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Influence of multidentate *N*-donor ligands on highly electrophilic zinc initiator for the ring-opening polymerization of epoxides

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ABSTRACT

A set of multidentate ligands have been synthesized and used to stabilize the putative highly electrophilic zinc species initiating ring-opening polymerization (ROP) of cyclohexene oxide (CHO) and propylene oxide (PO). Reaction of the bidentate C_2-chiral bis(oxazoline) ligand (^{R2,R3}BOX: R_2 = (4*S*)-*t*Bu, R_3 = H (**a**); R_2 = (4*S*)-Ph, R_3 = H (**b**); R_2 = (4*R*)-Ph, R_3 = (5*S*)-Ph (**c**)) with $Zn(R_1)_2$ (R_1 = Et (**1**), Me (**2**)) led to the heteroleptic three-coordinate complexes (^{R2,R3}BOX)ZnR_1, **1a**–**c** and **2a**, which were isolated in 92–96% yield. Next, two pyridinyl-functionalized *N*-heterocyclic carbene (NHC) ligands have been designed and synthesized: the 1,3-bis(2-pyridylmethyl)imidazolinium salt (**d**) and the protected NHC adduct 2-(2,3,4,5,6-pentafluorophenyl)-1,3-bis(2-pyridylmethyl)imidazolidine (**e**). The reaction of ligands **d** and **e** with $ZnEt_2$ led directly to the formation of (NHC)ZnEt(Cl) **3d** complex with ethane elimination and the adduct (NHC–C_6F_5(H))$ZnEt_2$ **4e**, respectively, in high yield. *In situ* combinations of selected complexes **1a**–**c**, **3d** and **4e** with $B(C_6F_5)_3$ (1 or 2 equivalents) give active systems for ROP, with high productivity (3.3–5.9 10^6 $g_{polym.}$ mol_{Zn}^{-1} h^{-1}) and high molecular weight (M_n up to 132 10^3 g mol^{-1}) for CHO polymerization. Although the *in situ* $B(C_6F_5)_3$-activated zinc species were not isolated, the sterically demanding BOX ligands (**1c** > **1b** > **1a**) and functionalized NHC ligands seem to enhance the stability of highly electrophilic zinc complexes over ligand redistribution, allowing a better control of the cationic ROP as reflected particularly for **3d** and **4e** complexes by their respective efficiency (42–88%).

1. Introduction

The ion pairs formed by cationic zinc complexes have recently attracted considerable interests due to their strong Lewis acidity [1]. For example, cationic zinc complexes generated *in situ* or isolated efficiently catalyze the intramolecular hydroamination/cyclization reactions [2–11] and the ROP of propylene oxide (PO), cycloxene oxide (CHO) and ϵ-caprolactone [12–15]. Generally, the organometallic chemistry of transition metal alkyls in the presence of cationizing reagents (*e.g.* $B(C_6F_5)_3$ [16–19], $[Ph_3C][B(C_6F_5)_4]$ [20], and $[HNRR'_2][B(C_6F_5)_4]$ [21]) proceed preferentially by alkyl abstraction [17,18,22–26], while main group metals such as zinc, aluminum and gallium alkyls with $B(C_6F_5)_3$ tend to provide alkyl/C_6F_5 exchange [27–36]. This ligand exchange may be totally suppressed, either by using neutral (or anionic) *N*,*N*′-chelating ligands or in a coordinating solvent (Et_2O), generating stable four- and even three-coordinate zinc alkyl or silylamide cations [12–15,37–40].

Toward the generation of the intriguing cationic zinc complexes, we were motivated to use bidentate and tridentate with *N*-donor ligands to enhance the stabilization of the highly reactive electrophilic zinc species. Here we report the synthesis of zinc alkyl complexes with bis(oxazoline) and *N*-heterocyclic carbene with pending hemilabile pyridine arms, their reactions with $B(C_6F_5)_3$ as cationizing reagents, and their reactivity in ring-opening polymerizations (ROP) of epoxides.

2. Results and discussion

2.1. Synthesis of bidentate *N*,*N*′-chelating BOX-zinc complexes

We have recently reported the synthesis of alkyl zinc(II) complexes (^{R2,R3}BOX)ZnEt **1a**, **1b** and **1c**, which are obtained straightforwardly from (^{R2,R3}BOX)H and $ZnEt_2$ (Scheme 1) [41]. Complex **2a** was obtained in similar manner in high yield (96%) by slow addition of 1 equivalent of neutral ligand (^{tBu,H}BOX)H to $ZnMe_2$ in hexane at room temperature (Scheme 1).

Complex **2a** was characterized by DRIFT, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopies. The NMR spectra show the expected set of signals for the BOX ligand and for the ZnMe group which is shifted in the high field region (^{1}H NMR: δ −0.11 ppm and $^{13}C\{^1H\}$ NMR: −10.5 ppm) in comparison with the starting material $ZnMe_2$ (^{1}H NMR: δ 0.51 ppm

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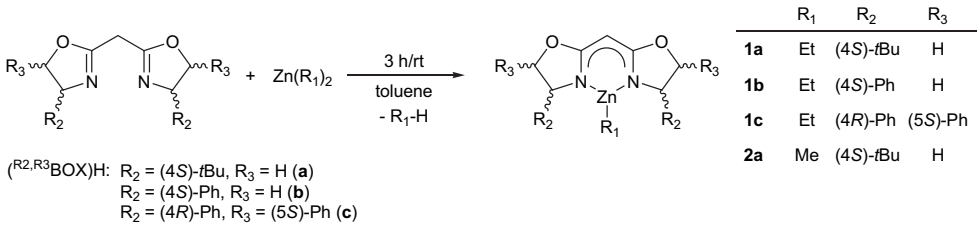


	R_1	R_2	R_3
1a	Et	(4*S*)-*t*Bu	H
1b	Et	(4*S*)-Ph	H
1c	Et	(4*R*)-Ph	(5*S*)-Ph
2a	Me	(4*S*)-*t*Bu	H

Scheme 1. Synthesis of bis(oxazoline) alkyl zinc complexes **1a**–**c** and **2a**.

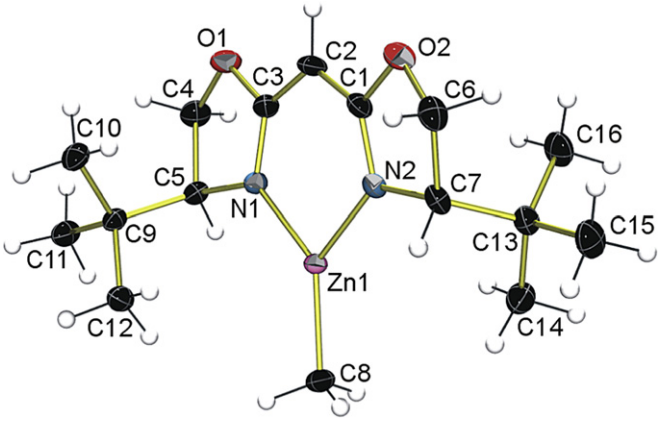


Fig. 1. Molecular structure of (^{tBu,H}BOX)ZnMe (**2a**). Selected bond lengths (Å) and angles (°) for **2a**: Zn(1)–C(8) 1.9543(11), Zn(1)–N(1) 1.9676(9), Zn(1)–N(2) 1.9628(9), N(1)–C(3) 1.3206(14), N(2)–C(1) 1.3248(14), C(1)–C(2) 1.3889(16), C(3)–C(2) 1.3923 (16), N(1)–Zn(1)–N(2) 93.13(4), N(1)–Zn(1)–C(8) 131.49(5), N(2)–Zn(1)–C(8) 132.34 (5), C(1)–C(2)–C(3) 122.88(10), C(2)–Zn(1)–C(8) 177.74(5).

and $^{13}C\{^1H\}$ NMR: −4.2 ppm) [42]. The structure of **2a** was confirmed by single-crystal X-ray diffraction and selected bond lengths and angles are given in Fig. 1. Compound **2a** crystallizes in the chiral tetragonal space group $P4_12_12$. The structure determined for **2a** shows that the zinc metal center adopts a slightly distorted trigonal geometry with a six-membered ring almost coplanar with the Zn(1) atom which is only displaced a) by 0.022(2) Å from the plane defined by N(1), N(2) and C(2) with a C(2)–Zn–C(8) angle close to 180° (177.74(5)°), and b) with the sum of angles of the Zn–N_2C core atoms close to 360° (sum 359.96(5)°). Moreover, both oxazolinyl rings are slightly twisted as seen from the torsion angles of ∠C(3)–N(1)–C(5)–C(4) = 17.43(11)° and ∠C(1)–N(2)–C(7)–C(6) = 17.52(11)°. The Zn–C distance and Zn–N distances are in the expected range of anionic bidentate *N,N′*-chelating zinc methyl compounds and comparable to β-diketoiminate, anilido-aldimine or aminotroponiminate ZnMe compounds with a trigonal geometry: (Zn(1)–C(8) 1.9543(11) Å and (Zn(1)–N(1) 1.9676(9) Å and Zn(1)–N(2) 1.9628(9) Å) [2–5,9,43,44].

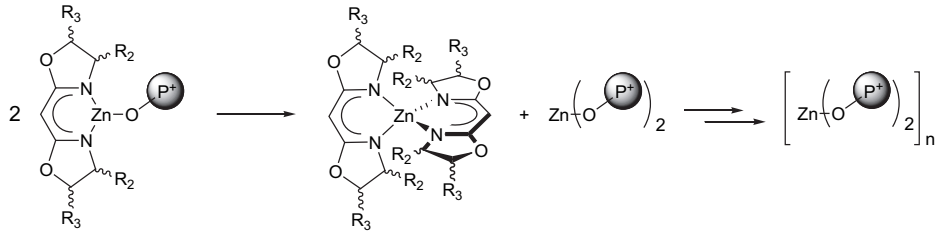
Systems based on cationic Zn(II) are well-known catalysts for the ROP of epoxides. In a first attempt, the complexes **1a**–**c** and **2a** were used and activated by 1 equivalent of $B(C_6F_5)_3$, increasing the Lewis acidity of the zinc center, under mild conditions for the polymerization of CHO. All complexes were found to be highly active with nearly quantitative yields after 1 min of reaction time (Table 1). These polymerization reactions were extremely exothermic with temperatures rising rapidly above 100 °C. For all cationic zinc complexes generated *in situ*, productivities reaching 5500–5900 $kg_{polym.}\ mol_{Zn}^{-1}\ h^{-1}$ and turn-over frequencies (TOFs) > 56,000 h^{-1} were observed. The polymers produced by the putative BOX divalent cationic zinc complexes were of reasonably high weight-average molecular weight ($86 < M_w < 108 \times 10^3$ g mol^{-1}), with a broad polydispersity (PDI = 2.9–5.7). The low number-average molecular weights measured (M_n < 37,000 g mol^{-1}) in comparison with the calculated M_n (98,140 g mol^{-1}) suggest significant ligand redistribution (assimilated to chain transfer here), most likely leading to the homoleptic BOX–Zn complexes and $Zn(OP^+)_2$ species which could furthermore decompose into $[Zn(OP^+)_2]_n$ polymeric aggregates as depicted in Scheme 2. This ligand redistribution in BOX–Zn systems, which has been previously demonstrated in the presence of donor ligands or solvents [41], seems to decrease with the bulkiness of BOX ligands. This observed trend (**1c** > **1b** > **1a**) indicates that the bulkier BOX ligands are better at "stabilizing" *in situ* the highly electrophilic zinc complexes generated and thus also at enhancing the cationic polymerization control (**1c**: M_n = 37,000 g mol^{-1} and **1a**: M_n = 15,000 g mol^{-1}). Note that the ligand redistribution itself might not be the whole reason explaining the low molecular weight and that side reactions such as deprotonation/chain transfer and/or back-biting (giving macrocyclic ethers) phenomena can also occur during the polymerization, albeit rather limited considering the high reactivity of the CHO monomer due to its strained 3-membered ring. Nevertheless, the observed apparent ligands dependency on the productivity could therefore also arise from the more or less efficient reaction of $B(C_6F_5)_3$ with the Zn-alkyl, or the formation of tight ion pairs, leading to a lower concentration of highly electrophilic zinc initiator in solution.

Preliminary investigations into the polymerization of propylene oxide catalyzed by the $B(C_6F_5)_3$-activated complexes **1a**–**c** revealed good productivity under mild conditions (Table 1). The same trend is

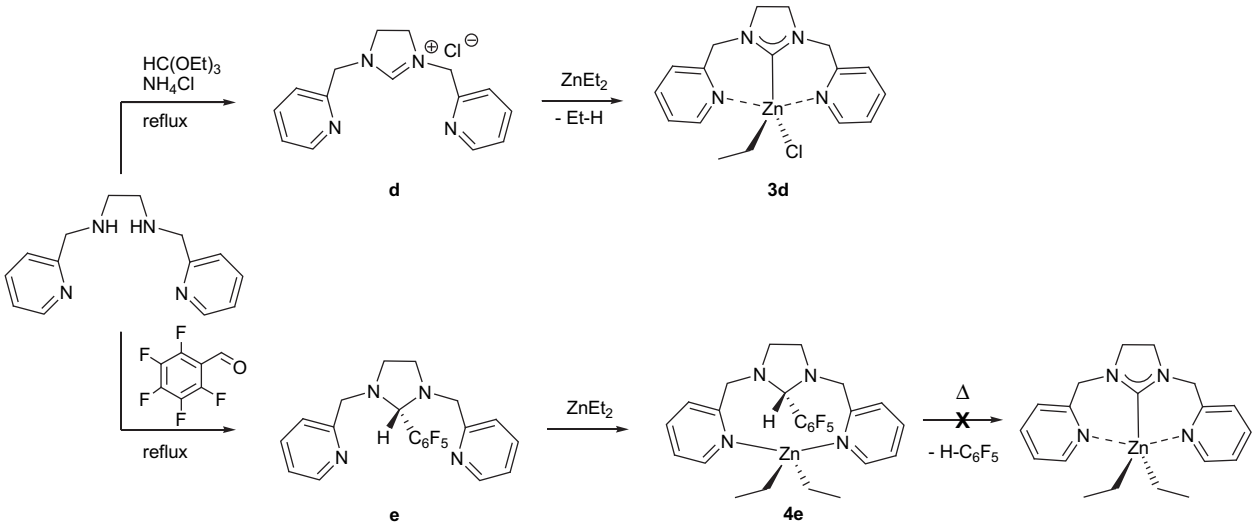
Table 1
Results from polymerization reactions using **1a**–**c** and **2a** complexes.

Initiator	Monomer	M/Cat ratio	Yield (%)	TOF (h^{-1})	Productivity ($kg_{polym.}\ mol_{Zn}^{-1}\ h^{-1}$)	M_w[c] ($\times 10^3$)	M_n[c] ($\times 10^3$)	PDI[d]
1a/$B(C_6F_5)_3$[a]	CHO	1000	94	56,312	5526	86	15	5.5
1b/$B(C_6F_5)_3$[a]	CHO	1000	100	60,121	5900	104	28	3.6
1c/$B(C_6F_5)_3$[a]	CHO	1000	100	60,121	5900	108	37	2.9
2a/$B(C_6F_5)_3$[a]	CHO	1000	96	57,520	5645	86	15	5.7
1a/$B(C_6F_5)_3$[b]	PO	1000	7	86	8.4	16.4	2.0	8.2
1b/$B(C_6F_5)_3$[b]	PO	1000	9	103	10.1	19.9	2.6	7.7
1c/$B(C_6F_5)_3$[b]	PO	1000	25	300	29.4	18.2	5.7	3.2

[a] Polymerization procedure: 21.2 μmol pre-catalyst, 5 mL toluene, 21.2 μmol $B(C_6F_5)_3$, 21.2 mmol CHO; 1 min at T_0 = 30 °C.
[b] Polymerization procedure: 21.2 μmol pre-catalyst, 5 mL toluene, 21.2 μmol $B(C_6F_5)_3$, 21.2 mmol PO; 30 min at T_0 = 30 °C.
[c] Determined by means of size exclusion chromatography (SEC). M_w = weight-average molecular weight; M_n = number-average molecular weight in g mol^{-1}.
[d] Polydispersity index = M_w/M_n.



Scheme 2. Illustration of ligand redistribution with BOX–Zn systems during the ROP.



Scheme 3. Synthesis of ligands **d** and **e**, and their reactivity with $ZnEt_2$.

observed (**1c** > **1b** > **1a**) for the polymerization of PO as was previously noted for the polymerization of CHO. The GPC data of the poly(propylene oxide) produced indicate an important amount of oligomers along with low molecular weight polymers, suggesting a substantial degradation of the cationic zinc species over time along with presumably side reactions such as deprotonation, inter- and intra-molecular (back-biting) chain transfer. Note that the observed weight-average molecular weights ($M_w = 15–20{,}000$ g mol^{-1}) show a higher formation of polymers than those reported for the same polymerization reaction initiated by cationic zinc and aluminum complexes (<3000 g mol^{-1}) [12–15,45,46].

All attempts to synthesize and isolate the BOX cationic zinc complexes failed and NMR-scale reactions with **1c** and 1 equivalent of $B(C_6F_5)_3$ in benzene-d_6 led to the formation of indistinct complexes. The ^{19}F NMR spectrum corroborates the presence of several cationic and neutral zinc complexes in solution, with ion pair $[(^{R2,R3}BOX)Zn]^+[EtB(C_6F_5)_3]^-$ and $(^{R2,R3}BOX)Zn(C_6F_5)/EtB(C_6F_5)_2$ as major species [31]. The lack of stabilization by the BOX ligands in these highly electrophilic zinc systems is presumably responsible for the presence of several zinc species in solution which also seems to be a major drawback regarding the control of the polymerization.

2.2. Synthesis of tridentate N,C,N′ chelating NHC zinc complexes

In order to stabilize the active cationic species the use of a strong σ-donor with potentially labile pending arms was investigated. The ability of *N*-heterocyclic carbenes to stabilize a wide range of metal complexes combined with the fact that the number of examples of functionalized NHC derivatives is rapidly growing renders this class of ligands highly interesting for the present study [47–49]. Herein, we report the synthesis and coordination of a NHC ligand functionalized by two pyridines. The latter are known to be poor Lewis bases and thus may be presumed to readily generate a vacant site.

So far, 1,3-bis(2-pyridylmethyl)imidazolidinylidene transition metal complexes (with W, Pd, Au, Ru) have been synthesized only by post-functionalization or indirect methods, and the synthesis and characterization of isolated 1,3-bis(2-pyridylmethyl)imidazolinium salts have so far not been reported [50,51]. Ligand **d** was prepared in high yield by a condensation reaction of *N*,*N*′-bis(2-pyridylmethyl)-ethane-1,2-diamine with an excess of triethyl orthoformate in the presence of ammonium chloride (Scheme 3). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **d** show characteristic peaks of the imidazolinium methyne group at 9.76 and 160.0 ppm, respectively, confirming the cyclization. The proton resonance of methyl pyridyl and the bridging methylic groups, appearing each as

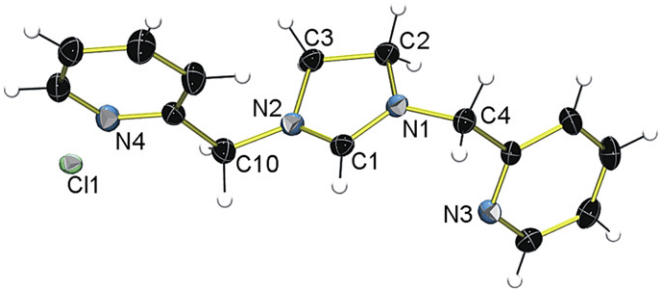


Fig. 2. Molecular structure of the 1,3-bis(2-pyridylmethyl)imidazolium chloride salt (d). Selected bond lengths (Å) and angles (°) for d: N(1)–C(1) 1.3131(15), N(2)–C(1) 1.3114(16), N(1)–C(2) 1.4733(15), N(1)–C(4) 1.4563(15), N(2)–C(3) 1.4815(16), N(2)–C(10) 1.4507(16), N(1)–C(1)–N(2) 113.27(11), C(1)–N(1)–C(4) 125.15(10), C(1)–N(2)–C(10) 125.30(11), C(1)–N(1)–C(2) 110.29(10), C(1)–N(2)–C(3) 110.02(10).

Table 2
Results from polymerization reactions using **3d** and **4e** complexes.

Initiator	Monomer	Yield (%)	TOF (h^{-1})	Productivity ($kg_{polym.}\ mol_{Zn}^{-1}\ h^{-1}$)	M_w[c] ($\times 10^3$)	M_n[c] ($\times 10^3$)	PDI[d]
3d/$B(C_6F_5)_3$[a]	CHO	57	34,038	3340	387	132	2.9
4e/$B(C_6F_5)_3$[a]	CHO	74	44,143	4332	176	82	2.1
4e/2 $B(C_6F_5)_3$[a]	CHO	100	60,121	5690	77	9	8.3
3d/$B(C_6F_5)_3$[b]	PO	43	345	33.8	–[e]	–[e]	–[e]

[a] Polymerization procedure: 21.2 μmol pre-catalyst, 5 mL toluene, 21.2 μmol or 42.4 μmol $B(C_6F_5)_3$ (1 or 2 equiv), 21.2 mmol CHO ($[CHO]_0/[cat]_0 = 1000:1$); 1 min at $T_0 = 30$ °C.
[b] Polymerization procedure: 21.2 μmol pre-catalyst, 5 mL toluene, 21.2 μmol $B(C_6F_5)_3$, 14.3 mmol PO ($[PO]_0/[cat]_0 = 675:1$); 30 min at $T_0 = 30$ °C.
[c] Determined by means of size exclusion chromatography (SEC). M_w = weight-average molecular weight; M_n = number-average molecular weight in g mol^{-1}.
[d] Polydispersity index M_w/M_n.
[e] Not determined.

a singlet at 4.99 and 4.01 ppm respectively, highlights the C_{2v} geometry. Ligand **d** was further characterized by X-ray crystallography and crystallizes as a well-separated ion pair as found in its reported unsaturated imidazolium analogs (Fig. 2) [52]. The shorter distances between N(1)–C(1) 1.3131(15) and C(1)–N(2) 1.3114 (16) Å in comparison to N(1)–C(2) 1.4733(15) and N(2)–C(3) 1.4815 (16) Å indicate a delocalization between N1–C1–N2 atoms.

With the aim to synthesize a (NHC)$ZnEt_2$ complex, repeated efforts to generate the free carbene prior to complexation using various bases such as $KN(SiMe_3)_2$, KO*t*Bu, *n*BuLi at low temperature and short reaction time led to a complicated mixture. Such reactivity is not surprising for this imidazolinium salt with its electrophilic pyridinylmethyl moieties in the presence of the nucleophilic carbene which tends to initiate the 1,2 migration rearrangement or enetetramines formation [53–58]. Attempts to generate a silver complex (from Ag_2O, Ag_2CO_3) were also thwarted by the presence of pyridinyl groups which can lead to a mixture of mono-, di- and polymeric compounds in solution as reported for similar bi- and tridentate NHC ligands [59–66]. In contrast, the imidazolinium salt reacts readily with $ZnEt_2$ in toluene to give (NHC)ZnEt(Cl) **3d** complex with ethane elimination (Scheme 3). The disappearance of the imidazolinium CH resonance in the ^1H NMR spectrum with a concomitant downfield shift to 206.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum reveals the coordination of the carbene to the metal. Surprisingly, both pyridinylmethyl and methylenic signals of the NHC ligand appear as a singlet (at 4.58 and 2.75 ppm, respectively), suggesting a highly fluxional process arising from the inherent weak interactions between the pyridine groups and zinc center [67]. In addition, the ^1H and $^{13}C\{^1H\}$ NMR resonances of the C_{ipso} from the pyridine ring (8.65 and 155.8 ppm, respectively) are only slightly shifted downfield, corroborating a weak coordination of the pyridine groups.

In order to form the free carbene *in situ*, we adapted the method developed by Waymouth and Hedrik, which does not need the presence of a base but in which the free carbene can be generated by thermal deprotection of pentafluorobenzene NHC adducts [68]. Thus, the protected adduct of 2-(2,3,4,5,6-pentafluorophenyl)-1,3-bis(2-pyridylmethyl)imidazolidine (**e**) was synthesized in high yield by condensation of *N*,*N*′-bis(2-pyridylmethyl)-ethane-1,2-diamine with pentafluoro-benzaldehyde catalyzed by acetic acid. The methyl pyridyl protons now appear as two sets of doublets centered at 3.87/3.81 ppm and the methylenic bridging protons resonate as a double doublet of doublets centered at 3.32/2.82 ppm, revealing the loss of C_{2v} symmetry. The complex (NHC–C_6F_5(H))$ZnEt_2$ **4e** is formed in high yield upon contacting the NHC adduct **e** with $ZnEt_2$ in toluene at room temperature (Scheme 3). Except for the appearance of the ethyl peaks at 1.57 and 0.39 ppm, no major changes in the ^1H and $^{13}C\{^1H\}$ spectra were observed, demonstrating the integrity of the ligand. Unfortunately, the thermal activation of the pentafluorobenzene NHC adduct **e**, involving temperatures ranging from 30 to 80 °C, both prior to reaction with $ZnEt_2$ and starting from complex **4e**, failed and led to unidentified mixtures of products.

Complexes **3d** and **4e** activated with $B(C_6F_5)_3$ (ratio 1:1) efficiently catalyze the polymerization of CHO under the aforementioned conditions (Table 2). The polymerization of CHO proceeds more slowly (polymer yield with **3d**: 57%; **4e**: 74% after 1 min) than with the cationized BOX-zinc systems, but the productivity remains consistently high (3.3 and 4.3 $\times 10^6$ $g_{polym.}\ mol_{Zn}^{-1}\ h^{-1}$). The polymers produced by **3d** and **4e** possess high molecular weights (>175 000 g mol^{-1}) with a moderately narrow polydispersity ($M_w/M_n > 2.9$). Interestingly, the multidentate *N*-donor ligands of the $B(C_6F_5)_3$-activated complexes **3d** and **4e** enhance the efficiency (I^*) of the polymerization of CHO, with an I^* corresponding to 42% and 88%, respectively ($I^* = M_n$(calculated)/M_n(measured) × 100), albeit to some extent at the expense of polymer yields. These results suggest that the "NHC" with pending hemilabile pyridine arms around the metal centers are more prone to stabilize the activated zinc species during the polymerization. Even though related cationic zinc species have previously been reported such as $[(DAD)ZnMe]^+[B(C_6F_5)_4]^-$ (DAD = diazadiene, $((2,6\text{-}iPr_2Ar)N{=}C(Me))_2$), or to a lesser extent $[(Et_2O)_3ZnX]^+[B(C_6F_5)_4]^-$ (X = Et, $N(SiMe_3)_2$) ion pairs [12,14] present nearly the same analogy with a common putative initiator as **4e**/$B(C_6F_5)_3$, it seems that the hemilabile pyridine groups in **4e** system suppress partially the ligand redistribution. However, when 2 equivalents of $B(C_6F_5)_3$ are used to activate the **4e** complex, the gain in productivity is enhanced (×1.4), but the control over ligand exchange is lost as previously observed with the BOX-systems or in these Cp-systems: $[Cp^{mes}Zn(TMEDA)]^+[EtB(C_6F_5)_3]^-$ and $Cp^{pyr}Zn(TMEDA)Et/B(C_6F_5)_3$ (Cp^{mes} = 3,5-$Me_2C_6H_3CH_2CMe_2C_5H_5$, Cp^{pyr} = *cyclo*-$C_4H_4NSiMe_2C_5H_5$, TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) [13].

The formation of poly(propylene oxide) by complex **4e** upon activation with 1 or 2 equivalents of $B(C_6F_5)_3$ was found to be negligible (≤5% yield) at room temperature. However, polymerization of PO could be achieved in moderate yield (43%) and productivity after 30 min by **3d** activated with 1 equivalent of B$(C_6F_5)_3$ at room temperature.

3. Conclusions

In summary, we have successfully prepared and structurally characterized neutral heteroleptic zinc alkyls complexes containing either bis(oxazoline), pyridinyl-functionalized NHC and its pentafluorobenzene adduct. The stabilization effect on the $B(C_6F_5)_3$-activated zinc species supported by the multidentate *N*-donor ligands operates most likely more efficiently with bulkier BOX and pyridinyl-functionalized NHC ligands, albeit not isolatable. Although the well-establish ring-opening and propagating cationic species are responsible for chain growth using the putative highly electrophilic zinc species as initiator, it seems that ligands with

hemilabile *N*-donors pendant arms are less prone to ligand redistribution and allow a better control over the molecular weights during cationic polymerization.

4. Experimental

4.1. General procedures

All operations were performed with rigorous exclusion of air and water, using standard Schlenk, high-vacuum and glovebox techniques (MB Braun MB200B-G; <1 ppm O_2, <1 ppm H_2O). Dichloromethane, hexane and toluene were purified by using *Grubbs* columns (MB Braun Solvent Purification System 800). Benzene-d_6, toluene-d_8, and chloroform-*d* (99.96% atom% D) were obtained from *Aldrich*, dried over sodium or CaH_2, vacuum transferred, degassed and filtered prior to use. 2,2′-Methylenebis[(4*S*)-4-tert-butyl-2-oxazoline] (**a**), 2,2′-methylenebis[(4*S*)-4-phenyl-2-oxazoline] (**b**), 2,2′-methylenebis[(4*R*,5*S*)-4,5-diphenyl-2-oxazoline] (**c**), ethane-1,2-diamine (99%), 2-pyridinecarboxaldehyde (99%), $NaBH_4$ (98.5%), pentafluoro-benzaldehyde (98%), triethyl orthoformate (98%), NH_4Cl (99%), acetic acid (ACS grade), anhydrous methanol (99.8%), $ZnMe_2$ (1 M solution in heptane) and $ZnEt_2$ (1 M in hexane) were purchased from *Aldrich* and used as received. Tris(pentafluorophenyl)boron was purchased from *Boulder Scientific Company* and used as received. *N*,*N*′-Bis(2-pyridylmethyl)-ethane-1,2-diamine [69] and complexes **1a**–**c** [41] were synthesized according to the literature. Cyclohexene oxide (CHO) and propylene oxide (PO) were purchased from *Aldrich* and were distilled from CaH_2 under vacuum following three freeze–pump–thaw cycles and stored at −37 °C in a glovebox.

The NMR spectra of air and moisture sensitive compounds were recorded using *J. Young* valve NMR tubes at 298 K on a *Bruker*-AVANCE-DMX400 spectrometer (5 mm BB, ^1H: 400.13 MHz; ^{13}C: 100.62 MHz) and a *Bruker*-BIOSPIN-AV500 and AV600 (5 mm BBO, ^1H: 500.13 MHz; ^{13}C: 125.77 MHz and 5 mm triple resonance inverse CryoProbe, ^1H: 600.13 MHz; ^{13}C: 150.91 MHz, respectively). ^1H and ^{13}C shifts are referenced to internal solvent resonances and reported in *parts per million* relative to TMS. IR spectra were recorded on a *Nicolet FT-IR Protégé 460* spectrometer with a DRIFT collector (Spectra-Tech™ Collector II™ from *Thermo Scientific*), and the samples were prepared in a glovebox and mixed in a KBr powder matrix before loading to the micro-cup. This cup is mounted into the well-sealed DRIFT dome (equipped with KBr windows). The spectra were averaged over 256 scans; the resolution was ±4 cm^{-1}. Elemental analyses of C, H and N were performed on an *Elementar Vario EL III*.

The molecular weights (M_n and M_w) and PDIs were determined by GPC-SEC. The chromatographic system consisted of a model GPCmax apparatus comprising isocratic pump, autosampler and degassing unit in a common housing, a model 302 TDA triple detector array detector comprising refractive index (RI), differential pressure (DP), low angle (7°) light scattering (LALS) and right angle (90°) laser light scattering (RALLS) detection with an integrated column oven all housed together and a model K-2501 UV-detector, all obtained from Viscotek (Houston, TX, USA). The sample loop permitted injection of fixed sample amounts and volumes of 100 μL of samples were injected onto the two SEC columns. For UV-detection a wavelength of 254 nm was chosen, whereas the laser wavelength for LALS- and RALS-detection was 670 nm. The volumes of the RI-, and LALS/RALLS measuring cells were 12 μl and 10 μl, respectively. The stationary phase system consisted of two ViscoGel™ GMH_{HR}-H columns (300 (L) × 7.8 mm (I.D.), 10 μm particle size, 100 Å pore size). Polystyrene PS-99K (M_w = 98,946, IV = 0.477) and PS-280K (M_w = 268,726, IV = 0.894) calibration standards for molecular weight calibration were obtained from Viscotek™ (PolyCAL TDS-PS standards). The PS-99K was used for conventional calibration and was dissolved in THF (1.153 mg mL^{-1}) and PS-280K was used as control experiment (2.458 mg mL^{-1}). Sample solutions (≈1.0 mg mL^{-1} in THF) were filtered through a syringe filter Whatmann® (0.45 μm pore size) prior to injection. Chromatographic separation of polyisoprene samples was performed at a column temperature of 40 °C with a flow-rate of 1 mL min^{-1} as well as the measurement of the RI-, UV-, LALS- and RALLS-responses. Rinsing of the sample syringe before and after injection of every sample performed with 300 μl of mobile phase.

4.2. Ligand syntheses

4.2.1. 1,3-Bis(2-pyridylmethyl)imidazolium chloride salt (**d**)

In a distillation apparatus *N*,*N*′-bis(2-pyridylmethyl)-ethane-1,2-diamine (8.44 g, 35.1 mmol) and NH_4Cl (2.00 g, 37.4 mmol) were dissolved in triethyl orthoformate (15.00 mL, 90.2 mmol) and the resulting solution stirred and heated to 110 °C until the evolution of EtOH ceased. After this time, the solvent was removed *in vacuo* to leave a brown solid, which was dissolved in CH_2Cl_2 and filtered through celite. The remaining solution was concentrated and layered with Et_2O to give colorless crystals of **d**. Yield: 8.05 g (79%). ^1H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ 9.76 (s, 1H, N–CH═N); 8.57 (dd, 2H, J = 5.0 Hz, 1.5 Hz, C_5H py); 7.74 (ddd, 2H, J = 7.8, 7.7, 1.5 Hz, C_3H py); 7.55 (dd, 2H, J = 7.7, 0.7 Hz, C_2H py); 7.30 (ddd, 2H, J = 7.8, 5.0, 0.7 Hz, C_4H py); 4.99 (s, 4H, N–CH_2-py); 4.01 (s, 4H, N–CH_2–CH_2–N). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 25 °C): δ 160.0 (s, N–CH═N); 152.4 (C_2 py); 149.5 (C_6 py); 137.2 (C_4 py); 123.3, 123.0 (C_3 py, C_5 py); 52.6 (s, N–CH_2-py), 48.6 (s, N–CH2–CH_2–N). Anal. Calcd for $C_{15}H_{17}ClN_4$ (288.78): C, 62.39; H, 5.93; N, 19.40%. Found: C, 61.17; H, 3.95; N, 12.57%.

4.2.2. 2-(2,3,4,5,6-Pentafluorophenyl)-1,3-bis(2-pyridylmethyl) imidazolidine (**e**)

N,*N*′-Bis(2-pyridylmethyl)-ethane-1,2-diamine (1.50 g, 6.28 mmol) and pentafluoro-benzaldehyde (1.23 g, 6.28 mmol) were dissolved in 2 mL of acetic acid and stirred at room temperature for 4 h. The solvent was removed *in vacuo* and the remaining solid was neutralized with an aqueous solution of Na_2CO_3. The aqueous solution was then extracted with CH_2Cl_2 and dried over $MgSO_4$. The volatiles were removed *in vacuo* to leave a brown oil. Yield: 1.72 g (65%). ^1H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ 8.41 (d, 2H, J = 5.0 Hz, C_6H py); 7.54 (dt, 2H, J = 7.6, 1.5, C_3H py); 7.29 (d, 2H, J = 7.6 Hz, C_4H py); 7.06 (dd, 2H, J = 7.6, 5.0 Hz, C_5H py); 4.81 (s, 1H, CH(C_6F_5)); 3.87 (d, 2H, J = 14.0 Hz, N–CH_aH_b-py); 3.81 (d, 2H, J = 14.0 Hz, N–CH_aH_b-py); 3.33 (ddd, 2H, J = 14.8 Hz, J = 9.6 Hz, J = 9.4 Hz, N–$CH_{a1}H_{b1}$–$CH_{a2}H_{b2}$–N); 2.80 (ddd, 2H, J = 14.8 Hz, J = 9.6 Hz, J = 9.4 Hz, N–$CH_{a1}H_{b1}$–$CH_{a2}H_{b2}$–N) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 25 °C): δ 158.8 (C_2 py); 149.1 (C_6 py); 136.5 (C_4 py); 122.6, 122.2 (C_3 py, C_5 py); 79.1 (CH–C_6F_5); 59.6 (N–CH_2-py); 52.0 (N–CH2–CH_2–N) ppm. IR (KBr, ν/cm^{-1}): 3083vw, 3062w, 3010w, 2932w, 2880w, 2824m, 2775vw, 1676m, 1651m, 1590s, 1570m, 1520vs, 1504vs, 1475s, 1433s, 1387m, 1337m, 1303m, 1252w, 1219w, 1148m, 1129m, 1046w, 997s, 960m, 944m, 893w, 880w, 836vw, 762s, 683w, 646vw, 623vw, 606vw, 577vw, 489vw, 466vw, 409w. Anal. Calcd for $C_{21}H_{17}F_5N_4$ (420.38): C, 60.00; H, 4.08; F, 22.60; N, 13.33%. Found: C, 61.17; H, 3.95; N, 12.57%.

4.3. Complexes syntheses

4.3.1. (^{tBu}BOX)ZnMe (**2a**)

To a solution of $ZnMe_2$ (0.38 mL of a 1 M solution in heptane, 0.38 mmol) in hexane (5 mL) was added a solution of (^{tBu,H}BOX)H (100 mg, 0.38 mmol) in hexane (10 mL). The colorless solution was stirred at ambient temperature for 5 h. The reaction mixture was dried *in vacuo* producing a white solid. The white solid was

solubilized in 5 mL toluene, filtered and concentrated to *ca.* 1 mL. Colorless crystals of **2a** were isolated at −37 °C after 3 days. Yield: 124.6 mg (96%). ^{1}H NMR (400.13 MHz, C_6D_6, 25 °C): δ 4.74 (s, 1H, HC_1); 3.87 (dd, 2H, J = 8.5, 3.3 Hz, H_aC_5); 3.64 (t, 2H, J = 8.5 Hz, HC_4); 3.38 (dd, 2H, J = 8.5, 3.3 Hz, H_bC_5); 0.72 (s, 18 H, C−$(CH_3)_3$); −0.11 (s, 3H, Zn−CH_3) ppm. ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 25 °C): δ 174.0 (C_2); 72.3 (C_4); 68.9 (C_5); 57.2 (C_1); 35.1 (C−$(CH_3)_3$), 26.4 (C−$(CH_3)_3$), −10.5 (Zn−CH_3) ppm. IR (KBr, ν/cm^{-1}): 3139vw, 3002w, 2952s, 2905m, 2886m, 2871m, 2844w, 1602s, 1552vs, 1469m, 1452m, 1394w, 1364w, 1346w, 1326w, 1329w, 1269w, 1233m, 1212w, 1197vw, 1155w, 1089s, 1054m, 1024m, 995m, 980w, 952vw, 932vw, 851vw, 825vw, 779w, 759w, 745m, 726vw, 713vw, 657m, 549m, 518vw, 479vw, 404vw. Anal. Calcd for $C_{16}H_{28}N_2O_2Zn$ (345.8): C, 55.57; H, 8.16; N, 8.10; O, 9.25; Zn, 18.91. Found: C, 55.30; H, 7.49; N, 7.96.

4.3.2. (NHC)ZnEt(Cl) (**3d**)

To a solution of 1,3-bis(2-pyridylmethyl)imidazolinium chloride (**d**) (100 mg, 0.34 mmol) in toluene (10 mL) was added a solution of $ZnEt_2$ (0.34 mL of a 1 M solution in hexane, 0.34 mmol). The orange dark solution was stirred at ambient temperature overnight. The reaction mixture was filtered and dried *in vacuo*, leading to a yellow-orange powder. Yield: 80 mg (60%). ^{1}H NMR (400.13 MHz, C_6D_6, 25 °C): δ 8.65 (d, 2H, J = 4.6 Hz, C_6H py); 7.16 (d, 2H, J = 7.7 Hz, C_4H py); 7.04 (dt, 2H, J = 7.7, 0.8 Hz, C_3H py); 6.59 (dd, 2H, J = 7.7, 6.2 Hz, C_5H py); 4.48 (s, 4H, N−CH_2-py); 2.75 (s, 4H, N−CH_2−CH_2−N); 1.85 (sb, 3H, Zn−CH_2CH_3); 0.79 (sb, 2H, Zn−CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (150.91 MHz, C_6D_6, 25 °C): δ 206.7 (N−C−N); 155.8 (C_2 py); 149.9 (C_6 py); 137.8 (C_4 py); 123.6, 123.3 (C_3 py, C_5 py); 53.3 (N−CH_2-py); 50.2 (N−CH2−CH_2−N); 14.6 (Zn−CH_2CH_3), 0.9 (Zn−CH_2CH_3) ppm. IR (KBr, ν/cm^{-1}): 3060w, 3024w, 3008w, 2922s, 2879s, 2844s, 2802m, 2709vw, 2278vw, 1671w, 1600s, 1571s, 1511vs, 1476s, 1461m, 1438s, 1359m, 1328vw, 1265m, 1224m, 1179w, 1154w, 1132vw, 1098vw, 1052m, 1017m, 994m, 958vw, 906w, 839vw, 811vw, 761m, 695vw, 660w, 640vw, 601m, 542vw, 502m, 466vw, 427w, 418w, 402w. Anal. Calcd for $C_{17}H_{22}ClN_4Zn$ (383.23): C, 53.28; H, 5.79; Cl, 9.25; N, 14.62; Zn, 17.06%. Found: C, 53.58; H, 5.8; N, 14.23%.

4.3.3. (NHC−C_6F_5(H))$ZnEt_2$ (**4e**)

To a solution of $ZnEt_2$ (0.59 mL of a 1 M solution in hexane, 0.59 mmol) in toluene (5 mL) was added a solution of 2-(2,3,4,5,6-pentafluorophenyl)-1,3-bis(2-pyridylmethyl)imidazolidine (**e**) (250 mg, 0.59 mmol) in toluene (10 mL). The dark orange solution was stirred at ambient temperature overnight. The reaction mixture was dried *in vacuo*, yielding a brown oil. Yield: 320 mg (91%). ^{1}H NMR (400.13 MHz, C_6D_6, 25 °C): δ 8.21 (d, 2H, J = 4.7 Hz, C_6H py); 6.86 (dt, 2H, J = 7.8, 1.5, C_3H py); 6.68 (d, 2H, J = 7.8 Hz, C_4H py); 6.46 (dd, 2H, J = 7.8, 4.7 Hz, C_5H py); 5.14 (s, 1H, CH(C_6F_5)); 3.81 (d, 2H, J = 14.4 Hz, N−CH_aH_b-py); 3.57 (d, 2H, J = 14.4 Hz, N−CH_aH_b-py); 3.00 (ddd, 2H, J = 14.4 Hz, J = 9.2 Hz, J = 8.4 Hz, N−$CH_{a1}H_{b1}$−$CH_{a2}H_{b2}$−N); 2.67 (ddd, 2H, J = 14.4 Hz, J = 9.2 Hz, J = 8.4 Hz, N−$CH_{a1}H_{b1}$−$CH_{a2}H_{b2}$−N), 1.57 (t, 3H, J = 7.9 Hz, Zn−CH_2CH_3); 0.39 (q, 2H, J = 7.9 Hz, Zn−CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 25 °C): δ 158.0 (C_2 py); 149.3 (C_6 py); 136.9 (C_4 py); 122.9, 122.8 (C_3 py, C_5 py); 78.2 (CH−C_6F_5); 59.2 (N−CH_2-py); 52.5 (N−CH2−CH_2−N); 13.9 (Zn−CH_2CH_3), 3.5 (Zn−CH_2CH_3) ppm. IR (KBr, ν/cm^{-1}): 3081vw, 3061w, 3008w, 2961w, 2927w, 2879w, 2823w, 2719vw, 1676w, 1651w, 1587s, 1569m, 1520s, 1502vs, 1475s, 1433s, 1392m, 1367m, 1347m, 1303w, 1288w, 1262vw, 1212vw, 1140w, 1134w, 1093vw, 1046vw, 1026w, 1000s, 946w, 893vw, 880vw, 841vw, 802vw, 795vw, 759m, 690vw, 659vw, 635vw, 623vw, 408w. Anal. Calcd for $C_{25}H_{27}F_5N_4Zn$ (543.14): C, 55.21; H, 5.00; F, 17.47; N, 10.30; Zn, 12.02%. Found: C, 55.58; H, 6.8; N, 10.23%.

4.4. Representative procedure for the ring-opening polymerization of epoxides

An oven-dried glass vial was loaded with a solution of precursor (21.2 μmol) in toluene (5 mL) followed by the addition of a solution of $B(C_6F_5)_3$ (1 equivalent, 21.2 μmol) in toluene (1 mL). This was allowed to stir for 15 min at room temperature. 2.14 mL of CHO or 1.48 mL of PO (21.2 mmol) was added to the freshly-made active catalyst and stirred at 30 °C, for the time indicated in Tables 1 and 2. *Caution*: the reaction is extremely exothermic when CHO is added (>100 °C). The reaction mixture was quenched with 1 mL of anhydrous methanol in a glovebox followed by an extra addition of methanol (20 mL) outside the glovebox to precipitate the polymer. The product was then dried *in vacuo* to a constant weight. The polymer yield was determined gravimetrically. All polymers showed an atatic microstructure determined by ^{1}H/^{13}C NMR [70].

4.5. X-ray crystallography and crystal structure determination

A crystal was selected in a glovebox and mounted inside a nylon loop containing Paratone-N cryoprotectant oil (*Hampton Research*). Raw data were absorption corrected using the SADABS multiscan method. Structure solution was performed by direct methods and model refinement using programs contained in the Bruker AXS APEX2 package [71]. Crystal data: for **2a**: from toluene. $C_{16}H_{28}N_2O_2Zn$, M = 345.77, tetragonal, space group $P4_12_12$ (No.92), a = b = 12.1279(5), c = 23.4565(10) Å, V = 3450.1(2) Å^3, Z = 8, ρ_{calc} = 1.331 g cm^{-3}, F(000) = 1472, μ(Mo-K$_\alpha$) = 1.430 mm^{-1}, λ = 0.71073 Å, T = 101(2) K. The 57,620 reflections measured on a Bruker AXS APEXII Ultra CCD area detector system yielded 5072 unique data (θ_{max} = 30.08°, R_{int} = 0.0347) [4963 observed reflections $I > 2\sigma(I)$]. R_1 = 0.0172, wR_2 = 0.0483. Crystal data: for **d**: from CH_2Cl_2/Et_2O layer. $C_{15}H_{17}ClN_4$, M = 288.78, monoclinic, space group $P2_1/n$ (No. 14), a = 8.3324(3), b = 19.0521(6), c = 9.8245(3) Å, β = 112.87°, V = 1437.00(8) Å^3, Z = 4, ρ_{calc} = 1.335 g cm^{-3}, F(000) = 608, μ(Mo-K$_\alpha$) = 0.262 mm^{-1}, λ = 0.71073 Å, T = 123(2) K. The 24,233 reflections measured on a Bruker AXS APEXII Ultra CCD area detector system yielded 4377 unique data (θ_{max} = 30.50°, R_{int} = 0.0327) [4111 observed reflections $I > 2\sigma(I)$]. R_1 = 0.0420, wR_2 = 0.1158.

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Appendix A. Supplementary material

CCDC 799049 (**2a**) and CCDC 799050 (**d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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