Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 4669

www.rsc.org/dalton

PAPER

Dimethylaluminium iminophosphoranylenamides and iminophosphoranylanilides: Synthesis, characterisation, and their controlled ring-opening polymerisation of ε-caprolactone†

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Received 7th December 2010, Accepted 4th February 2011
DOI: 10.1039/c0dt01713b

A series of aluminium iminophosphoranylenamide complexes, $[Me_2Al\{N(Ar)C(Ph)=CHP(Ph_2)=N\text{-}Ar^1\}]$ (Ar = Ph, Ar^1 = *p*-MeC_6H_4 (**9**); Ar = Ph, Ar^1 = *o*-ClC_6H_4 (**10**); Ar = Ph, Ar^1 = *o*-FC_6H_4 (**11**); Ar = *p*-MeC_6H_4, Ar^1 = *o*-FC_6H_4 (**12**)), were synthesised by the reactions of $ArN=C(Ph)CH_2P(Ph_2)=NAr^1$ (**5–8**) with $AlMe_3$ in toluene. Similar reactions between *o*-$\{ArN=P(Ph_2)\}C_6H_4NHC(Ph)=CHP(Ph_2)=NAr$ (Ar = *p*-MeC_6H_4, **13**), and $AlMe_3$ in toluene generates aluminium iminophosphoranylanilide, **14**. All new compounds were characterised by NMR spectroscopy and elemental analysis. The molecular structures of complexes **9** and **14** were further characterised by single-crystal X-ray structure determination. In the presence of benzyl alcohol (BnOH) each of the complexes is catalytically active for the ring-opening polymerisation (ROP) of ε-caprolactone (ε-CL), and complex **14** has the highest activity among them.

Introduction

Synthetic polyesters such as poly(ε-caprolactone) (PCL), poly(lactide) (PLA), poly(glycolide) (PGA) and their copolymers have found wide applications in the biomedical and pharmaceutical fields due to their biodegradable, biocompatible, and permeability properties.[1–3] Among the polymers, PCL shows specific advantages such as its miscibility with different commercial polymers,[4] its adhesive properties at low temperature,[4c] and its ability to disperse pigments.[1h,5] It is also ideally suited for long-term drug delivery due to its slow degradation in comparison to other polymers.[2a] An efficient way to synthesise the polyesters is the ROP of cyclic esters catalysed/initiated by metal complexes. This polymerisation method allows good control on the molecular weight, molecular weight distribution, polymer architecture and end functionality.[6] So far, a number of metal catalysts or initiators have been reported, including magnesium, aluminium, zinc, tin, and rare earth metal complexes supported by various ligands.[3,7] On the other hand, ancillary ligands play important roles in stabilising central metal ions and tuning the catalytic properties of the complexes. Nitrogen-based polydentate ligands such as β-diketiminate ligands (**A**, Chart 1) have attracted considerable attention.[3,8] For example, magnesium, zinc, and tin(II) complexes bearing β-diketiminate ligands exhibit excellent catalytic properties in the ROP of cyclic esters.[3,8g–p] Recently, aluminium β-diketiminate complexes were reported to be active catalysts for the ROP of ε-CL. However, the complexes showed relatively low activity and poor control in the polymerisation.[9] We intend to devise ligands that offer a steric environment similar to diimines, while the electronic characteristics are different, improving the catalytic properties of the aluminium complexes. Bis(iminophosphoranyl)methanides and iminophosphoranylenamides (**B** and **C**, Chart 1) are good candidates for such a study. Iminophosphoranes essentially behave as strong π and σ donor ligands and do not exhibit π-accepting capacity in contrast to imines.[10] These properties of iminophosphoranes in the ancillary ligands may provide a proper electronic environment at the metal centre for the catalysis. As a first step, we synthesised aluminium complexes supported by iminophosphoranylenamides and studied their catalytic behaviour in the ROP of ε-CL. A structurally related aluminium iminophosphoranylanilide complex was also studied. Here we report the results.

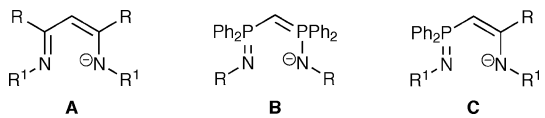

Chart 1

Results and discussion

Synthesis and characterisation of compounds 3–12 and 14

Synthesis of compounds **3–12** is illustrated in Scheme 1. α-(Diphenylphosphino)imine **3** and **4** were synthesised by lithiation

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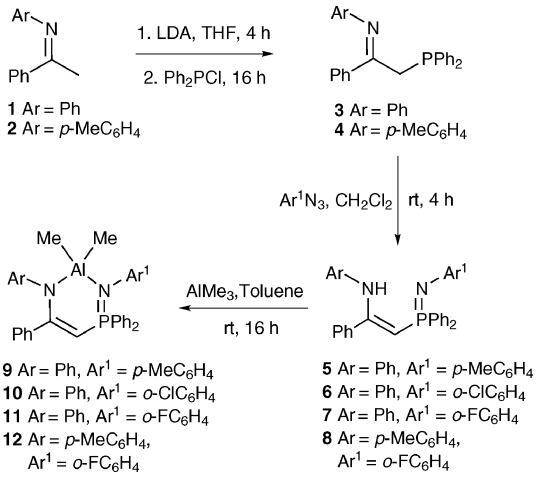
† CCDC reference numbers 803993–803994. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01713b



Scheme 1 Synthesis of aluminium complexes **9–12**.

of **1** or **2** with lithium diisopropylamide and the lithiated species were then treated with chlorodiphenylphosphine in THF. Treatment of **3** and **4** with aryl azides in dichloromethane at room temperature for 4 h generated iminophosphoranylenamines **5–8**. Compound **5** was purified by washing with *n*-hexane after removing the solvent from the reaction mixture, while compounds **6–8** were re-crystallised from diethyl ether. Reaction of **5–8** with $AlMe_3$ in toluene at room temperature for 16 h afforded complexes **9–12** as yellow crystalline solids. Complexes **9–12** were purified by re-crystallising from diethyl ether (**9** and **12**) or a mixed solvent of diethyl ether and *n*-hexane (**10** and **11**).

Each of compounds **3–12** were characterised by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis. NMR spectra of **3** indicate the presence of four isomers in $CDCl_3$ at room temperature. The ^{1}H NMR spectrum exhibits four sets of signals at δ 3.50–3.66, 3.66–6.74, 5.56–5.66, and 5.72–5.76 ppm, respectively, in the ratio of 17 : 2 : 3 : 1. This is attributed to the presence of the imine (δ 3.50–3.66 and 3.66–6.74 ppm) and enamine (δ 5.56–5.66 and 5.72–5.76 ppm) isomers. Both imine and enamine have *E* and *Z* isomers. Hence compound **3** has four isomers (**D–G**, Chart 2) and the ratio of the enamine to the imine is about 1 : 5. Four signals of the ^{31}P NMR of compound **3** at δ –17.03, –22.85, –26.56, and –36.32 ppm are also consistent with the four isomers. NMR spectra of compound **4** also show the presence of four isomers and the ratio of the enamine to the imine is about 1 : 4 based on the ^{1}H NMR spectrum.

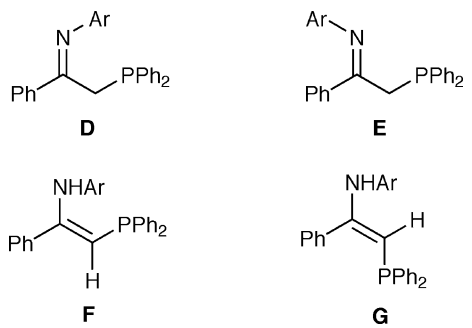


Chart 2 The isomers of **3** (Ar = Ph) and **4** (Ar = *p*-MeC_6H_4).

^{1}H NMR spectrum of each of compounds **5–8** displays a singlet at about 11 ppm, which is assigned to an NH group. This means that each of **5–8** exists in an enamine form and the high frequency chemical shifts indicate the presence of hydrogen bonds in the molecules. Meanwhile, we also observed trace amounts of imine isomer in each case from their respective ^{1}H and ^{31}P NMR spectra. These phenomena are consistent with those observed by us and other groups previously.[11]

Complexes **9–12** gave satisfactory elemental analytical results. ^{1}H NMR spectra of each of complexes **9**, **11**, and **12** exhibits only one Al–Me signal, showing the two methyl groups to be chemically equivalent. ^{1}H NMR spectrum of complex **10** exhibits two Al–Me signals (δ –0.09 and 0.01 ppm, respectively). This was further confirmed by its ^{13}C NMR spectrum in which two Al–Me signals appear at δ –8.01 and –7.73 ppm, respectively. ^{31}P NMR spectra of each of complexes **9–12** exhibits one signal as a multiplet. The structure of complex **9** was also determined by single-crystal X-ray diffraction analysis. The ORTEP drawing is shown in Fig. 1, along with selected bond lengths and angles. The central aluminium atom has a distorted tetrahedral geometry with the N1–Al–N2 angle [99.34(11)°] narrower than the C35–Al–C35 angle [118.67(16)°]. The six-membered chelate ring adopts a twist conformation. Each of the N1 and N2 atoms is approximately in a planar environment. The C1–C2–C3–N1 atoms also lie on a plane. The Al–N bond distances of 1.901(3) Å and 1.925(2) Å are shorter than the corresponding distances in [Me_2Al{N(2,6-$Pr^i_2C_6H_3$)C(Me)=CHP(Ph_2)=N(2,6-$Pr^i_2C_6H_3$)}] (≡ $LAlMe_2$) [1.932(2) and 1.943(2) Å, respectively].[11c] The C2–N1 distance of 1.382(4) Å is longer than the corresponding distance in [$LAlMe_2$] [1.353(3) Å], while the C1–C2 distance of 1.362(4) Å in complex **9** is shorter than the corresponding distance in [$LAlMe_2$] [1.383(4) Å].[11c] The P–N distance of 1.622(2) Å is longer than a formal double bond and is normal for a coordinated iminophosphorane, while the P–C1 distance of 1.741(3) Å is in between that of a formal single and double bond.[12,13]

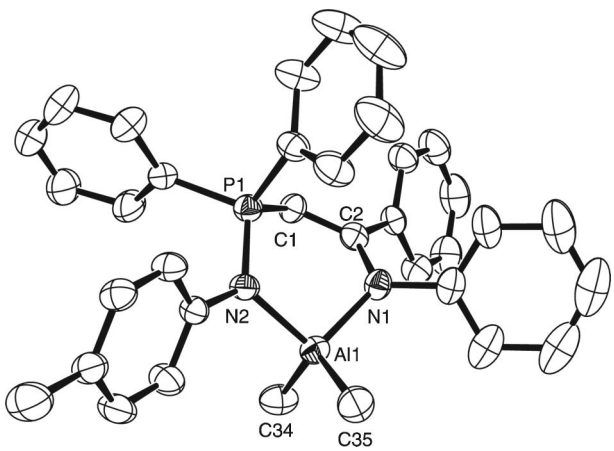
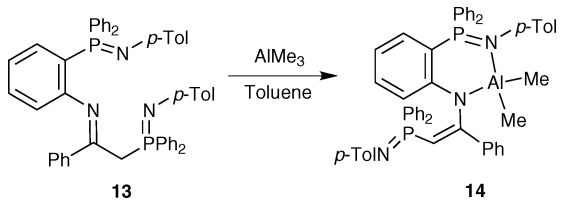


Fig. 1 Molecular structure of complex **9** shown with 30% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.901(3), Al(1)–N(2) 1.925(2), Al(1)–C(34) 1.947(4), Al(1)–C(35) 1.961(3), P(1)–N(2) 1.622(2), P(1)–C(1) 1.741(3), N(1)–C(2) 1.382(4), C(1)–C(2) 1.362(4), N(1)–Al(1)–N(2) 99.34(11), N(1)–Al(1)–C(34) 108.33(14), C(34)–Al(1)–C(35) 118.67(16), P(1)–N(2)–Al(1) 116.51(13), C(2)–N(1)–Al(1) 119.1(2), N(2)–P(1)–C(1) 110.35(14), C(2)–C(1)–P(1) 122.4(2), C(2)–N(1)–Al(1) 119.1(2), C(1)–C(2)–N(1) 119.9(3).

Complex **14** was synthesised from **13** and $AlMe_3$ as shown in Scheme 2. Compound **13** was prepared according to the procedure we reported previously[14] and characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy and elemental analysis. Both ^1H and ^{31}P NMR spectra show that **13** exists in three isomers with a ratio of 3 : 2 : 2. Among the isomers the imine isomer accounts for about 30% and the two enamine isomers account for about 70%. Treatment of **13** with $AlMe_3$ in toluene at room temperature for 16 h and then at 110 °C for 8 h afforded, after re-crystallisation using diethyl ether, a yellow crystalline complex, **14**, in 63% yield. Complex **14** gave satisfactory elemental analytical results. Its ^1H NMR spectrum exhibits a single Al–Me signal, indicating the two methyl groups to be at the same chemical environment. The ^{31}P NMR spectrum displays two signals, being consistent with its molecular structure.



Scheme 2 Synthesis of complex **14**.

The structure of complex **14** was also determined by single-crystal X-ray diffraction techniques and the ORTEP drawing is presented in Fig. 2, along with selected bond lengths and angles. In the solid state, the nitrogen atom of one of the iminophosphoranyls (that attached on the C=C double bond) does not coordinate to the central metal. The aluminium atom is four coordinate and the geometry at the aluminium atom is a distorted tetrahedron. The chelate metal ring adopts a twist conformation, which is different from that of $[Me_2Al\{N(Dipp)C_6H_4(2\text{-}\{P(Ph_2)=NMes\}\}]$. The structure of the latter reveals that the Al atom protrudes from an idealized plane in the chelate metal ring.[15] The N–Al–N angle of 98.39(10)° is close to that reported [98.39(10)°], but the C–Al–C angle of 119.76(15)° is markedly wider than the corresponding angle in $[Me_2Al\{N(Dipp)C_6H_4(2\text{-}\{P(Ph_2)=N\text{-}Mes\}\}]$ [113.7(2)°].[15] The Al–N distances of 1.946(2) Å and 1.906(2) Å are longer than the corresponding distances in $[Me_2Al\{N(Dipp)C_6H_4(2\text{-}\{P(Ph_2)=NMes\}\}]$ [1.926(3) Å and 1.891(3) Å][15] and the distances in complex **9** [1.925(2) Å and 1.901(3) Å]. The P1–N1 distance of 1.623(2) Å is almost the same as that in complex **9** [1.622(2) Å]. The P2–N3 distance of 1.569(2) Å is shorter than the P1–N1 distance and is indicative of a P=N double bond.[13]

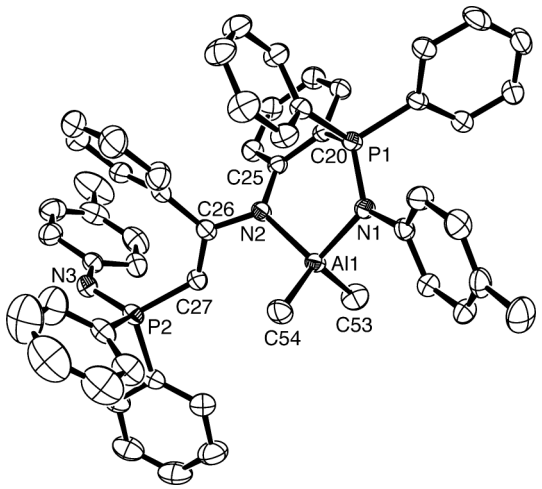


Fig. 2 Molecular structure of complex **14** shown with 30% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.946(2), Al(1)–N(2) 1.906(2), Al(1)–C(53) 1.962(3), Al(1)–C(54) 1.978(3), P(1)–N(1) 1.623(2), P(1)–C(20) 1.792(3), N(2)–C(25) 1.394(3), P(2)–N(3) 1.569(2), P(2)–C(27) 1.795(3), C(26)–C(27) 1.354(4), N(1)–Al(1)–N(2) 98.39(10), N(2)–Al(1)–C(53) 110.66(13), N(1)–Al(1)–C(53) 109.91(13), C(53)–Al(1)–C(54) 119.76(15), P(1)–N(1)–Al(1) 118.09(12), C(25)–N(2)–Al(1) 121.37(17), N(1)–P(1)–C(20) 109.81(12).

Ring-opening polymerisation of ε-caprolactone

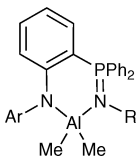
The ROPs of ε-CL in toluene using **9–12** and **14** as the catalysts, in the presence of BnOH at various temperatures, have been systematically conducted as shown in Table 1. Thus, an aluminium complex was treated with 1 equiv of BnOH in toluene at room temperature for 1 h and then 200 equiv of ε-CL was added into the mixture at a preset temperature. The data in Table 1 show that in the presence of benzyl alcohol all the complexes are active

Table 1 Ring-opening polymerisation of ε-CL catalysed by organoaluminium complexes (**9–12** and **14**) in the presence of benzyl alcohol[a]

Entry	Cat.	Temp. (°C)	Time (min)	Conversion (%)[b]	M_n (GPC)[c]	M_n (Calcd)[d]	Yield (%)	PDI[e]
1	**9**	110	11	99	19 200	19 814	95	1.24
2	**9**	90	60	100	18 600	19 070	94	1.27
3	**9**	70	210	99	17 700	18 082	94	1.20
4	**10**	110	15	98	18 000	21 405	95	1.21
5	**10**	90	40	98	18 600	19 596	93	1.19
6	**10**	70	90	99	14 200	19 104	94	1.18
7	**10**	50	210	77	13 100	14 646	72	1.11
8	**11**	90	45	96	18 100	17 832	92	1.14
9	**11**	70	76	97	18 300	17 931	93	1.19
10	**12**	110	20	99	18 700	18 115	99	1.23
11	**12**	90	60	100	22 500	19 900	96	1.25
12	**12**	70	210	100	19 900	16 835	95	1.22
13	**14**	70	25	94	31 400	34 996	90	1.21
14	**14**	50	42	78	26 500	25 220	74	1.21

[a] All polymerisations were carried out in toluene; $[CL]_0 : [Al]_0 : [BnOH]_0 = 200 : 1 : 1$, $[CL]_0 = 2$ M. [b] Measured by ^1H NMR spectra. [c] Calculated from the molecular weight of ε-CL, times the conversion of monomer and the ratio of $[CL]_0/[BnOH]_0$, plus the molecular weight of BnOH. [d] Obtained from GPC analysis and calibrated against polystyrene standard, multiplied by 0.56.[16] [e] Obtained from GPC analysis, PDI = polydispersity index.

for the ROP of ε-CL. GPC (Gel Permeation Chromatography) analysis shows that the molecular weights of the polymers match the calculated values very well. The polydispersities are also very narrow, ranging from 1.11 to 1.27. These results imply that the catalytically active species are quite stable during the reaction process even at 110 °C and the polymerisations are well controlled (see below on kinetic studies). Each of complexes **9–12** and **14** exhibits higher catalytic activity than the aluminium β-diketiminate complexes.[9] This is ascribed to the stronger electron-donating effect of iminophosphorane than imine. In order to establish reaction order in monomer and metal concentration, and compare the catalytic activity of the complexes, kinetic studies of ε-CL polymerisation catalysed by the complexes in the presence of BnOH were performed. Plots of $\ln([\varepsilon\text{-CL}]_0/[\varepsilon\text{-CL}])$ *versus* time using **9–12** and **14** are shown in Fig. 3. Each of the plots exhibit a good linear relationship, indicating the polymerisation reaction proceeds with first-order dependence on monomer concentration. The first-order kinetics implies that the concentration of active species remains unchanged. The plots also reveal that each of the polymerisations catalysed by **9–12** has an induction period under the polymerisation conditions. At first we guessed that formation of catalytically active species requires a period of time at the reaction temperature. In order to verify our guess we mixed complex **10** and an equiv. of BnOH in toluene and stirred the solution at 60 °C for 60 min. The polymerisation of ε-CL using the mixture mentioned above as catalyst displayed an induction period of about 50 min, shorter than that previous (about 80 min). Hence it seems that the induction period is partially caused by the reaction of the complex with BnOH. It was also noted that the induction period changes with polymerisation temperatures. For example, the induction period of the polymerisation catalysed by **12** at 70 °C is about 20 min, while at 60 °C it is about 110 min. From Fig. 3 we can obtain a catalytic activity order of **14** > **11** ≥ **10** > **12** > **9** at 60 °C. The higher activity of complex **11** than complex **12** means that an electron-donating group on the phenyl ring of the Ar group decreases the catalytic activity. Higher activity of both complexes **10** and **11** compared to **9** implies that an electron-donating group on the phenyl ring of the Ar[1] group also reduces the catalytic activity. These facts seem contradictory with the inference mentioned above. However, although a stronger donor capability of iminophosphorane than imine may lead to a higher catalytic activity of complexes **9–12** than aluminium β-diketiminate complexes, a proper electronic environment at the metal centre is critical for the catalysis. An electron-withdrawing group on the phenyl ring of the ligands in complexes **9–12** may tune the whole electron effect of the ligand to a more proper condition for the catalysis. Complex **14** displays the highest catalytic activity among the complexes. This result is also a sharp contrast to that of anilidoiminophosphorane aluminium complexes (**H** in Chart 3). The latter showed poor catalytic activity and gave polymers with much lower molecular weights than calculated ones.[8e] The reason for the higher activity of **14** may be that an additional nitrogen atom of iminophosphoranyl coordinates to the aluminium atom of the active catalyst during the polymerisation process, which stabilises the central metal ion and changes the electronic environment of the central metal.



Ar = 2,6-$Pr^i_2C_6H_3$
R = 2,6-$Pr^i_2C_6H_3$ or $SiMe_3$

H

Chart 3

Plots of the number-average molecular weights (M_n) of the PCL catalysed by **10**, **12** and **14** in the presence of BnOH, and the polydispersities as functions of monomer conversions, are shown in Fig. 4–6, respectively. In each case, the number-average molecular weight follows a linear relationship in monomer conversion and polydispersity values remain low, further proving the controlled character of the polymerisations.

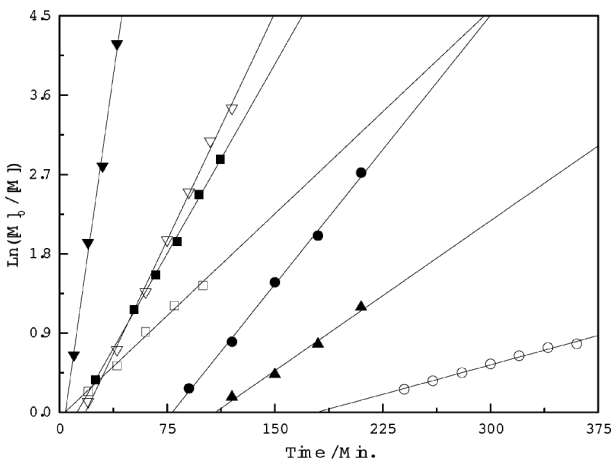


Fig. 3 Plots of $\ln([M]_0/[M])$ *versus* time for the polymerisation of ε-CL catalysed by **9** (○, 60 °C), **10** (●, 60 °C), **11** (■, 60 °C), **12** (▲, 60 °C; ▽,70 °C) and **14** (□, 40 °C; ▼, 60 °C). Conditions: Solvent: toluene; $[M]_0/[Al]/[BnOH]_0 = 200:1:1$, $[M]_0 = 2$ M.

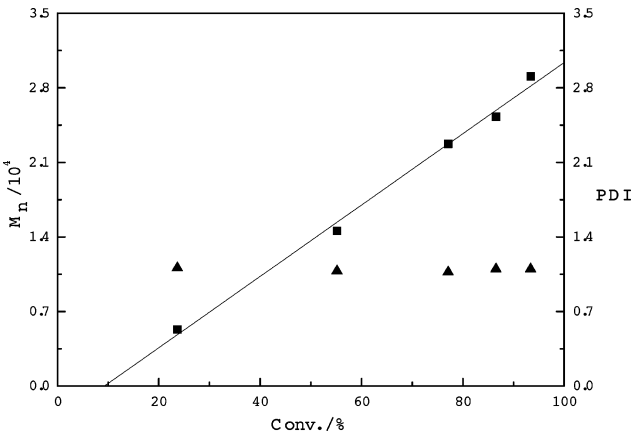


Fig. 4 Plots of PCL M_n (■ obtained from GPC analysis) and polydispersity (▲, M_w/M_n) as a function of ε-CL conversion using complex **10** at 60 °C. $[M]_0:[Al]_0:[BnOH]_0 = 200:1:1$, $[M]_0 = 2$ M.

To understand the polymerisation process, we attempted to isolate the reaction product of **14** with 1 equiv of BnOH. However, a mixture identified by ^{1}H NMR spectroscopy was always obtained. We guess that the obtained alkoxyaluminium compounds

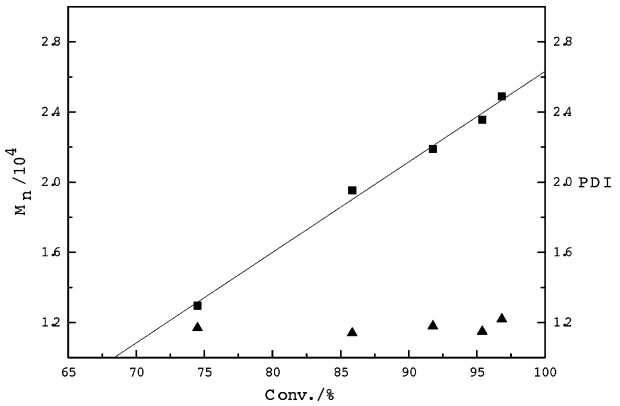


Fig. 5 Plots of PCL M_n (■ obtained from GPC analysis) and polydispersity (▲, M_w/M_n) as a function of ε-CL conversion using complex **12** at 70 °C. $[M]_0 : [Al] : [BnOH] = 200 : 1 : 1$, $[M]_0 = 2$ M.

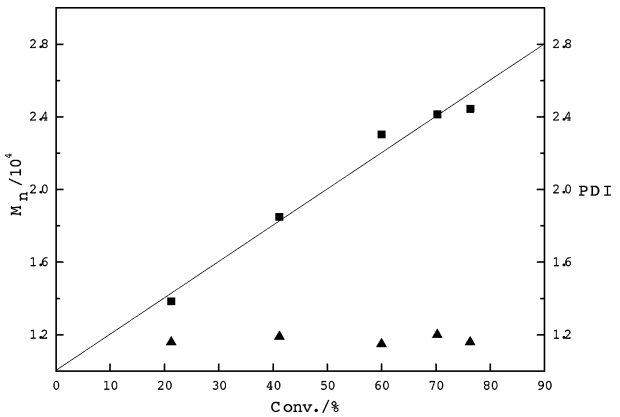


Fig. 6 Plots of PCL M_n (■ obtained from GPC analysis) and polydispersity (▲, M_w/M_n) as a function of ε-CL conversion using complex **14** at 40 °C. $[M]_0 : [Al] : [BnOH] = 200 : 1 : 1$, $[M]_0 = 2$ M.

may have different structures in solution and they exist in an equilibrium. One of the equilibrium components is an active catalyst for the ROP and its concentration remains constant. Hence, although the reaction between the complexes and BnOH forms a mixture, the catalysed polymerisation still proceeds in an almost living manner. The end group analysis of the PCL (entry 3 in Table 1), using ^{1}H NMR spectrum as shown in Fig. 7, proves that the PCL is capped with a benzyloxy group (H_g) on one end and a hydroxymethyl group (H_f) on the other end. Further more, the integration ratio between H_e and H_g is about 174, which is to say the molecular weight of PCL is about 19 814 g mol^{-1} and this value is close to the calculated value. This implies that the polymerisation may be initiated through insertion of the benzyl alkoxyl group to ε-CL followed by ring opening *via* acyl-oxygen cleavage.

Conclusions

We have synthesised and characterised a series of dimethylaluminium complexes supported by iminophosphoranylenamide ligands (**9–12**) or iminohosphoranylanilide ligand (**14**). In the presence of BnOH each of the complexes is an efficient catalyst for the ROP of ε-CL. Complex **14** shows the highest catalytic activity among the complexes, and in complexes **9–12** the substituents

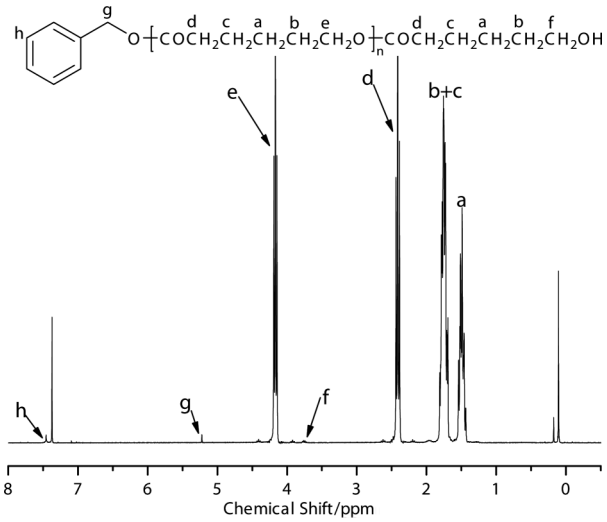


Fig. 7 ^{1}H NMR spectrum of PCL (entry 3 in Table 1) in $CDCl_3$.

on the phenyl rings attached to coordinated nitrogen atoms affect the catalytic activity remarkably through electronic effects. Kinetic studies reveal that each of the polymerisation reactions catalysed by **10**, **12**, and **14** follows the first-order kinetics in the concentration of monomer and the number-average molecular weight follows a linear relationship in monomer conversion. These results show that the polymerisations proceed in a controlled manner.

Experimental

General

All air- or moisture-sensitive manipulations were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium/benzophenone (*n*-hexane, THF and Et_2O) or $CaH_2(CH_2Cl_2)$ and degassed prior to use. Compounds **1**, **2**[17] and 2-$(Ph_2P)C_6H_4N{=}C(Ph)CH_2PPh_2$[14] were prepared using the procedure described in literature. Chlorodiphenylphosphine was purchased from Acros Organics and distilled prior to use. Diisopropylamine was dried with NaOH and distilled prior to use. *n*-BuLi was purchased from Acros Organics and used as received. $AlMe_3$ was purchased from Alfa-Aesar and used as received. $CDCl_3$ and C_6D_6, purchased from Cambridge Isotope Laboratories, were de-gassed and stored over 4 Å molecular sieves ($CDCl_3$) or Na/K alloy (C_6D_6). ε-Caprolactone, purchased from Acros Organics, was stirred over CaH_2 for 24 h and distilled under vacuum. NMR spectra were recorded on a Bruker av300 spectrometer at ambient temperature. The chemical shifts of ^{1}H and ^{13}C NMR spectra were referenced to internal solvent resonances or TMS; the ^{31}P NMR spectra were referenced to external 85% H_3PO_4. Elemental analysis was performed by the Analytical Center of University of Science and Technology of China. Gel permeation chromatography (GPC) measurements were performed on a Waters 150C instrument equipped with UltraStyragel columns (103, 104, and 105 Å) and a 410 refractive index detector, using monodispersed polystyrene as the calibration standard. THF was used as the eluent at a flow rate of 1 cm^3 min^{-1}.

Synthesis of PhC(=NAr)CH_2PPh_2 (Ar = Ph, 3; Ar = *p*-MeC_6H_4, 4)

A solution of **1** (4.00 g, 20.9 mmol) in THF (20 cm^3) was added dropwise to a stirred THF solution of *i*-Pr_2NLi (22.5 mmol, prepared *in situ* from *n*-BuLi and *i*-Pr_2NH in THF) at 0 °C. The stirring continued at 0 °C for 4 h and then a solution of Ph_2PCl (4.97 g, 22.5 mmol) in THF (20 cm^3) was transferred to the reaction mixture. The resultant mixture was stirred for 16 h at room temperature. Volatiles were removed from the mixture under reduced pressure and the yellow residue was extracted with CH_2Cl_2 (60 cm^3). The extract was distilled to dryness under reduced pressure. The residual solid was re-crystallised from a mixed solvent of diethyl ether and *n*-hexane to afford yellow crystals of **1** (4.51 g, 58%), (Found: C, 82.11, H, 5.80, N, 3.50. $C_{26}H_{22}NP$ requires C, 82.30, H, 5.84, N, 3.69). mp 100–102 °C. ^{1}H NMR ($CDCl_3$): δ 3.50–3.66 (m, CH_2), 3.66–3.74 (m, CH_2), 5.56–5.66 (m, =CH), 5.72–5.86 (m, =CH), 6.28–6.68 (m, Ar), 6.70–7.64 (m, Ar), 7.74–7.95 (m, Ar). ^{13}C NMR ($CDCl_3$): δ 31.46 (d, J = 23 Hz), 42.67 (d, J = 16.2 Hz), 106.05 (d, J = 4.5 Hz), 119.32, 119.49, 120.79, 123.05, 127.81, 128.13, 128.16, 128.36, 128.54, 128.64, 128.78, 128.90, 129.06, 130.46, 132.56, 132.81, 132.93, 133.05, 133.20, 133.31, 137.12, 137.33, 138.88, 150.83, 165.47, 165.60. ^{31}P NMR ($CDCl_3$): δ –17.03 (m), –22.85 (m), –26.56 (m), –36.32 (m).

By using the same procedure as for synthesis of **3**, compound **4** was obtained in 58% yield, (Found: C, 82.24, H, 6.10, N, 3.38; $C_{27}H_{24}NP$ requires C, 82.42, H, 6.15, N, 3.56). mp 108–110 °C. ^{1}H NMR ($CDCl_3$): δ 2.17 (s, Me), 2.29 (s, Me), 3.56 (s, CH_2), 3.64 (s, CH_2), 5.51 (t, J = 1.8 Hz, =CH), 5.64 (d, J = 4.4 Hz, =CH), 6.27 (d, J = 6.9 Hz, Ar), 6.34 (d, J = 6.9 Hz, Ar), 6.49 (d, J = 7.2 Hz, Ar), 6.85 (d, J = 7.7 Hz, Ar), 6.96 (d, J = 7.7 Hz, Ar), 7.15–7.52 (m, Ar), 7.82 (d, J = 7.8 Hz, Ar). ^{13}C NMR ($CDCl_3$): δ 17.39, 20.65, 20.95, 31.30 (d, J = 22.8 Hz), 42.79 (d, J = 16.2 Hz), 87.21, 88.64, 104.80, 119.45, 119.77, 120.78, 121.47, 127.26, 127.90, 128.02, 128.09, 128.12, 128.30, 128.45, 128.50, 128.58, 128.66, 128.82, 128.99, 129.07, 129.16, 129.35, 129.39, 129.48, 129.62, 129.72, 129.85, 130.29, 130.44, 130.89, 131.03, 131.36, 131.48, 131.56, 132.28, 132.37, 132.54, 132.69, 132.79, 132.95, 133.06, 133.21, 133.31, 135.33 (d, J = 7.1 Hz), 135.59 (d, J = 7.1 Hz), 137.40 (d, J = 16.2 Hz), 139.15, 148.33, 160.82, 165.61 (d, J = 9.7 Hz). ^{31}P NMR ($CDCl_3$): δ –16.91 (m), –22.90 (m), –26.55 (m), –36.71 (m).

Synthesis of *p*-MeC_6H_4N=$P(Ph_2)CH$=C(Ph)NHPh (5)

A solution of *p*-methylphenyl azide (0.77 g, 5.80 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to a stirred solution of **3** (2.00 g, 5.27 mmol) in CH_2Cl_2 (30 cm^3) at 0 °C. The mixture was stirred at 0 °C for 10 min. and then at room temperature for 4 h. The solvent was removed under reduced pressure and the residue was washed with *n*-hexane and dried under vacuum to give a yellow powder of **5** (2.12 g, 83%), (Found: C, 81.05, H, 6.03, N, 5.72; $C_{33}H_{29}N_2P{\cdot}0.06CH_2Cl_2$ requires C, 81.09, H, 5.99, N, 5.72). mp 98–100 °C. ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 3H, Me), 4.57 (d, J = 22.5 Hz, 1H, CH), 6.60 (d, J = 8.4 Hz, 2H, C_6H_4), 6.73 (d, J = 8.1 Hz, 2H, Ar), 6.79 (d, J = 7.8 Hz, 1H, Ph), 6.83 (d, J = 7.8 Hz, 2H, Ph), 7.04 (t, J = 7.8 Hz, 2H, Ph), 7.21–7.33 (m, 4H, Ph), 7.36–7.49 (m, 7H, Ph+C_6H_4), 7.78 (d, J = 7.5 Hz, 2H, Ph), 7.81 (d, J = 7.2 Hz, 2H, Ph), 11.44 (broad, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.64, 86.80 (d, J = 49 Hz), 115.36, 120.81, 121.23, 121.45, 121.83, 122.38, 122.62, 128.25, 128.42, 128.60, 128.66, 128.75, 129.43, 129.36, 129.44 (d, J = 1.3 Hz), 130.96 (d, J = 10.6 Hz), 131.39 (d, J = 2.7 Hz), 131.85, 131.98, 138.21, 141.84, 147.96 (d, J = 4.8 Hz), 159.63. ^{31}P NMR ($CDCl_3$): δ 2.42 (m).

Synthesis of *o*-ClC_6H_4N=$P(Ph_2)CH$=C(Ph)NHPh (6)

A solution of *o*-chlorophenyl azide (0.97 g, 6.32 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to a stirred solution of **3** (2.00 g, 5.27 mmol) in CH_2Cl_2 (30 cm^3) at 0 °C. The mixture was stirred at 0 °C for 10 min. and then at room temperature for 4 h. Solvent was removed *in vacuo*. The residual solid was washed with *n*-hexane and dried under vacuum to give a yellow powder of **6** (2.05 g, 77%). The compound was pure enough for the next step. Further purification was carried out by re-crystallisation of the crude product from diethyl ether. (Found: C, 76.03, H, 5.17, N, 5.28; $C_{32}H_{26}ClN_2P$ requires C, 76.11, H, 5.19, N, 5.55). mp 150–152 °C. ^{1}H NMR ($CDCl_3$): δ 4.55 (d, J = 23.4 Hz, 1H, CH), 6.49–6.57 (m, 2H, Ar), 6.71–6.75 (m, 3H, Ar), 6.83 (t, J = 6.9 Hz, 1H, Ar), 7.03 (t, J = 7.8 Hz, 2H, Ar), 7.20–7.34 (m, 4H, Ar), 7.37–7.52 (m, 8H, Ar), 7.79 (d, J = 8.1 Hz, 2H, Ar), 7.83 (d, J = 8.1 Hz, 2H, Ar), 11.09 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 86.18 (d, J = 129.6 Hz), 117.79, 121.42 (d, J = 12.3 Hz), 122.15, 122.75, 126.63, 128.31, 128.39, 128.46, 128.74 (d, J = 11.5 Hz), 129.38 (d, J = 20.7 Hz), 131.60, 131.94 (d, J = 9.8 Hz), 132.85, 138.25 (d, J = 15.9 Hz), 141.81, 147.93, 160.23. ^{31}P NMR ($CDCl_3$): δ 4.31 (m).

Synthesis of *o*-FC_6H_4N=$P(Ph_2)CH$=C(Ph)NHPh (7)

Compound **7** was synthesised using the same procedure as for **6**. Thus, the reaction of **3** (2.00 g, 5.27 mmol) with *o*-fluorophenyl azide (0.80 g, 5.80 mmol) in CH_2Cl_2 (40 cm^3) gave, after work-up, compound **7** (2.06 g, 80%), (Found: C, 78.41, H, 5.34, N, 5.59; $C_{32}H_{26}FN_2P$ requires C, 78.67, H, 5.36, N, 5.73). mp 184–186 °C. ^{1}H NMR ($CDCl_3$): δ 4.46 (d, J = 23.7 Hz, 1H, CH), 6.50–6.73 (m, 5H, Ar), 6.82 (t, J = 7.2 Hz, 1H, Ar), 6.92–6.98 (m, 1H, Ar), 7.06 (t, J = 7.8 Hz, 2H, Ar), 7.22–7.33 (m, 3H, Ar), 7.37–7.52 (m, 8H, Ar), 7.76–7.83 (m, 4H, Ar), 11.66 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 86.06 (d, J = 130.8 Hz), 115.22 (d, J = 20.8 Hz), 117.47 (d, J = 7.4 Hz), 121.44, 121.46, 121.58, 122.68 (d, J = 2.6 Hz), 122.86 (d, J = 2.6 Hz), 123.68 (d, J = 3.4 Hz), 128.24, 128.36, 128.45, 128.55, 128.66, 128.81, 129.34, 131.60 (d, J = 2.2 Hz), 131.94 (d, J = 10 Hz), 133.10, 138.33 (d, J = 16.2 Hz), 141.82, 160.09. ^{31}P NMR ($CDCl_3$): δ 5.97 (m).

Synthesis of *o*-FC_6H_4N=$P(Ph_2)CH$=C(Ph)NH(*p*-MeC_6H_4) (8)

A solution of *o*-fluorophenyl azide (0.77 g, 5.6 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to a stirred solution of **4** (2.00 g, 5.08 mmol) in CH_2Cl_2 (30 cm^3) at 0 °C. The mixture was stirred at 0 °C for 10 min. and then at room temperature for 4 h. The solvent was removed under vacuum. The residual solid was washed with *n*-hexane and dried under vacuum to give a yellow powder of **8** (1.94 g, 76%). The compound was pure enough for the next step. Further purification was carried out by re-crystallisation of the crude product from diethyl ether. (Found: C, 77.66, H, 6.10, N, 5.10; $C_{33}H_{28}FN_2P{\cdot}0.6Et_2O$ requires C, 77.72, H, 6.26, N, 5.12). mp 136–138 °C. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, J = 6.9 Hz, Et_2O), 2.19

(s, 3H, Me), 3.47 (q, J = 6.9 Hz, Et_2O), 4.40 (d, J = 24 Hz, 1H, CH), 6.51–6.68 (m, 5H, Ar), 6.87 (d, J = 8.4 Hz, 2H, Ar), 6.90–6.98 (m, 1H, Ar), 7.20–7.34 (m, 3H, Ar), 7.21–7.32 (m, 3H, Ar), 7.40–7.52 (m, 8H, Ar), 7.76–7.82 (m, 8H, Ar), 11.58 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 15.40 (Et_2O), 20.74, 65.96 (Et_2O), 84.98 (d, J = 131.1 Hz), 115.18 (d, J = 20.7 Hz), 117.39 (d, J = 7.2 Hz), 121.57, 122.76 (d, J = 13.1 Hz), 123.63 (d, J = 3.5 Hz), 128.38, 128.61, 128.77, 129.14, 129.22, 131.06, 131.53 (d, J = 2.3 Hz), 131.91 (d, J = 10 Hz), 132.07, 133.22, 138.44 (d, J = 16.3 Hz), 139.27, 160.36. ^{31}P NMR ($CDCl_3$): δ 6.03 (m).

Synthesis of [Me_2Al{N(Ph)C(Ph)═CHP(Ph_2)═N(*p*-MeC_6H_4)}] (9)

$AlMe_3$ (0.50 cm^3, 2.3 M solution in hexane, 1.15 mmol) was added dropwise to a stirred solution of **5** (0.50 g, 1.03 mmol) in toluene (30 cm^3) at room temperature. The mixture was stirred at room temperature for 16 h. Solvents were removed under vacuum and the residue was dissolved in diethyl ether. The solution was filtered and the filtrate was concentrated to generate yellow crystals of **9** (0.42 g, 75%), (Found: C, 77.43, H, 6.28, N, 5.16; $C_{35}H_{34}AlN_2P$ requires C, 77.76, H, 6.34, N, 5.18). mp 228–230 °C. ^{1}H NMR (C_6D_6): δ 0.05 (s, 6H, AlMe), 1.91 (s, 3H, Me), 4.65 (d, J = 25.2 Hz, 1H, CH), 6.62 (t, J = 7.2 Hz, 1H, Ar) 6.69 (d, J = 8.4 Hz, 2H, Ar), 6.78–7.03 (m, 15H, Ar), 7.37–7.40 (m, 2H, Ar), 7.66–7.73 (m, 4H, Ar). ^{13}C NMR (C_6D_6): δ –7.65, 21.00, 83.20 (d J = 121 Hz), 122.54, 126.65, 127.26 (d, J = 33.54 Hz), 128.39, 128.64, 128.95, 129.11, 129.27, 130.05, 130.27, 132.51, 133.44 (d, J = 10.1 Hz), 142.38, 142.46, 142.42 (d, J = 6.1 Hz), 150.30, 172.70. ^{31}P NMR (C_6D_6): δ 20.59 (m).

Synthesis of [Me_2Al{N(Ph)C(Ph)═CHP(Ph_2)═N(*o*-ClC_6H_4)}] (10)

Synthesis of complex **10** follows the same procedure as for **9**. Reaction of $AlMe_3$ (0.29 cm^3, 2.3 M solution in hexane, 0.667 mmol) with **6** (0.30 g, 0.594 mmol) in toluene (30 cm^3) afforded, after re-crystallisation from a mixed solvent of diethyl ether and *n*-hexane, yellow crystals of **10** (0.24 g, 71%), (Found: C, 72.53, H, 5.59, N, 4.87; $C_{34}H_{31}AlClN_2P$ requires C, 72.79, H, 5.57, N, 4.99). mp 138–140 °C. ^{1}H NMR (C_6D_6): δ –0.09 (s, 3H, AlMe), 0.01 (s, 3H, AlMe), 4.46 (d, J = 24 Hz, 1H, CH), 6.44–6.54 (m, 1H, Ar), 6.58–6.73 (m, 2H, Ar), 6.82–7.10 (m, 14H, Ar), 7.13–7.23 (m, 1H, Ar), 7.42–7.50 (m, 2H, Ar), 7.55–7.65 (m, 2H, Ar), 7.72–7.82 (m, 2H, Ar). ^{13}C NMR (C_6D_6): δ –8.01, –7.73, 77.94 (d, J = 120.4 Hz), 122.65, 126.06 (d, J = 3 Hz), 126.74, 127.36 (d, J = 2.7 Hz), 128.58, 128.70, 128.95, 129.01, 129.16, 130.21, 130.68 (d, J = 2.4 Hz), 131.83 (d, J = 4.9 Hz), 132.30, 132.58, 132.87 (d, J = 10.3 Hz), 133.58 (d, J = 9.7 Hz), 142.17 (d, J = 7.6 Hz), 142.32, 142.52, 150.09, 173.20. ^{31}P NMR (C_6D_6): δ 22.64 (m).

Synthesis of [Me_2Al{N(Ph)C(Ph)═CHP(Ph_2)═N(*o*-FC_6H_4)}] (11)

Synthesis of complex **11** follows the same procedure as for **9**. Treatment of **7** (0.30 g, 0.62 mmol) with $AlMe_3$ (0.3 cm^3, 2.3 M solution in hexane, 0.69 mmol) in toluene (30 cm^3) yielded a yellow crystalline solid of **11** (0.18 g, 53%), (Found: C, 74.86, H, 5.66, N, 5.22; $C_{34}H_{31}AlFN_2P$ requires C, 74.99, H, 5.74, N, 5.14). mp 180–182 °C. ^{1}H NMR (C_6D_6): δ 0.19 (s, 6H, $AlMe_2$), 4.82 (d, J = 25.5 Hz, 1H, CH), 6.63–6.73 (m, 2H, Ar), 6.75–6.84 (m, 2H, Ar), 6.96–7.23 (m, 14H, Ar), 7.56–7.60 (m, 2H, Ar), 7.86–7.93 (m, 4H, Ar). ^{13}C NMR (C_6D_6): δ –8.23, 82.31 (d, J = 120.6 Hz), 116.49 (d, J = 21.4 Hz), 122.54, 124.40, 125.21 (d, J = 7.4 Hz), 126.55, 128.65, 128.83, 128.99, 129.31, 130.26, 130.40 (d, J = 7.9 Hz), 132.54 (d, J = 2.1 Hz), 133.29 (d, J = 10.2 Hz), 141.66 (d, J = 15.2 Hz), 150.11, 173.00. ^{31}P NMR (C_6D_6): δ 22.88 (m).

Synthesis of [Me_2Al{N(*p*-MeC_6H_4)C(Ph)═CHP(Ph_2)═N(*o*-FC_6H_4)}] (12)

Synthesis of complex **12** follows the same procedure as for **9**. Reaction of **8** (0.30 g, 0.60 mmol) with $AlMe_3$ (0.29 cm^3, 2.3 M solution in hexane, 0.667 mmol) in toluene (30 cm^3) afforded a yellow crystalline solid of **12** (0.22 g, 67%), (Found: C, 75.19, H, 5.97, N, 4.92; $C_{35}H_{33}AlFN_2P$ requires C, 75.25, H, 5.95, N, 5.01). mp 146–148 °C. ^{1}H NMR (C_6D_6): δ 0.04 (s, 6H, AlMe), 1.89 (s, 3H, Me), 4.59 (d, J = 25.8 Hz, 1H, CH), 6.45–6.55 (m, 2H, Ar), 6.62 (t, J = 7.8 Hz, 1H, Ar), 6.69–6.76 (m, 4H, Ar), 6.85–7.08 (m, 10H, Ar), 7.43 (d, J = 7.2 Hz, 2H, Ar), 7.70 (d, J = 8.4 Hz, 2H, Ar), 7.74 (d, J = 8.1 Hz, 2H, Ar). ^{13}C NMR (C_6D_6): δ –8.22, 21.06, 81.37 (d, J = 121 Hz), 116.52 (d, J = 24.5 Hz), 124.39, 125.15 (d, J = 7.3 Hz), 126.52, 128.79, 128.95, 129.25, 130.29, 130.44, 131.66, 132.45 (d, J = 2.3 Hz), 133.34 (d, J = 10.2 Hz), 141.87 (d, J = 14.8 Hz), 147.49, 173.14. ^{31}P NMR (C_6D_6): δ 22.91 (m).

Synthesis of 2-{*p*-MeC_6H_4N═P(Ph_2)}C_6H_4N═C(Ph)-$CH_2P(Ph_2)$═N(*p*-MeC_6H_4) (13)

Synthesis of complex **13** follows a similar procedure to 2-{PhN═P(Ph_2)}C_6H_4N═C(Ph)$CH_2P(Pr^i_2)$═NPh.[17] To a solution of 2-(Ph_2P)C_6H_4N═C(Ph)CH_2PPh_2 (1.05 g, 1.863 mmol) in CH_2Cl_2 (40 cm^3) was added *p*-$MeC_6H_4N_3$ (0.57 g, 4.28 mmol) at room temperature and the mixture was stirred overnight. Volatiles were removed *in vacuo* and the residue was dissolved in Et_2O. The solution was filtered and the filtrate was concentrated to give yellow crystals of **13**·0.5Et_2O (1.31 g, 87%), (Found: C, 79.84, H, 6.28, N, 5.25. $C_{52}H_{45}N_3P_2$·0.5Et_2O requires C, 79.98, H, 6.21, N, 5.18.), mp 182–184 °C. ^{1}H NMR ($CDCl_3$): δ 1.20 (t, J = 7.2 Hz, Et_2O), 2.06, 2.10, 2.13, 2.17, 2.20, 2.25 (Me), 3.27 (d, J = 12.4 Hz,CH_2), 3.47 (q, J = 7.2 Hz, Et_2O), 5.23 (d, J = 15.6 Hz, ═CH), 5.80 (dd, J = 4.4, 8 Hz, Ar), 5.85 (d, J = 14 Hz, ═CH), 5.95 (b, Ar), 6.21 (d, J = 8 Hz, Ar), 6.37 (d, J = 6.8 Hz, Ar), 6.60–6.76 (m, Ar), 6.80 (d, J = 8 Hz, Ar), 6.86–6.98 (m, Ar), 7.05–7.26 (m, Ar), 7.31–7.46 (m, Ar), 7.48–7.60 (m, Ar), 7.62–7.67 (m, Ar), 7.73 (dd, J = 7.2, 11.6 Hz, Ar), 7.87 (dd, J = 7.2, 12 Hz, Ar), 10.78 (s, NH). ^{13}C NMR ($CDCl_3$): δ 15.40, 20.60, 20.65, 20.75, 65.96, 98.47 (d, J = 93.6 Hz), 118.73 (d, J = 21.1 Hz), 120.17, 120.31, 121.69 (d, J = 14.1 Hz), 122.37, 122.62 (d, J = 13.1 Hz), 122.82 (d, J = 11.1 Hz), 123.10, 123.36, 123.37 (d, J = 18.1 Hz), 123.59 (d, J = 10.1 Hz), 127.05, 127.36, 127.56, 128.02 (d, J = 12.1 Hz), 128.18, 128.33 (d, J = 4.4 Hz), 128.54 (d, J = 12.1 Hz), 128.74 (d, J = 12.1 Hz), 128.95, 129.06, 129.35, 129.57, 130.23, 130.95, 131.22, 131.65 (d, J = 9 Hz), 131.98, 132.09, 132.19, 132.24, 132.55, 132.83 (d, J = 9.6 Hz), 133.25 (d, J = 9.2 Hz), 133.35, 134.92, 135.81 (d, J = 3.8 Hz), 146.29, 146.99, 148.21 (d, J = 11 Hz), 149.17, 149.56, 153.94, 156.57. ^{31}P NMR ($CDCl_3$): δ –3.22, –0.34, 1.04, 1.86, 9.22, 11.91.

Table 2 Details of the X-ray structure determinations of complexes **9** and **14**

	9	**14**·0.13$C_8H_{16}O_2$
empirical formula	$C_{35}H_{34}AlN_2P$	$C_{54}H_{50}AlN_3P_2$·0.13$C_8H_{16}O_2$
fw	540.59	848.67
T (K)	298(2)	294(2)
λ (Å)	0.71073	0.71070
crystal system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	12.3833(13)	10.7891(12)
b (Å)	13.9861(14)	15.4618(14)
c (Å)	18.4732(18)	17.1493(18)
α (deg)	90	63.402(8)
β (deg)	90.1360(10)	72.448(9)
γ (deg)	90	89.894(9)
V (Å^3)	3199.4(6)	2409.0(4)
Z	4	2
D_{calcd} (g cm^{-3})	1.122	1.169
$F(000)$	1144	896
μ (mm^{-1})	0.138	0.148
θ range for data collecn (deg)	1.64 to 25.02	1.50 to 27.80
no. of reflns collected	16 587	20 945
no. of indep reflns (R_{int})	5650 (0.1109)	11 148 (0.0435)
restraints/params	0/355	10/566
goodness of fit on F^2	1.046	1.010
final R indices[a] [$I > 2\sigma(I)$]	$R_1 = 0.0612$ $wR_2 = 0.1311$	$R_1 = 0.0631$, $wR_2 = 0.1794$
R indices (all data)	$R_1 = 0.1220$, $wR_2 = 0.1503$	$R_1 = 0.1033$, $wR_2 = 0.2035$
largest diff peak and hole [e Å^{-3}]	0.297 and –0.350	0.739 and –0.368

[a] $R_1 = \sum \|\|F_o\| - |F_c\|\| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{\frac{1}{2}}$

Synthesis of [Me_2Al\{N\{2-(*p*-MeC_6H_4N=$P(Ph_2)$)C_6H_4\}-C(Ph)=CHP(Ph_2)=N(*p*-MeC_6H_4)\}] (14)

$AlMe_3$ (0.31 cm^3, 2.3 M solution in hexane, 0.713 mmol) was added dropwise to a stirred solution of **13** (0.50 g, 0.646 mmol) in toluene (20 cm^3) at room temperature. The mixture was then stirred at room temperature for 16 h and then again at 110 °C for 8 h. The resulting solution was cooled back to room temperature and the solvent was removed *in vacuo*. The residue was dissolved in diethyl ether and filtered. The filtrate was concentrated under reduced pressure to form yellow crystals of **14** (0.34 g, 63%), (Found: C, 77.06, H, 5.99, N, 4.96; $C_{54}H_{50}AlN_3P_2$·0.6Et_2O requires C, 77.47, H, 6.46, N, 4.81). mp 238–240 °C. ^{1}H NMR (C_6D_6): δ –0.13 (s, 6H, AlMe), 1.85 (s, 3H, Me), 2.33 (s, 3H, Me), 6.22 (d, J = 16.5 Hz, 1H, CH), 6.29–6.35 (m, 1H, Ar), 6.64–6.73 (m, 5H, Ar), 6.79–7.16 (m, 20H, Ar), 7.30 (d, J = 8.1 Hz, 2H, Ar), 7.36–7.40 (m, 1H, Ar), 7.47–7.54 (m, 4H, Ar), 8.04–8.11 (m, 4H, Ar). ^{13}C NMR (C_6D_6): δ –6.74, 20.87, 21.40, 101.55 (d, J = 89.3 Hz), 119.57 (d, J = 14 Hz), 124.22 (d, J = 20.2 Hz), 124.93, 125.22, 126.20, 126.23 (d, J = 9.7 Hz), 127.51, 127.85 (d, J = 8.7 Hz), 128.36, 128.51, 129.02, 129.43 (d, J = 12.4 Hz), 130.04, 130.26 (d, J = 1.8 Hz), 130.49 (d, J = 2.7 Hz), 131.28, 131.70 (d, J = 12.1 Hz), 132.42 (d, J = 9 Hz), 133.47 (d, J = 2.9 Hz), 134.45 (d, J = 10.3 Hz), 134.60 (d, J = 2 Hz), 135.19, 136.64, 139.50 (d, J = 3.3 Hz), 142.72 (d, J = 5.2 Hz), 150.98 (d, J = 2.1 Hz), 157.73 (d, J = 3.9 Hz), 168.56 (d, J = 8.3 Hz). ^{31}P NMR ($CDCl_3$): δ –12.58 (m), 29.12 (m).

Single crystals of complex **14** suitable for X-ray diffraction analysis were grown from a mixed solvent of THF and *n*-hexane.

X-ray crystallography

Single crystals of complexes **9** and **14**·0.13$C_8H_{16}O_2$ were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Bruker Smart CCD area-detector or a Rigaku Saturn CCD area detector with graphite-monochromated Mo K_α radiation. Unit-cell dimensions were obtained with least squares refinement. Data collection and reduction were performed using the SMART (for **9**)[18] or CrystalClear (Rigaku Corporation, 2005) software (for **14**). Absorption corrections were applied using the SADABS[19] (for **9**) or REQAB program[20] (for **14**). The structures were solved by direct methods using SHELXS-97[21] and refined against F^2 by full-matrix least-squares using SHELXL-97.[22] Hydrogen atoms were placed in calculated positions. The co-crystallised THF molecule in **14**·0.13$C_8H_{16}O_2$ disordered over an inversion centre was refined with geometrical restraints. Crystal data and experimental details of the structure determinations are listed in Table 2.

Polymerisation of ε-CL catalysed by complexes 9–12 and 14

A typical polymerisation procedure is exemplified by the synthesis of PCL using complex **9** as a catalyst in the presence of benzyl alcohol (Table 1, entry 1). Complex **9** (0.0122 g, 0.0226 mmol) and toluene (2 cm^3) were added successively into a Schlenk tube. After the complex dissolved, benzyl alcohol (0.2 cm^3, 0.1128 M in toluene, 0.0226 mmol) was added at room temperature. The mixture was stirred at room temperature for 1 h. The Schlenk tube was put into an oil bath which was preset at 110 °C. After 10 min. ε-CL (0.515 g, 4.512 mmol) was added *via* a syringe. After the solution was stirred for 11 min. the polymerisation reaction was terminated by addition of several drops of glacial acetic acid. After stirring at room temperature for 0.5 h, the resulting viscous solution was diluted with THF and then dropped into cool methanol with stirring. The white precipitate was collected by

filtration under reduced pressure and washed with cool methanol and dried under vacuum, giving a white solid (0.4907 g, 95%).

For the GPC analysis, the sample was dissolved in dichloromethane, passed through a short neutral aluminium oxide column, precipitated in methanol and dried under vacuum.

For the kinetic studies, samples were taken from the reaction mixture using a syringe at a desired time interval.

Acknowledgements

We thank the National Natural Science Foundation of China (Grant No. 20972146) and the Foundation for Talents of Anhui Province (Grant No. 2008Z011) for financial support. We also thank Prof. D.-Q. Wang and Prof. H.-B. Song for the crystal structure determination and Prof. S.-Y. Liu for the GPC analysis.

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