) 3.52 (d, CH_2, 2H) 3.06 (d, CH_2, 2H) 1.92 (s, ^{t}Bu, 18H) 1.46 (s, ^{t}Bu, 18H) 1.28, 2.79 and 3.08 (t, d, d, pip-C*H* 8H). ^{13}C NMR (C_6D_6): δ 157.44 (q, Ar-*C*) 140.33 (Ar-*C*H) 139.36 (Ar-*C*H) 124.59 (q, Ar-*C*) 122.92 (q, Ar-*C*) 120.04 (q, Ar-*C*) 58.31 (CH_2) 49.83 (pip-CH_2) 48.19 (pip-CH_2) 35.96 (q, ^{t}Bu) 34.39 (q, ^{t}Bu) 32.15 (CH_3, ^{t}Bu) 30.63 (CH_3, ^{t}Bu). *Anal.* Calc. for $C_{34}H_{52}AlN_2O_2$: C, 70.02; H, 8.99; N, 4.80. Found: C, 70.08; H, 9.01; N, 4.83%.

4.6. Synthesis of ethoxy aluminium-N,N-bis(benzyl-3,5-di-tert-butyl-phenol)piperazine (**6**)

$AlEt_2OEt$ (0.612 mL of a 1.6 M solution in diethyl ether, 0.979 mmol) was added dropwise to a solution of 1 (0.508 g, 0.98 mmol) in toluene (50 mL) at 50 °C. The reaction was stirred at 50 °C until the evolution of gas had ceased (approx. 30 min). The mixture was refluxed at 110 °C for 5 h. The solvent was removed *in vacuo* and the resulting solid was washed with pentane (10 mL) three times. The product was pumped dry to give a white solid. (Yield: 59%). ^{1}H NMR (C_6D_6): δ 7.67 (d, Ar-*H*, 2H) 6.82 (d, Ar-*H*, 2H) 3.52 (d, CH_2, 2H) 3.06 (d, CH_2, 2H) 1.92 (s, ^{t}Bu, 18H) 1.46 (s, ^{t}Bu, 18H) 1.28, 2.79 and 3.08 (t, d, d, pip-C*H* 8H). ^{13}C NMR (C_6D_6): δ 158.68 (q, Ar-*C*) 139.44 (q, Ar-*C*H) 138.43 (q, Ar-*C*H) 124.17 (Ar-*C*) 123.06 (Ar-*C*) 120.38 (q, Ar-*C*) 67.85 (CH_2–OEt) 58.45 (CH_2) 50.42 (pip-CH_2) 47.66 (pip-CH_2) 36.00 (q, ^{t}Bu) 34.33 (q, ^{t}Bu) 32.19 (CH_3, ^{t}Bu) 30.61 (CH_3, ^{t}Bu) 25.85 (pip-CH_2) 21.16 (CH_3–OEt). *Anal.* Calc. for $C_{36}H_{57}AlN_2O_3$: C, 72.94; H, 9.69; N, 4.73. Found: C, 73.05; H, 9.62; N, 4.81%.

4.7. Synthesis of methoxy aluminium-N,N-bis(benzyl-3,5-di-tert-butyl-phenol)piperazine (**7**)

KOMe (0.0260 g, 0.363 mmol) was added to a stirred solution of L(AlCl) 5 (0.212 g, 0.363 mmol) in THF (3 mL) at room temperature and the mixture was stirred overnight. The resulting suspension was filtered and the solvent was removed *in vacuo* to give a white solid. (Crude yield: 53%). ^{1}H NMR (C_6D_6): δ 7.60 (d, Ar-*H*, 2H) 6.80 (d, Ar-*H*, 2H) 3.49 (d, CH_2, 2H) 3.47 (s, OMe, 3H) 3.01 (d, CH_2, 2H) 1.91 (s, ^{t}Bu, 18H) 1.43, 1.40 (s, ^{t}Bu, 18H) 2.95, 2.75, 1.24 and 1.15 (d, d, d, d, pip-C*H* 8H). ^{13}C NMR (C_6D_6): δ 158.70 (q, Ar-O) 139.63 (q, Ar-*C*) 138.54 (q, Ar-*C*) 124.22 (Ar-*C*H) 123.06 (Ar-*C*H) 120.53 (q, Ar-*C*) 67.86 (benzyl CH_2) 50.07 (pip-CH_2) 47.91 (pip-CH_2) 36.01 (q, ^{t}Bu) 34.36 (q, ^{t}Bu) 32.20 (CH_3, ^{t}Bu) 30.46 (CH_3, ^{t}Bu) 25.85 (OMe). *Anal.* Calc. for $C_{35}H_{55}AlN_2O_3$: C, 72.63; H, 9.58; N, 4.66. Found: C, 72.65; H, 9.43; N, 4.72%.

4.8. Synthesis of iso-propoxy aluminium-N,N-bis(benzyl-3,5-di-tert-butyl-phenol)piperazine (**8**)

KO^{i}Pr (0.0410 g, 0.415 mmol) was added to a stirred solution of L(AlCl) 5 (0.242 g, 0.415 mmol) in THF (3 mL) at room temperature

Table 3
Crystallographic data for compounds **2**, **4** and **5**.

	didi-AlMe·0.5(thf) (**2**)	didi-$(AlEt_2)_2$ (**4**)[a]	didi-AlCl·0.5(hexane) (**5**)[b]
Chemical formula	$C_{35}H_{55}N_2O_2Al·0.5(C_4H_8O)$	$C_{42}H_{72}N_2O_2Al$	$C_{34}H_{52}N_2O_2Al·0.5(C_6H_{14})$
Formula weight	598.84	690.98	626.29
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal size (mm^3)	0.25 × 0.20 × 0.15	0.30 × 0.20 × 0.15	0.30 × 0.20 × 0.05
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	*C*2/*c* (No. 15)
a (Å)	35.0777(9)	10.8533(2)	28.1541(7)
b (Å)	10.2547(3)	11.5608(3)	10.1962(2)
c (Å)	24.5710(5)	17.9027(4)	25.8789(7)
α (°)	90	77.901(1)	90
β (°)	115.898(1)	85.052(1)	94.211(1)
γ (°)	90	78.674(1)	90
V ($Å^3$)	7950.8(3)	2151.25(8)	7408.9(3)
Z	8	2	8
D_{calc} ($mg\ m^{-3}$)	1.00	1.07	1.12
Absorption coefficient (mm^{-1})	0.08	0.10	0.16
θ Range for data collection (°)	3.46–26.02	3.50–26.05	3.40–25.96
Measured/independent reflections/R_{int}	23029/7769/0.057	35726/8491/0.053	57004/7222/0.113
Reflections with [$I > 2\sigma(I)$]	5414	6699	4990
Data/restraints/parameters	7769/0/372	8491/0/433	7222/5/385
Goodness-of-fit on F^2	1.085	1.010	1.068
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.080$, $wR_2 = 0.238$	$R_1 = 0.044$, $wR_2 = 0.109$	$R_1 = 0.087$, $wR_2 = 0.215$
R indices (all data)	$R_1 = 0.115$, $wR_2 = 0.264$	$R_1 = 0.062$, $wR_2 = 0.119$	$R_1 = 0.139$, $wR_2 = 0.237$
Largest difference in peak and hole (e $Å^3$)	0.89 and −0.44	0.36 and −0.23	1.04 and −0.71

[a] Two independent molecules both lying on inversion centres.
[b] The poorly defined hexane solvate was included with isotropic C atoms and geometry restraints.

Table 4
Crystallographic data for compounds **7**, **8**, **9** and **10**.

	didi-AlOEt·(ether) (**6**)	didi-AlO^{i}Pr·(**8**)	didi-AlO^{t}Bu·(ether) (**9**)[a]	didi-AlOTf·3(toluene)·(**10**)[b]
Chemical formula	$C_{42}H_{72}N_2O_3Al·(C_4H_{10}O)$	$C_{37}H_{59}N_2O_3Al$	$C_{38}H_{61}N_2O_3Al·(C_4H_{10}O)$	$C_{35}H_{52}F_3N_2O_5SAl·(C_7H_8)$
Formula weight	666.94	606.84	694.99	973.23
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal size (mm^3)	0.30 × 0.25 × 0.20	0.24 × 0.20 × 0.20	0.4 × 0.4 × 0.3	0.40 × 0.20 × 0.20
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$ (No. 19)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	10.1265(2)	14.1909(3)	25.6699(3)	10.4927(1)
b (Å)	16.6979(5)	27.5448(5)	14.8465(2)	28.9080(3)
c (Å)	23.8931(8)	18.9434(3)	24.7492(3)	18.1928(2)
α (°)	90	90	90	90
β (°)	90	90	116.089(1)	97.741(1)
γ (°)	90	90	90	90
V ($Å^3$)	4040.1(2)	7404.7(2)	8471.10(18)	5468.01(10)
Z	4	8	8	4
D_{calc} ($mg\ m^{-3}$)	1.10	1.09	1.09	1.18
Absorption coefficient (mm^{-1})	0.09	0.09	0.09	0.13
θ Range for data collection (°)	3.41–26.02	3.40–26.05	3.45–26.02	3.43–26.04
Measured/independent reflections/R_{int}	22598/7872/0.064	30156/7197/0.047	80666/16487/0.061	61951/10735/0.059
Reflections with [$I > 2\sigma(I)$]	5742	5865	12881	7512
Data/restraints/parameters	7872/0/425	7197/0/402	16487/30/881	10735/91/604
Goodness-of-fit on F^2	1.025	1.042	0.995	1.004
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.060$, $wR_2 = 0.124$	$R_1 = 0.046$, $wR_2 = 0.108$	$R_1 = 0.067$, $wR_2 = 0.165$	$R_1 = 0.083$, $wR_2 = 0.212$
R indices (all data)	$R_1 = 0.096$, $wR_2 = 0.141$	$R_1 = 0.060$, $wR_2 = 0.116$	$R_1 = 0.089$, $wR_2 = 0.183$	$R_1 = 0.119$, $wR_2 = 0.239$
Largest difference in peak and hole (e $Å^3$)	0.32 and −0.32	0.28 and −0.24	0.92 and −0.81	1.38 and −0.72

[a] The methyl C atoms of the disordered C(31) ^{t}Bu group were left isotropic and SADI geometry restraints were applied.
[b] One of the toluene solvates is disordered and was included with SADI geometry restraints, isotropic C atoms and H atoms omitted.

and the mixture was stirred overnight. The resulting suspension was filtered and the solvent was removed *in vacuo* to give a white solid. (Crude yield: 70%). ^{1}H NMR (C_6D_6): δ 7.58 (d, Ar-*H*, 2H) 6.81 (d, Ar-*H*, 2H) 4.29 (t, ^{i}Pr-C*H*, 1H) 3.68 (d, CH_2, 2H) 2.95 (d, CH_2, 2H) 1.90 (s, ^{t}Bu, 18H) 1.44 (s, ^{t}Bu, 18H) 3.15 and 2.80 (d, d, pip-C*H* 4H) 1.05 (d, ^{i}Pr-CH_3). ^{13}C NMR (C_6D_6): δ 161.23 (q, Ar-O) 140.97 (q, Ar-*C*) 139.27 (q, Ar-*C*) 124.18 (Ar-*C*H) 123.05 (Ar-*C*H) 120.18 (q, Ar-*C*) 62.95 (^{i}Pr-*C*H) 58.70 (benzyl CH_2) 50.83 (pip-*C*H_2) 47.26 (pip-*C*H_2) 36.08 (q, ^{t}Bu) 34.40 (q, ^{t}Bu) 32.37 (*C*H_3, ^{t}Bu) 30.81 (*C*H_3, ^{t}Bu) 28.05 (^{i}Pr-*C*H_3). *Anal*. Calc. for $C_{37}H_{59}AlN_2O_3$: C, 73.23; H, 9.80; N, 4.62. Found: C, 73.29; H, 9.87; N, 4.58%.

4.9. Synthesis of tert-butoxy aluminium-N,N-bis(benzyl-3,5-di-tert-butyl-phenol)piperazine (**9**)

KO^{t}Bu (0.0190 g, 0.170 mmol) was added to a stirred solution of L(AlCl) 5 (0.0990 g, 0.170 mmol) in THF (3 mL) at room temperature and the mixture was stirred overnight. The resulting suspension was filtered and the solvent was removed *in vacuo* to give a white solid. (Yield: 72%). ^{1}H NMR (C_6D_6): δ 7.57 (d, Ar-*H*, 2H) 6.75 (d, Ar-*H*, 2H) 4.05 (d, CH_2, 2H) 2.72 (d, CH_2, 2H) 1.79 (s, ^{t}Bu, 18H) 1.46 (s, O^{t}Bu, 9H) 1.40 (s, ^{t}Bu, 18H) 3.02, 2.81, 1.82 and 1.09 (d, d, d, d, pip-C*H* 8H). ^{13}C NMR (C_6D_6): δ 158.12 (q, Ar-O)

139.19 (q, Ar-*C*) 138.03 (q, Ar-*C*) 127.94 (q, O^{t}Bu) 125.72 (Ar-*C*H) 123.15 (Ar-*C*H) 120.43 (q, Ar-*C*) 67.91 (benzyl CH_2) 59.28 (O^{t}Bu, CH_3) 51.56 (pip-CH_2) 45.89 (pip-CH_2) 36.08 (q, ^{t}Bu) 34.32 (q, ^{t}Bu) 32.23 (*C*H$_3$, ^{t}Bu) 31.64 (*C*H$_3$, ^{t}Bu). *Anal.* Calc. for $C_{38}H_{61}AlN_2O_3$: C, 73.51; H, 9.90; N, 4.51. Found: C, 73.50; H, 9.85; N, 4.51%.

4.10. Synthesis of aluminium-N,N-bis(benzyl-3,5-di-tert-butyl-phenol)piperazine triflate (**10**)

AgOTf (0.0890 g, 0.346 mmol) was added to a stirred solution of L(AlCl) 5 (0.202 g, 0.346 mmol) in THF (3 mL) at room temperature and the mixture was stirred overnight. The resulting suspension was filtered and the solvent was removed *in vacuo* to give a white solid. (Yield: 43%). ^{1}H NMR (C_6D_6): δ 7.59 (d, Ar-*H*, 2H) 6.69 (d, Ar-*H*, 2H) 3.65 (br d, C*H*$_2$, 2H) 3.19 (br d, C*H*$_2$, 2H) 1.79 (s, ^{t}Bu, 18H) 1.38 (s, ^{t}Bu, 18H) 2.82, 2.58 and 1.10 (br d, d, d, pip-C*H* 6H). ^{13}C NMR (C_6D_6): δ 161.21 (q, Ar-*C*) 144.57 (Ar-*C*H) 142.07 (Ar-*C*H) 129.95 (CF_3) 129.70 (q, Ar-*C*) 127.51 (q, Ar-*C*) 123.71 (q, Ar-*C*) 62.70 (*C*H$_2$) 53.99 (pip-*C*H$_2$) 51.95 (pip-*C*H$_2$) 40.41 (q, ^{t}Bu) 38.91 (q, ^{t}Bu) 36.54 (*C*H$_3$, ^{t}Bu) 35.19 (*C*H$_3$, ^{t}Bu). *Anal.* Calc. for $C_{35}H_{52}AlF_3N_2O_5S$: C, 60.33; H, 7.52; N, 4.02. Found: C, 60.26; H, 7.57; N, 3.98%.

4.11. Polymerisation studies

To a 50 mL ampoule fitted with a Teflon stopcock and stirrer bar was added the appropriate quantity (9.5, 6.4, 4.8 or 3.8 mg) of compound **3**. Two milliliter of a 0.28 M stock solution of caprolactone in toluene (0.56 mmol) was added to the reaction vessel. The stopcock was closed and the reaction was stirred for a set period of time at the appropriate temperature (RT/60 °C). The reaction was quenched with a few drops of 3 M HCl and stirred for 5 min. The polymer was precipitated with ethanol and left to dry on a crystallizing dish for 24 h. The polymers were weighed to obtain yields. ^{1}H NMR ($CDCl_3$, 293 K): δ 4.05 (t, 2H, CH_2) 2.30 (t, 2H, CH_2) 1.65 (t, 4H, CH_2) 1.20 (t, 2H, CH_2). ^{13}C{1H} NMR ($CDCl_3$, 293 K): δ 173.5 (*C*=O) 64.0 (*C*H$_2$) 34.0 (CH_2) 28.2 (CH_2) 25.5 (CH_2) 24.5 (CH_2).

4.12. Crystal structure determinations

Data were collected at 173 K on a Nonius Kappa CCD diffractometer, k(Mo Kα) = 0.71073 Å. Details of the crystal data, intensity collection and refinement are listed in Tables 3 and 4. The structures were refined with SHELXL-97 [25].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.016.

References

[1] O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, Chem. Rev. 104 (2004) 6147.
[2] B.J. O'Keefe, M.A. Hillmyer, W.B. Tolman, J. Chem. Soc., Dalton Trans. (2001) 2215.
[3] J.-M. Vion, R. Jerome, P. Teyssie, M. Aubin, R.E. Prud'homme, Macromolecules 19 (1986) 1828.
[4] S. Gong, H. Ma, Dalton Trans. (2008) 3345.
[5] J. Liu, N. Iwasa, K. Nomura, Dalton Trans. (2008) 3978.
[6] N. Iwasa, S. Katao, J. Liu, M. Fujiki, Y. Furukawa, K. Nomura, Organometallics 28 (2009) 2179.
[7] H. Du, X. Pang, H. Yu, X. Zhuang, X. Chen, D. Cui, X. Wang, X. Jing, Macromolecules 40 (2007) 1904.
[8] L.M. Alcazar-Roman, B.J. O'Keefe, M.A. Hillmyer, W.B. Tolman, Dalton Trans. (2003) 3082.
[9] M. Haddad, M. Laghzaoui, R. Welter, S. Dagorne, Organometallics 28 (2009) 4584.
[10] A. Arbaoui, C. Redshaw, D.L. Hughes, Chem. Commun. (2008) 4717.
[11] M.-A. Munoz-Hernandez, T.S. Keizer, P. Wei, S. Parkin, D.A. Atwood, Inorg. Chem. 40 (2001) 6782.
[12] H.M. Niemeyer, J. Mol. Struct. 57 (1979) 241.
[13] M. Ostermeier, C. Limberg, B. Ziemer, Z. Anorg. Allg. Chem. 632 (2006) 1287.
[14] O. Schlager, K. Wieghardt, A. Rufinska, B. Nuber, J. Chem. Soc., Dalton Trans. 1659–1668 (1996).
[15] J. Lloyd, S.Z. Vatsadze, D.A. Robson, A.J. Blake, P. Mountford, J. Organomet. Chem. 591 (1999) 114.
[16] J.D. Farwell, P.B. Hitchcock, M.F. Lappert, G.A. Luinstra, A.V. Protchenko, X.-H. Wei, J. Organomet. Chem. 693 (2008) 1861.
[17] S. Mohanty, D. Suresh, M.S. Balakrishna, J.T. Mague, Tetrahedron 64 (2008) 240.
[18] C.-T. Chen, C.-A. Huang, B.-H. Huang, Dalton Trans. (2003) 3799.
[19] P.A. Cameron, V.C. Gibson, C. Redshaw, J.A. Segal, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (2002) 415.
[20] J. Scott, S. Gambarotta, I. Korobkov, Q. Knijinenburg, B. de Bruin, P.H.M. Budzelaar, J. Am. Chem. Soc. 127 (2005) 17204.
[21] M.-A. Munoz-Hernandez, T.S. Keizer, S. Parkin, Y. Zhang, D.A. Atwood, J. Chem. Cryst. 30 (2000) 219.
[22] B. Qian, D.L. Ward, M.R.I. Smith, Organometallics 17 (1998) 3070.
[23] D. Vidovic, M. Findlater, G. Reeske, A.H. Cowley, J. Organomet. Chem. 692 (2007) 5683.
[24] For other aluminium-based lactide polymerisation catalysts, see Refs. [6,8,10,18] and A. Amgoune, L. Lavanant, C.M. Thomas, Y. Chi, R. Welter, S. Dagorne, J.-F. Carpentier, Organometallics 24 (2005) 6279.
[25] G.M. Sheldrick, In SHELXL-97, Program for the Refinement of Crystal Structures, 1997.