

Abnormal N-heterocyclic carbene main group organometallic chemistry: a debut to the homogeneous catalyst

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Abnormal N-heterocyclic carbene (aNHC) adducts of zinc(II) (**1**) and aluminum(III) (**2**) were synthesized. The compounds were characterized by NMR spectroscopy and elemental analysis. The solid state structures of these complexes (**1** and **2**) were determined by single crystal X-ray study. Furthermore, these organozinc and organoaluminum adducts (**1** and **2**) were tested for the ring opening polymerization of cyclic esters. These adducts were found to be quite efficient catalysts for the polymerization of cyclic esters such as *rac*-lactide (*rac*-LA), ϵ -caprolactone (ϵ -CL), and δ -valerolactone (δ -VL). Furthermore, aNHC zinc adduct has been used as catalyst for the synthesis of a tri-block copolymer.

Introduction

The carbenes have been considered as important species in organic chemistry ever since the first evidence of their existence. Much of the early carbene chemistry was established in 1950s by Skell,¹ and little later, it was Fischer and co-workers who first introduced carbenes into the light of inorganic and organometallic chemistry in 1964.² Followed by the report by Arduengo and co-workers and others,³ N-heterocyclic carbenes (NHCs) have established themselves as extremely valuable catalysts in organic synthesis.⁴ While most of these studies considered the transition metal N-heterocyclic carbene complexes as catalysts only a very limited number of main group metal NHC adducts were tested as efficient catalysts for homogeneous polymerization catalysis.⁵

Recently, Bertrand and co-workers isolated a new class of NHC called abnormal N-heterocyclic carbene (aNHC) in which the carbene centre is no longer located between the two nitrogen atoms as commonly observed in the case of Arduengo NHC (normal NHC or *n*NHC) but is generated between nitrogen and carbon atoms.⁶ The isolation of aNHC has been envisaged as the new cornerstone in the field of organometallic catalysis with its superior potential to bind strongly with

catalytically active metal centre by virtue of its strong σ donation capability over its normal NHC counterpart.⁷

The metal chemistry of aNHC was originally inspired by a report of Faller, Crabtree and co-workers in 2001 where an unprecedented mode of coordination of NHC (abnormal mode of coordination) with the Ir centre was observed.⁸ In fact the signature of the superior catalytic ability of aNHC in comparison to its normal counterpart has been earlier authenticated by a seminal study of Lebel and co-workers⁹ and later on other studies documented similar observations.¹⁰ In this regard, recently we have established that the isolable abnormal N-heterocyclic carbene [1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-5-ylidene]⁶ can be used efficiently in metal free ring opening polymerization.¹¹ More recently, we used the same aNHC to synthesize halobridged palladium dimers for Suzuki–Miyaura cross coupling of challenging aryl chloride substrates delivering excellent yield at room temperature under very low-catalyst loading (0.005 mol%).¹² The main group chemistry of aNHC is itself in its infancy with a very few reports dealing with their synthesis and characterization as documented by Roesky *et al.*,¹³ Robinson *et al.* and others,¹⁴ however, the application of main group metal complexes of aNHC toward catalysis has not been reported. As part of our ongoing search for the development of green ROP catalysts, recently we reported the use of organozinc and organoaluminum complexes of phenalenyl ligands as efficient catalyst for producing biocompatible cyclic polyesters.¹⁵ Our choice of metals has remained the same while developing the main group based organometallic catalysts of aNHC ligand. Herein we introduce aNHC organozinc (**1**) and aNHC organoaluminum (**2**) adducts as catalysts for the ring opening polymerization of cyclic

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†Electronic supplementary information (ESI) available: Crystallographic details, NMR (¹H and ¹³C) spectroscopy, polymerization results, additional kinetic data, DFT calculation details and crystallographic data in CIF. CCDC 919364 and 919365. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51802g



esters. Catalytic efficacy of **1** was tested for different cyclic ester monomers like *rac*-lactide (*rac*-LA), ϵ -caprolactone (ϵ -CL), and δ -valerolactone (δ -VL), whereas the adduct **2** was investigated for polymerization of *rac*-LA monomer.

Results and discussion

Syntheses of adducts **1** and **2**

The *a*NHC adducts, **1** and **2** were prepared by the treatment of ZnEt₂ and AlMe₃, respectively with the *a*NHC ligand generated *in situ* in the reaction medium by the treatment of imidazolium salt **1A** and 2 equivalents of the base KN(SiMe₃)₂ in THF (Scheme 1).

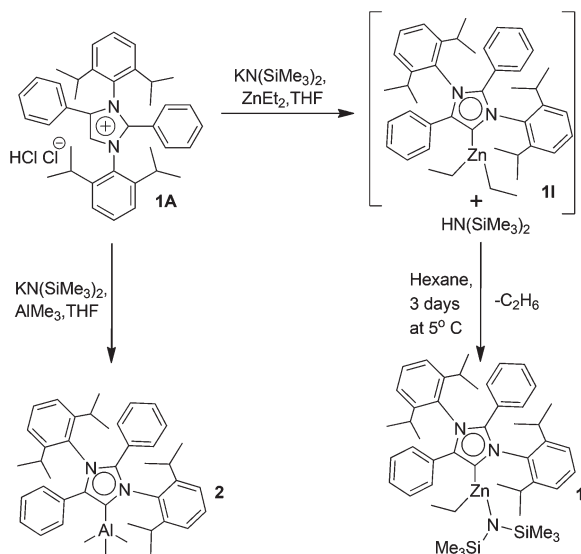
The compound **1** was characterized as an unprecedented one bearing amido and alkyl groups attached to the same Zn(II) centre. The formation of **1** can be explained by considering the formation of an intermediate compound **1I** and free HNSiMe₃, which subsequently reacts during the period of crystallization process under elimination of one molecule of ethane. The formation of compound **1I** was confirmed by the ¹H NMR spectrum recorded immediately after the reaction and before the crystallization process (see ESI, Fig. S3†). The ¹H NMR spectrum of compound **1I** recorded in C₆D₆ immediately after the reaction exhibited a characteristic triplet at δ 1.67 ppm and a quartet at δ 0.72 ppm with an intensity of 6 and 4 protons, respectively as determined by comparing the other proton resonances. This result reveals the formation of a diethyl zinc adduct of the *a*NHC (**1I**, see ESI, Fig. S3†) as an intermediate compound which subsequently leads to the formation of **1** by reacting with free HN(SiMe₃)₂ present in the reaction medium. The reaction mixture also exhibits the characteristic singlet peak at δ 0.1 ppm assigned to the free HN(SiMe₃)₂.¹⁶ The reaction mixture was subsequently extracted with hexane and kept at 5 °C for three days when the

compound **1I** slowly converted to the yellow crystals of compound **1**. The synthesis of compound **1** has been reproduced several times. Compound **1** was characterized by the ¹H and ¹³C NMR spectroscopy and elemental analysis. The ¹H NMR spectrum of compound **1** showed the characteristic new triplet at δ 1.63 ppm and a quartet at δ 0.69 ppm with an intensity of 3 and 2 protons, respectively along with another new 18 proton resonance at δ 0.34 ppm supporting the formation of compound **1** (see ESI, Fig. S4†). The presence of Zn(Et) and ZnN-(SiMe₃)₂ groups in **1** was also supported by the ¹³C NMR spectroscopy (see ESI, Fig. S5†). The ¹³C resonances at δ 14.0 and δ 6.0 ppm indicate the presence of ethyl group attached to the zinc centre.^{14a} The signal at δ 8.1 ppm in ¹³C NMR spectrum reveals the presence of trimethylsilyl amide group attached to the zinc centre.¹⁷ Compound **2** was synthesized by the reaction of *in situ* generated *a*NHC followed by the addition of AlMe₃ in the reaction medium (Scheme 1). The singlets at δ -0.45 ppm in ¹H NMR spectrum and at δ -5.22 ppm in ¹³C NMR spectrum are assigned to the CH₃ groups attached to the aluminium(III) centre in **2** (see ESI, Fig. S6 and S7†).^{14c}

X-ray crystal structures of **1** and **2**

The suitable single crystal for X-ray crystallography of adducts **1** and **2** were developed from the hexane solution at 5 °C (see Experimental section).

The selected bond lengths as well as angles observed in **1** and **2** are presented in Table 1. The molecular structure as determined by X-ray crystallographic study confirmed the structure of **1** (Fig. 1a). The molecular structure of **1** shows a trigonal planar geometry around the zinc centre (Fig. 1a). The Zn–C(*a*NHC) distance in compound **1** was determined as 2.061 Å which is comparable with the bond distance observed (2.022 Å) for Zn–C(abnormal NHC) bond distance reported in the literature.^{14a} The Zn–C(Et) and Zn–N(SiMe₃)₂ bond distances in **1** are determined to be 2.008 Å and 1.976 Å,



Scheme 1 Syntheses of organozinc (**1**) and organoaluminum (**2**) adducts of abnormal NHC.

Table 1 Selected bond distances and bond angles for **1** and **2**

1			
Bond distance (Å)		Bond angle (°)	
Zn1–C9	2.061(2)	N1–Zn1–C9	115.38(7)
Zn1–C1	2.008(2)	N1–Zn1–C1	120.34(8)
Zn1–N1	1.9767(15)	C1–Zn1–C9	124.10(8)
Si1–N1	1.6991(17)	Si1–N1–Si2	123.45(10)
Si2–N1	1.6981(18)	N2–C9–C40	103.17(16)
C1–C2	1.526(3)	Zn1–C9–N2	122.36(13)
2			
Bond distance (Å)		Bond angle (°)	
Al1–C21	2.1043(19)	C21–Al1–C22	107.34(3)
Al1–C22	1.988(2)	C21–Al1–C23	108.36(9)
Al1–C23	2.003(2)	C21–Al1–C24	112.74(8)
Al1–C24	1.998(2)	C22–Al1–C23	108.77(9)
C14–C21	1.379(3)	N1–C21–C14	102.81(15)
N1–C21	1.415(2)	C23–Al1–C24	107.52(9)



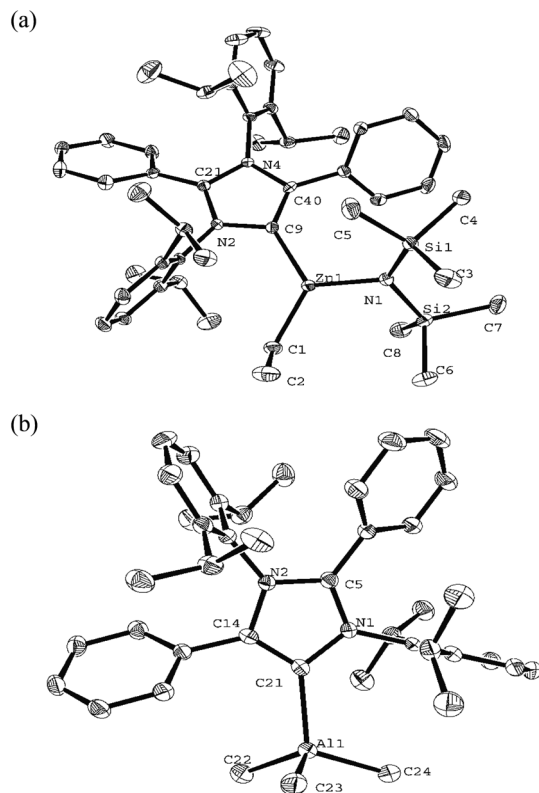


Fig. 1 Molecular structures with 50% ellipsoids: (a) adduct **1**; (b) adduct **2**. H atoms are removed for the sake of clarity.

respectively. These values fall well within the reported values in literature for relevant Zn-*a*NHC and Zn-*n*NHC adducts.^{14a,17} In organoaluminum *a*NHC adduct **2**, the aluminium centre adopts a distorted tetrahedral geometry (Fig. 1b). The Al-C(*a*NHC) bond distance observed in **2** (2.104 Å) is comparable with the literature report for *a*NHC-AlMe₃ adduct (2.033 Å) reported by Robinson *et al.*^{14c}

Stability of adducts **1** and **2**

We checked the stability of these adducts **1** and **2** on heating. The adducts **1** and **2** were found thermally stable on heating in toluene-*d*₈. Adduct **1** is stable up to 75 °C whereas **2** is stable under refluxing condition in toluene-*d*₈ (see ESI, Fig. S11 and S12†). This implies a stable adduct formation using the *a*NHC ligand, despite its known thermal instability in the free carbene state as reported earlier.⁶ We further checked the stability of these adducts by performing DFT calculation. The DFT optimized structures of **1** and **2** show strong resemblance with the crystal structures. The formation energies of adducts **1** and **2** are both exothermic ($\Delta H_{298} = -53.7$ kcal mol⁻¹ for **1** and -62.8 kcal mol⁻¹ for **2**) and exergonic ($\Delta G_{298} = -8.8$ kcal mol⁻¹ for **1** and -25.6 kcal mol⁻¹ for **2**). The bond lengths Zn-C(*a*NHC) = 2.162 Å and Al-C(*a*NHC) = 2.130 Å and the formation energies of **1** and **2** (*vide supra*) are well within the range calculated by Frenking *et al.*¹⁸ To understand the nature of the Zn-C(*a*NHC) and Al-C(*a*NHC) bonds we have performed Natural Bond Orbital analysis. The Wiberg bond

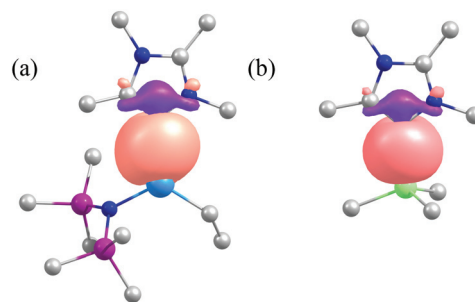


Fig. 2 Natural bond orbitals of (a) **1** and (b) **2** showing the C(carbene)-Zn and C(carbene)-Al bonds (see Computational details). Hydrogen atoms are removed for the sake of clarity. Colour code: C grey, N blue, Si magenta, Zn cyan, Al green.

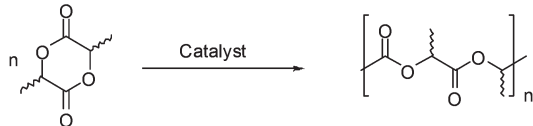
indices for the above bonds are 0.798 and 0.905 respectively. Both the carbene-organozinc and organoaluminum bonds are single bonds with occupancy of 1.993 and 1.923 e, respectively suggesting a similar type of bond strength (see Fig. 2). The sp² hybridized bonds contain substantial contribution (~85%) from the more electronegative carbene carbon (see Fig. 2). Furthermore, to quantify the electron density present in the bonds we have performed AIM (Atoms in Molecules) calculations. The electron density at the bond critical points (BCPs) of Zn-C(*a*NHC) and Al-C(*a*NHC) are 0.071 and 0.053, respectively with a Laplacian of -0.048 and -0.049 . The bond formation entails an overall charge transfer of 0.241 and 0.258 e from the *a*NHC component to the organozinc and organoaluminium fragments in **1** and **2**, respectively.

Polymerization of cyclic esters

There have been enormous interests to develop new catalytic systems for the synthesis of biodegradable and biocompatible polycaprolactide (PCL), polylactide (PLA), and polyvalerolactone (PVL) by ring opening polymerization catalysis.¹⁹ The access of stable Zn-*a*NHC (**1**) and Al-*a*NHC (**2**) adducts prompted us to test their potential as catalysts for ring opening polymerization (ROP) of *rac*-lactide under various reaction conditions (Table 2). All polymerization screenings were performed under dry nitrogen atmosphere in the presence or absence of benzyl alcohol (BnOH) as initiator in a toluene solution of monomer and in the presence of catalyst (see the Experimental section). It was found that adduct **1** readily polymerizes the *rac*-lactide, ϵ -caprolactone and δ -valerolactone monomers under ambient temperature (Table 2 and Table S2 of ESI†). The polymerization results reveal that the catalyst **1** falls among the best NHC based zinc catalysts in terms of activity reported in the literature.^{5b,c,17} The organoaluminum adduct **2** polymerizes *rac*-lactide at 100 °C (see Table 2). The polymerization results presented in Table 2 reveal that the polymerization rate decreases as the monomer ratio gradually increases keeping other variants constant (see entries 3–7, Table 2). The gradual increase of the concentration of the monomer also leads to a linear increment of the observed molecular weight of the polymer and this may be attributed to the controlled nature of the polymerization (also see below,



Table 2 Results of ring opening polymerization of *rac*-lactide using **1** and **2** as catalysts^a

								
Entry	Cat. [C]	[M] : [C] : [ROH]	Con. ^b (%)	Time	<i>M_n</i> (cal) ^c	<i>M_n</i> (GPC) ^d	PDI	<i>P_m</i> ^e
1	1	200 : 1 : 0	99	15 min	28 650	20 808	1.25	—
2	1	100 : 1 : 1	99	15 min	14 256	9451	1.21	0.62
3	1	50 : 1 : 2	99	15 min	3708	8053	1.27	0.63
4	1	100 : 1 : 2	99	15 min	7236	11 682	1.11	0.62
5	1	150 : 1 : 2	84	15 min	9180	13 044	1.13	0.56
6	1	200 : 1 : 2	84	26 min	12 204	17 330	1.09	0.58
7	1	250 : 1 : 2	80	26 min	14 508	19 414	1.11	0.57
8 ^f	2	50 : 1 : 3	90	8 h	2268	5316	1.08	0.47
9 ^f	2	100 : 1 : 3	76	14 h	3756	9253	1.11	0.48
10	<i>a</i> NHC	100 : 1 : 1	90	15 min	14 400	12 586	1.27	—
11	[N(Me) ₂ ,N(Me)-PLY]ZnEt	100 : 1 : 1	96	4 h	14 500	7900	1.16 ^{15b}	—
12	<i>n</i> NHC-Zn(OBn) ₂	130 : 1 : 0	96	20 min	9400	17 200	1.25	0.40 ^{5b}
13	<i>n</i> NHC-GaMe ₂ OMe ^g	50 : 1 : 0	99	30 min	7200	21 700	1.94	0.78 ^{5a}

^a At ambient temperature, in toluene as solvent. ^b Measured by ¹H NMR. ^c *M_n*(calcd) = (*M*/*I*) × conv. × 144 + *M*_{end group}. ^d Determined by GPC in THF. ^e Parameter *P_m* is the probability to give *meso* enchainment between monomer units and is determined from the methine region of the homonuclear decoupled ¹H NMR spectrum. ^f At 100 °C. ^g Reaction was performed at −20 °C.

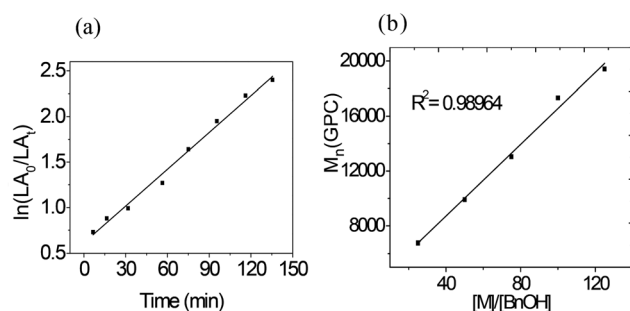


Fig. 3 (a) Polymerization of *rac*-LA using *a*NHC based organozinc adduct **1** under [*rac*-LA]₀ : [catalyst] : [BnOH] = 150 : 1 : 2 ratio in 5 mL toluene at 25 °C: logarithmic plot of *rac*-LA consumption as a function of time showing a linear increase. (b) Polymerization of *rac*-LA using organozinc adduct **1** under [catalyst] : [BnOH] = 1 : 2 ratio in 5 mL toluene at 25 °C.

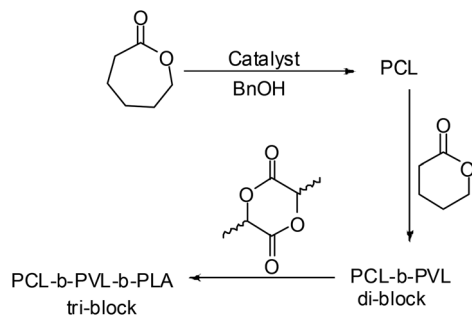
Fig. 3b). When the adduct **1** is used as catalyst in the absence of any initiator, the resulting polymer reveals the presence of −N(SiMe₃)₂ as the end group (see ESI, Fig. S9†) of the polymers which indicates that the initiation of polymerization process takes place through the nucleophilic insertion mechanism in which the zinc centre acts as a Lewis acceptor. However, in the presence of BnOH as initiator, the end group analysis revealed the presence of benzyloxy moiety (see ESI, Fig. S10†). This finding supports the formation of the dibenzyloxy zinc compound on treatment of **1** with two equivalents of BnOH (see ESI, Fig. S8†). The kinetic studies revealed that the polymerization in the presence of benzyl alcohol is first order with respect to monomer concentration and controlled in nature (Fig. 3 and also see ESI, Fig. S1†) as determined by kinetic studies with the help of ¹H NMR spectroscopy. The plot of ln (*LA*₀/*LA*_{*t*}) versus time provided a straight line with positive slope and this result indicates a first order reaction with

respect to the *rac*-lactide concentration. The controlled nature of the polymerization using the catalyst **1** is revealed in the plots of molecular weight [*M_n* (GPC)] vs. monomer to benzyl alcohol ratio which shows the gradual increase of molecular weight in a linear fashion with monomer to benzyl alcohol. The homonuclear decoupling ¹H NMR spectra indicate that the catalyst **1** is non-stereoselective in nature and the catalyst **2** provides atactic polylactide (see Table 2 and Fig. S2 of ESI†). We compared the relative catalytic activity of adduct **1** with that of the free *a*NHC reported earlier¹¹ (entries 2 and 10 of Table 2) which precludes the involvement of free carbene in the catalysis. The results of polymerization obtained by using the catalyst **1** are comparable with other related organozinc catalysts (see Table 2, entries 11–13) reported in the literature.^{5a,b,15b} Furthermore, the thermal stability of these adducts (**1** and **2**, discussed above, see also ESI†) ascertained by variable temperature NMR studies do not support the dissociation of these adducts in solution into free carbene.

Block copolymerization

Biodegradable polymers such as polyesters and polycarbonates produced by ring-opening polymerizations, including poly(ε-caprolactone), poly(*p*-dioxanone), poly(trimethylene carbonate), poly(glycolic acid), and poly(lactic acid), have met broad acceptance for medical uses owing to their low toxicity, degradation properties, and ease of synthesis.²⁰ Unfortunately, many times a single polymer cannot fulfill all the requirements for an intended application when two monomers are often copolymerized or two or more polymers are blended with each other to alter properties such as degradation rate, flexibility, and strength. A representative example is vicryl, a commercially available poly(lactide-*co*-glycolide) suture produced by Ethicon. Thus there have been enormous interests to





Scheme 2 Synthesis of tri-block copolymer.

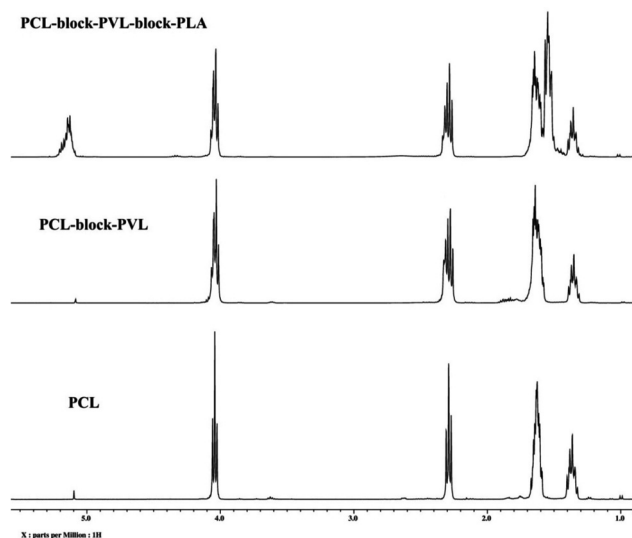


Fig. 4 Stack plots for synthesis of tri-block copolymer using catalyst **1** in CDCl_3 .

develop new catalytic systems for the synthesis of biodegradable and biocompatible copolymers. The controlled nature of polymerization using **1** as catalyst motivated us to check its efficiency in the block copolymerization process. The catalytic ability of **1** for block copolymerization was tested using ϵ -CL, δ -VL, *rac*-LA (Scheme 2) monomers in successive fashion at room temperature.

The tri-block copolymer was synthesized using 0.0097 mmol catalyst **1** and 100 equivalent (0.97 mmol) of each monomer ϵ -CL, δ -VL, *rac*-LA and 2 equivalents (0.0194 mmol) of benzyl alcohol at room temperature using toluene as solvent (5 mL). First, ϵ -CL was completely polymerized, followed by addition of the second monomer δ -VL to the polymerizing reaction mixture and further polymerization was done to its complete conversion to the di-block copolymer. Subsequently, a solution of *rac*-LA monomer was added to the polymerizing reaction mixture. The tri-block copolymer was isolated by precipitation on adding the methanol to the reaction mixture. The ^1H spectrum and mono modal nature of the resulting copolymer in GPC (see Fig. 4 and 5) confirm the formation of a tri-block copolymer.

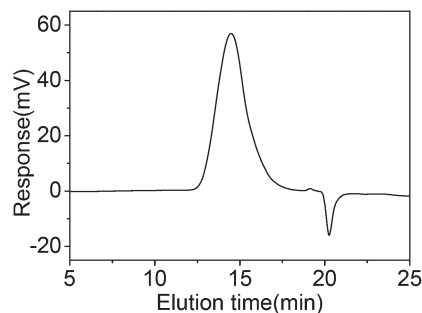


Fig. 5 GPC curve of PCL-block-PVL-block-poly(*rac*-LA) revealing a monomodal nature after tri-block copolymerization.

Summary and conclusions

In summary, this study reports the synthesis and characterization of stable organozinc and organoaluminum adducts of *a*NHC for development of main group based homogeneous catalysis. The present study demonstrates the synthesis and characterization of *a*NHC-Zn(Et)(N(SiMe₃)₂) (**1**) and *a*NHC-AlMe₃ (**2**) adducts. These *a*NHC adducts were used as catalysts in the ring opening polymerization reaction. *a*NHC-organozinc (**1**) adduct efficiently catalyzed the ring opening polymerization of different cyclic esters in a controlled manner. The controlled nature of polymerization of the catalyst *a*NHC-organozinc adduct **1** was further utilized in the synthesis of the tri-block copolymer.

Experimental section

General methods and instrumentation

All manipulations were carried out using standard Schlenk line and MBraun glovebox maintained at or below a 0.1 ppm of O₂ and H₂O level, utilizing glasswares that were oven-dried (130 °C) and evacuated while hot prior to use. All solvents were distilled from Na/benzophenone and were degassed by purging with dinitrogen. C₆D₆ was dried over sodium/potassium alloy and stored over activated 4 Å molecular sieves. NMR samples were prepared inside a glovebox. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 500 MHz and Jeol ECS 400 MHz spectrometers. Chemical shifts (δ) downfield from the reference standard were assigned positive values. Elemental analyses were performed using a Perkin Elmer 2400 CHN analyzer. GPC measurements were performed on a Waters 515 isocratic high-performance liquid chromatography (HPLC) pump system equipped with a differential Waters 2414 Refractive Index detector using THF (HPLC grade) as an eluant running at 1.0 mL min⁻¹. The chromatographic columns HT.3 (WAT 045920) and HT.4 (WAT 045935) were used. Molecular weight and molecular weight distributions were calculated using polystyrene as standard.

Single crystal X-ray structural analysis

Shock cooled crystals were selected and mounted under nitrogen atmosphere using the X-TEMP2.²¹ The data of *a*NHC



organozinc (1) and *a*NHC organoaluminum (2) adducts were measured on a Bruker TXS-Mo rotating anode with Helios mirror optics and APEX II detector with D8 goniometer. Diffractometers were equipped with a low temperature device and used MoK α radiation, $\lambda = 71.073$ pm. The data of 1 and 2 were integrated with Saint.²² The structures were solved by direct methods (Shelxs-97) and refined by full-matrix least-squares methods against F^2 (Shelxl-97).²³ All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in Table S1 of ESI.†

Computational details

All calculations were performed with Gaussian09 Quantum code.²⁴ Geometries are optimised using ONIOM (MO:MO)²⁵ method implemented in Gaussian09 program package. As a higher level we have specified whole molecule except four phenyl fragments connecting to the imidazole ring. This higher level was treated using BP86 functional²⁶ with triple-zeta quality basis sets (TZVP).²⁷ Low level of the ONIOM was treated with HF/STO-3G level of theory.²⁸ Geometries were optimized without any symmetry constraints. Harmonic force constants were computed at the optimized geometries to characterize the stationary points as minima or saddle points. Single point calculations were performed of the optimized geometries using BP86 functional incorporating higher basis sets (TZVP) for all atoms. NBO analysis²⁹ was performed to understand the nature of bonding in *a*NHC–Zn and *a*NHC–Al bonds. For NBO study we have done a single-point calculation of the optimized structures of 1 and 2 with replacing the phenyl substituents with methyl groups. The charge distribution around the carbene centre was analyzed using Weinhold's NPA (Natural Population Analysis) approach. Wiberg bond indices were also calculated to quantify covalent interactions.³⁰ We have applied Bader's AIM (Atoms-in-molecule)³¹ concept to characterize the electron distribution in the *a*NHC–Zn and *a*NHC–Al complexes. Any bonded pair of atoms has a bond path, *i.e.* a connecting line with maximum electron density. The bond critical (BCP) is a point on this line where the gradient of the density is equal to zero. The magnitude of the electron density (ρ) and its Laplacian ($\nabla^2\rho$) at the BCP provide information about the strength and type of bond. The Laplacian indicates whether the density is locally concentrated ($\nabla^2\rho < 0$) or depleted ($\nabla^2\rho > 0$). Natural bond orbitals are plotted in the Chemcraft visualization software.³²

Starting materials

Carbene salt was prepared according to the literature procedure.⁶ ϵ -CL and δ -VL were purchased from Sigma-Aldrich and dried over freshly ground CaH₂ and distilled before use.

rac-LA and other reagents were purchased from Sigma-Aldrich and recrystallized from dry toluene before use.

Synthesis of adduct 1

In a 100 mL Schlenk flask, carbene salt, 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium salt (1A) (1 mmol, 615 mg) was taken and kept under vacuum for 3 h. Subsequently, potassium bis(trimethylsilyl)amide (2 mmol, 400 mg) was added to the Schlenk flask and kept at -80 °C. Then THF (20 mL) was added to the mixture. The mixture was stirred for 1 h at same temperature and then warmed to room temperature when it was additionally stirred for 1 h. The solution became green. Again the solution was taken to -80 °C and zinc diethyl (1 mL, 1 M in hexane) solution was added and slowly taken to room temperature followed by stirring for 12 h at room temperature. Subsequently, the reaction mixture was dried under vacuum and extracted with hexane. The reaction mixture was filtered through the celite pad and the filtrate was kept at 5 °C for 3 days to grow yellow crystals (334 mg, 0.42 mmol, 42%) of the title compound. ¹H NMR (C₆D₆, 500 MHz, 298 K): δ 7.54 (2H, d, $J = 7.5$ Hz, ArH), 7.22 (1H, t, $J = 8.5$ Hz, ArH), 7.13–7.08 (5H, m, ArH), 6.97 (1H, t, $J = 8.5$ Hz, ArH), 6.85 (4H, d, $J = 7.5$ Hz, ArH), 6.56–6.51 (3H, m, ArH), 3.07–3.06 (2H, m, CH(CH₃)₂), 2.78–2.72 ((2H, m, CH(CH₃)₂), 1.63 (3H, t, $J = 9$ Hz, Zn CH₂CH₃), 1.57 (6H, d, $J = 7$ Hz, CH(CH₃)₂), 0.88 (12H, d, $J = 9$ Hz, CH(CH₃)₂), 0.78 (6H, d, $J = 6.5$ Hz, CH(CH₃)₂), 0.48–0.45 (2H, m, Zn CH₂CH₃), 0.34 (18H, s, $-N\{Si(CH_3)_3\}_2$) ppm. ¹³C NMR (C₆D₆, 100 MHz, 298 K): δ 165.3 (Zn–C_aNHC), 145.4 (ArC), 145.2 (ArC), 144.4 (ArC), 141.4 (ArC), 135.9 (ArC), 131.3 (ArC), 130.9 (ArC), 130.7 (ArC), 130.2 (ArC), 130.1 (ArC), 129.8 (ArC), 128.6 (ArC), 128.6 (ArC), 128.4 (ArC), 127.9 (ArC), 125.4 (ArC), 125.4 (ArC), 124.3 (ArC), 28.9 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 23.7 (CH(CH₃)₂), 23.5 (CH(CH₃)₂), 23.3 (CH(CH₃)₂), 14.0 (Zn CH₂CH₃), 8.1 ($-N\{Si(CH_3)_3\}_2$), 6.1 (Zn CH₂CH₃). Melting point 172–174 °C. Anal. Calcd for C₄₇H₆₇N₃Si₂Zn: C, 70.95; H, 8.49; N, 5.28 Found: C, 70.68; H, 8.23; N, 5.11.

Synthesis of adduct 2

In a 100 mL Schlenk flask, carbene salt 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium salt (1A) (1 mmol, 615 mg) was taken and kept under vacuum for 3 h. Subsequently potassium bis(trimethylsilyl)amide (2 mmol, 400 mg) was added and THF (20 mL) was added to the mixture. The reaction mixture was then cooled -80 °C and stirred for 1 h. The reaction mixture was then warmed to room temperature and additionally stirred for 1 h. During this period, the solution became green. Further the solution was taken to -80 °C and aluminum trimethyl (0.5 mL, 2 M in toluene) solution was added and stirred for 12 h at room temperature. Finally the reaction mixture was dried under vacuum and extracted with hexane. The hexane extract was filtered through a celite pad and the filtrate was kept at 5 °C for 3 days to grow colourless crystals (287 mg, 0.47 mmol, 47%) of the title compound. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 7.78 (2H, d, $J = 8.4$ Hz, ArH), 7.29 (1H, t, $J = 7.6$ Hz, ArH), 7.12–7.08 (4H, m, ArH), 6.99–6.94



(2H, m, ArH), 6.90 (2H, d, $J = 7$ Hz, ArH), 6.77 (2H, d, $J = 8.4$ Hz, ArH), 6.56–6.48 (3H, m, ArH), 2.97–2.95 (2H, m, $\text{CH}(\text{CH}_3)_2$), 2.84–2.83 (2H, m, $\text{CH}(\text{CH}_3)_2$), 1.55 (6H, d, $J = 8.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.86–0.82 (12H, m, $\text{CH}(\text{CH}_3)_2$), 0.68 (6H, d, $J = 8.4$ Hz, $\text{CH}(\text{CH}_3)_2$), -0.45 (9H, s, $\text{Al}(\text{CH}_3)_3$) ppm. ^{13}C NMR (C_6D_6 , 100 MHz, 298 K): δ 159.8 ($\text{Al}-\text{C}_{\text{NHC}}$), 145.5 (ArC), 145.4 (ArC), 143.2 (ArC), 143.1 (ArC), 135.6 (ArC), 132.1 (ArC), 131.6 (ArC), 131.2 (ArC), 130.9 (ArC), 130.2 (ArC), 130.1 (ArC), 129.7 (ArC), 125.2 (ArC), 124.9 (ArC), 124.3 (ArC), 29.2 ($\text{CH}(\text{CH}_3)_2$), 28.8 ($\text{CH}(\text{CH}_3)_2$), 24.6 ($\text{CH}(\text{CH}_3)_2$), 24.1 ($\text{CH}(\text{CH}_3)_2$), 23.7 ($\text{CH}(\text{CH}_3)_2$), 23.4 ($\text{CH}(\text{CH}_3)_2$), -5.2 ($\text{Al}(\text{CH}_3)_3$) ppm. Melting point 246–248 °C (decomposition). Anal. Calcd for $\text{C}_{42}\text{H}_{53}\text{AlN}_2$: C, 82.31; H, 8.72; N, 4.57 Found: C, 82.49; H, 8.82; N, 4.46.

General procedure for the ring-opening polymerization (ROP) of cyclic esters

In a single necked tube fitted with standard ground joint, a toluene solution (2 mL) of catalyst (0.0097 mmol catalyst) and BnOH (required amount) were loaded inside the glovebox at room temperature. The solution was stirred for 5 min, and then cyclic ester (required amount) was added to the solution and the tube was closed with a glass stopper. The reaction mixture was stirred at appropriate temperature. The polymerization mixture was quenched by addition of water (0.2 mL) and diluted with dichloromethane. The resultant solution was poured into rapidly stirred methanol (400 mL) solution. The ring-opened polymer was collected as the methanol insoluble white precipitates by filtration and was dried under reduced pressure.

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