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Synthesis and catalytic activity of three-coordinate zinc cations

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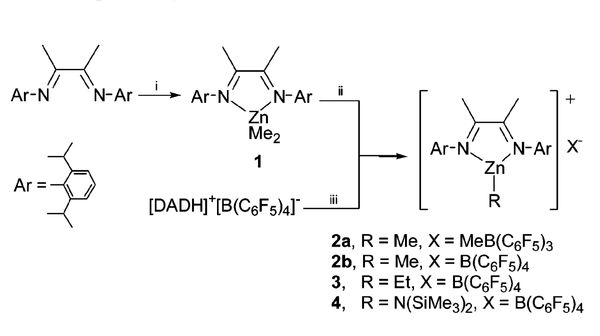
Reaction between DADZnR$_2$ and either B(C$_6$F$_5$)$_3$ or ZnR$_2$ and [DADH][B(C$_6$F$_5$)$_4$] affords three-coordinate alkyl and amide zinc cations which are active for the ring opening polymerisation of epoxides and ε-caprolactone [DAD = (MeC=NC$_6$H$_3$Pr$^i_2$-2,6)$_2$].

Zinc complexes of sterically hindered ligands have attracted considerable attention in recent years as catalysts for the formation of polyesters. For example, zinc aryloxides,[1–3] carboxylates[4,5] and bulky diketiminato complexes[6] catalyse the alternating copolymerisation of cyclohexene oxide with carbon dioxide to give polycarbonates. Coates *et al.* and Chisholm *et al.* found a number of diketiminato,[7,8] tris(pyrazolato)borate[9] and iminophenolato[10] complexes that were highly active catalysts for the ring-opening polymerisation of lactides but were found to be unreactive towards the homopolymerisation of propene oxide (PO) and even cyclohexene oxide (CHO). We report here the synthesis of cationic three-coordinate zinc complexes that are suitable for the homopolymerisation of epoxides and lactones.

The addition of the diazadiene ligand (MeC=NC$_6$H$_3$Pr$^i_2$-2,6)$_2$ (DAD) to a solution of ZnMe$_2$ in light petroleum affords the complex ZnMe$_2$(DAD) **1** as a deep orange precipitate. This adduct is susceptible to dissociation under vacuum.[11] Treatment of a solution of **1** in hexanes with B(C$_6$F$_3$)$_3$ in a 1 : 1 ratio at 0 °C generates [ZnMe(DAD)]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ **2a** as an orange solid.† Alkyl/C$_6$F$_5$ exchange, as seen in the reaction of zinc alkyls with B(C$_6$F$_5$)$_3$ in the absence of donor ligands,[12] is not observed. Alternatively, the alkyl and amido zinc cations are readily prepared by the reaction of [DADH]$^+$[B(C$_6$F$_5$)$_4$]$^-$ with ZnR$_2$ [R = Me, Et, N(SiMe$_3$)$_2$] to give the [B(C$_6$F$_5$)$_4$]$^-$ salts **2b**, **3** and **4**, respectively (Scheme 1).



Scheme 1 Reagents and conditions: i, hexanes, ZnMe$_2$ 0 °C; ii, B(C$_6$F$_5$)$_3$, hexanes, 2 h, 23 °C; iii, ZnR$_2$, dichloromethane, 30 min, 23 °C.

The ^{1}H and ^{11}B NMR spectra of **2a** show singlets at δ 0.45 and −11.9, respectively, indicative of a non-coordinated [MeB(C$_6$F$_5$)$_3$]$^-$ anion. This is confirmed by the ^{19}F NMR data.[13] The metal centre is therefore three-coordinate, even in the case of the [MeB(C$_6$F$_5$)$_3$]$^-$ anion which is well-known for its tendency to give methyl-bridged zwitterions. In spite of the steric hindrance of the DAD ligand the cation in **2a** is still very reactive, and in solutions containing an excess of **1** rapid exchange of all methyl ligands is observed. There was no indication for the formation of the methyl-bridged binuclear cation [{(DAD)ZnMe}$_2$(μ-Me)]$^+$, even at −80 °C.

The X-ray crystal structure of **2b** confirmed the trigonal-planar coordination geometry of the metal centre (angle sum 359.6°) (Fig. 1). ‡ The Zn–N distances of, on average, 2.040(2) Å are longer than those of the neutral diketiminato complexes {HC(MeC=NAr)$_2$}ZnX (X = NPr$^i_2$, OBu^t),[7,8] while the N(1)–Zn–N(2) angle is more acute, 80.10(8)°. Although a number of three-coordinate neutral and anionic zinc alkyl complexes are known,[14,15] complex **2a** appears to be the first structurally characterised example of a cationic zinc centre with such a low coordination number.[16,17]

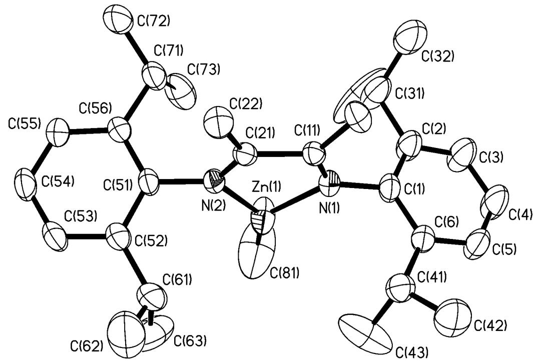


Fig. 1 Structure of the [ZnMe(DAD)]$^+$ cation with thermal ellipsoids at 50% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn–C(81) 1.914(4), Zn–N(1) 2.035(2), Zn–N(2) 2.045(2), N(1)–C(11) 1.286(3), N(1)–C(1) 1.458(3); C(81)–Zn–N(1) 136.3(2), C(81)–Zn–N(2) 143.2(2), N(1)–Zn–N(2) 80.10(8).

Complexes **2** catalyse the polymerisation of epoxides and ε-caprolactone under mild conditions. The exotherm of the rapid polymerisation of CHO was moderated by dilution with toluene and ice bath cooling. The polymer molecular weight increases with time, with a polydispersity of about 2 (Table 1). Activities increase with time due to the rise in temperature; there is no induction period.

The polymerisation of PO proceeds more slowly, producing polymers with molecular weights of 30–40000 g mol^{-1}, regardless of reaction time (Table 2).

The polymerisation of ε-caprolactone at room temperature was slow but accelerated on heating to 60 °C. The resulting polymer gave M_w values of up to 40000, with polydispersities close to 1 (Table 3). Methyl methacrylate was slowly polymerised at 25 °C to give polymer with 70% syndiotacticity.

This high catalytic activity, compared to neutral zinc complexes, is no doubt due to the increased Lewis acidity of the cationic metal centre. Zinc dialkyls activated with water or alcohols are known to polymerise epoxides, most probably *via* a coordinated anionic mechanism.[18] Investigations on the polymerisation mechanism of these cationic systems are currently the subject of further studies.

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Table 1 Polymerisation of cyclohexene oxide with complex **2b**[a]

Time/min	Conversion (%)	Activity/kg mol^{-1} h^{-1}	M_w	M_w/M_n
0.5	2.6	3036	53000	4.1
1	10.8	6361	69000	2.0
1.5	22.3	8771	97000	1.5
2	28.7	8493	113000	2.3
2.5	39.0	9224	117000	1.9
3	44.9	8843	119000	1.5
3.5	48.7	8220	145000	1.9
4	49.0	7247	—	—
4.5	50.9	6683	163000	2.3
5	54.3	6419	177000	1.8

[a] Conditions: CHO (CHO : Zn = 10000 : 1) was injected into a stirred suspension of 10 µmol of **2b** in 50.5 mL toluene precooled to 0 °C. 2.5 mL aliquots were removed every 30 s and quenched with HCl–MeOH to precipitate the polymer.

Table 2 Polymerisation of propylene oxide with complex **2b**[a]

Time/h	Conversion (%)	Activity/kg mol^{-1} h^{-1}	M_w	M_w/M_n
1	0.8	4.76	33000	6.4
7	23.4	19.41	38000	4.0
24	51.6	12.49	35000	1.9
72	73.3	5.92	29000	1.9

[a] Conditions: 25 µmol of **2b** was stirred with 10000 equiv. of propylene oxide at 23 °C. Aliquots of 2.5 mL were removed at the times shown and quenched in methanol.

Table 3 Polymerisation of ε-caprolactone with complex **2b**[a]

Time/min	Conversion (%)	Activity/kg mol^{-1} h^{-1}	M_w	M_w/M_n
30	4.4	10.1	23000	2.0
45	9.9	15.1	38000	1.1
60	12.7	14.7	40000	1.1

[a] Conditions: 93.5 µmol of **2b** was stirred in 40 mL toluene at 60 °C. 10 mL of ε-caprolactone was injected. 5 mL aliquots were removed at times shown and quenched in HCl–MeOH to precipitate the polymer.

Notes and references

† Synthesis and spectroscopic data: **2a**: To a stirred solution of DAD (1.25 g, 3.1 mmol) in 25 mL hexanes at 0 °C was injected $ZnMe_2$ (1.54 mL of a 2 M solution in hexanes, 3.08 mmol) followed by $B(C_6F_5)_3$ (1.58 g, 3.1 mmol, in 25 mL hexanes) to give a pale orange suspension. After stirring for 2 h, the solid was filtered off, washed with hexanes and dried to give an orange powder (2.42 g, 2.39 mmol, 77%). ^{1}H NMR (CD_2Cl_2, 20 °C, 300.13 MHz): δ 7.5–7.3 (m, 6 H, Ar-*H*), 2.50 (s, 6 H, N=CC*H*$_3$), 2.45 (sept, 4 H, J = 6.8 Hz, MeC*H*Me), 1.26 (d, 12 H, J = 6.8 Hz, C*H*$_3$CHC*H*$_3$), 1.20 (d, 12 H, J = 6.8 Hz, C*H*$_3$CHC*H*$_3$), 0.45 (br s, 3H, BMe), −0.38 (s, 3H, ZnMe). ^{13}C NMR (CD_2Cl_2, 20 °C, 75.48 MHz): δ 175.0 (C=N), 138.3 (*o*-C), 137.7 (*ipso*-C), 130.1 (*p*-C), 125.6 (*m*-C), 30.2 (Me$_2$*C*H), 24.2 (*Me*$_2$CH), 22.8 (*Me*$_2$CH), 19.9 (N=C*C*H$_3$), −14.6 (ZnMe). ^{11}B NMR (CD_2Cl_2, 20 °C, 96.29 MHz): δ −11.9. ^{19}F NMR (CD_2Cl_2, 20 °C, 282.4 MHz): δ −133.52 (d, 6 F, J = 12.8 Hz, *o*-F), −165.54 (t, 3 F, J = 20.6 Hz, *p*-F), −168.22 (t, 6 F, J = 20.6 Hz, *m*-F). Anal. calc. for $C_{48}H_{46}BF_{15}N_2Zn$: C, 56.97; H, 4.58; N, 2.77. Found: C, 56.30; H, 4.50; N, 2.65%.

2b. From $ZnMe_2$ (3.5 mmol) and $[DADH]^+[B(C_6F_5)_4]^-$ (3.65 g, 3.37 mmol) in 75 mL dichloromethane at room temperature. Workup as for **2a** afforded **2b** as a fine orange powder (3.8 g, 32.3 mmol, 97%). Crystals suitable for X-ray analysis were grown from dichloromethane at −26 °C. ^{1}H NMR (CD_2Cl_2, 20 °C, 300.13 MHz): δ −0.37 (s, 3 H, ZnMe). ^{13}C NMR (CD_2Cl_2, 20 °C, 75.48 MHz): δ −14.6 (ZnMe). ^{11}B NMR (CD_2Cl_2, 20 °C, 96.29 MHz): δ −13.7. ^{19}F NMR (CD_2Cl_2, 20 °C, 282.4 MHz): δ −133.51 (br d, 8 F, *o*-F), −164.06 (t, 4 F, J = 20.6 Hz, *p*-F), −167.96 (br t, 8 F, J = 20.6 Hz, *m*-F). (DAD resonances are essentially identical to **2a** and are omitted here). Anal. calc. for $C_{53}H_{43}BF_{20}N_2Zn$: C, 54.68; H, 3.72; N, 2.41. Found: C, 54.46; H, 3.67; N, 2.35%.

3: Preparation analogous to **2b**. Yield 0.58 g (0.49 mmol, 74%). ^{1}H NMR (CD_2Cl_2, 20 °C, 300.13 MHz): δ 0.86 (t, 3 H, J = 8.0 Hz, Zn–CH$_2$C*H*$_3$), 0.54 (q, 2 H, J = 8.0 Hz, Zn–C*H*$_2$CH$_3$). ^{13}C NMR (CD_2Cl_2, 20 °C, 75.48 MHz): δ 10.8 (Zn–CH$_2$*C*H$_3$) 0.88 (Zn–*C*H$_2$CH$_3$). (DAD and borate resonances omitted). Anal. calc. for $C_{54}H_{45}BF_{20}N_2Zn$: C, 55.05; H, 3.85; N, 2.38. Found: C, 53.72; H, 3.82; N, 2.20%.

4: Preparation analogous to **2b**. Yield 3.8 g (32.3 mmol, 97%). ^{1}H NMR (CD_2Cl_2, 20 °C, 300.13 MHz): δ −0.20 (s, 18 H, SiMe$_3$). ^{13}C NMR (CD_2Cl_2, 20 °C, 75.48 MHz): δ 5.0 (s, 18 H, SiMe$_3$). (DAD and borate resonances omitted). Anal. calc. for $C_{58}H_{58}BF_{20}N_3Si_2Zn$: C, 53.20; H, 4.46; N, 3.21. Found: C, 52.47; H, 4.45; N, 3.05%.

‡ Crystal data for **2b**: $C_{53}H_{43}BF_{20}N_2Zn$, M = 1164.1, monoclinic, space group $P2_1/n$ (no. 14), a = 16.234(3), b = 19.980(4), c = 17.443(4) Å, β = 112.81(3)°, V = 5215(2) Å^3, Z = 4, D_c = 1.483 g cm^{-3}, $F(000)$ = 2360, T = 140(1) K, μ(Mo-Kα) = 5.8 cm^{-1}, λ(Mo-Kα) = 0.71069 Å, 15871 reflections measured, 8851 unique (R_{int} = 0.028), F^2 refinement, R_1 = 0.0417 [$I > 2\sigma(I)$], wR_2 = 0.115 (all data). CCDC reference number 186246. See http://www.rsc.org/suppdata/dt/b2/b208165m/ for crystallographic data in CIF or other electronic format.

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