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Cationic and charge-neutral calcium tetrahydroborate complexes and their use in the controlled ring-opening polymerisation of *rac*-lactide[†]

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The first cationic main group tetrahydroborate complexes are reported. $[Ca(BH_4)(THF)_5][BPh_4]$ and the charge neutral $(Tp'^{Bu,Me})Ca(BH_4)(THF)$ are initiators for the living ring opening polymerization of *rac*-lactide, the latter producing PLA with high levels of heterotactic enrichment. These represent a new class of ROP initiators for main group metals.

The last decade has witnessed an exponential increase in activity in the synthesis, structures, reactivity and catalytic applications of compounds of the heavier alkaline earth (Ae) metals.¹ Most of this research has centered on calcium, the ionic radius of which is very similar to that of ytterbium, and which is abundant, non-toxic and inexpensive. Nonetheless, both the general solution chemistry and catalytic applications of this element remain considerably underdeveloped.

The ring-opening polymerization (ROP) of cyclic esters such as ε -caprolactone (ε -CL) and lactide (LA) towards biocompatible and biodegradable polymers is an area of considerable current interest.² Although calcium's lighter congener, Mg, and the lanthanides are highly developed for ROP, only a handful of well-defined, heteroleptic initiators of the type (L)Ca–X (X = amide or aryloxide) have been reported.^{3,4}

In the last 5–8 years lanthanide tetrahydroborates,⁵ either as "ligand-free" $Ln(BH_4)_3(THF)_x^6$ or heteroleptic (L)Ln(BH₄) systems,⁷ have become well-established as effective initiators for the polymerisation of a range of cyclic esters and other monomers. However, no main group borohydride has been established in this regard.⁵ Furthermore, in terms of both initiating efficiency and molecular weight control, (L)Ln–BH₄ systems are better controlled than the corresponding amides, (L)Ln–NR₂,^{7a} and comparable to alkoxides, (L)Ln–OR.^{6c} Drawing upon the potential parallels with the lanthanides, we set out to develop calcium tetrahydroborate complexes as a new class of main group initiators for the ROP of *rac*-LA.

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Initial studies using commercially available Ca(BH₄)₂(THF)₂ and ε-CL or rac-LA in THF gave disappointing performances, in contrast to the well-controlled trivalent Ln(BH₄)₃(THF)₃ systems (La = Ln, Sm, Nd).⁶ However, bearing in mind very recent reports of mono- and di-cationic ROP initiators, 4a,8,9 we carried out the reaction of Ca(BH₄)₂(THF)₂ with [Et₃NH][BPh₄] in THF at -78 °C. This gave [Ca(BH₄)(THF)₅][BPh₄] (1-BPh₄) in 51% recrystallized yield (Scheme 1).† As discussed below, 1-BPh₄ is an effective initiator for the ROP of rac-LA. The ¹H NMR spectrum of **1–BPh₄** shows a 1 : 1 : 1 : 1 guartet at -0.19 ppm for the BH₄ ligand (${}^{1}J_{1H^{11}B} = 82$ Hz) which appears at -36.1 ppm in the ¹¹B NMR spectrum. The IR spectrum is consistent with a κ^3 bound BH₄ ligand.^{5f} Recalling the recently reported successful dicationic yttrium ROP initiator $[(Tpm)Y(O^{i}Pr)(THF)_{3}]^{2+}$,^{8b} we treated **1–BPh₄** with HC(3,5- Me_2pz_3 (Tpm) in dichloromethane at -78 °C which gave 2-BPh₄ in 74% yield. The Tpm-supported half-sandwich cation $[(Tpm)Ca(BH_4)(THF)_2]^+$ (2⁺) also possesses a κ^3 bound BH₄ ligand (δ (¹H) = 0.15 ppm (¹J_{1H¹¹B} = 82 Hz); $\delta(^{11}B) = -35.6$ ppm in CD₂Cl₂). ¹H and ¹¹B NMR showed that 2^+ does not undergo redistribution (e.g. to [(Tpm)₂Ca]²⁺ and Ca(BH₄)₂(THF)₂) in THF-d₈ at RT or 70 °C.

The solid state structures of the tetrahydroborate cations $[Ca(BH_4)(THF)_5]^+$ (1⁺) and $[(Tpm)Ca(BH_4)(THF)_2]^+$ (2⁺)



Scheme 1 Synthesis of new calcium tetrahydroborate complexes. $[BPh_4]^-$ anions are omitted for 1^+ and 2^+ .

[†] Electronic supplementary information (ESI) available: 1st order plot for consumption of *rac*-LA using **1–BPh**₄; additional plots of M_n vs. *rac*-LA converted using **1–BPh**₄, **2–BPh**₄ and **3**; experimental and characterising data; CIF data for **1–BPh**₄ and **2–BPh**₄. CCDC 796412–796413. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc04348f



Fig. 1 Molecular structures of $[Ca(BH_4)(THF)_5]^+$ (1⁺, left) and $[(Tpm)Ca(BH_4)(THF)_2]^+$ (2⁺, right). The H atoms of the κ^3 -BH₄ ligands were located from Fourier difference maps and positionally and isotropically refined. C-bound H atoms omitted.

are shown in Fig. 1. The only previously structurally characterized calcium tetrahydroborate compounds are Ca(BH₄)₂(dme)₂ and Ca₂(BH₄)₂(diglyme)₂.¹⁰ A number of cationic tetrahydroborate compounds have been reported for the d- and f-block elements.^{8*b*,9,11} However, although the anionic complexes [Zn(BH₄)₃]⁻ and [Al(BH₄)₄]⁻ are known (having κ^2 -BH₄ ligands),¹² no cationic tetrahydroborate complexes have yet been described for any main group element. Fully-authenticated cationic main group hydrides of the type [(L)MH₂]⁺ are also few in number, and are established only for M = Al and Ga.¹³

1–BPh₄ rapidly polymerized 200 equivs ε -CL to 100% conversion within 2 min at RT in THF giving α, ω -dihydroxy telechelic PCL of the form HO(CH₂)₅C(O)–[PCL]–O(CH₂)₆OH as determined by ¹H NMR spectroscopy and MALDI-ToF-MS analysis. The formation of α, ω -dihydroxy telechelic PCL is a particular characteristic of (L)Ln(BH₄)-initiated ε -CL ROP and the mechanism of formation has been studied in detail.^{7a,b,d} The formation of dihydroxy PCL with **1–BPh₄** is consistent with an analogous mechanism.

Very good agreement between measured and predicted $M_{\rm n}$ was found for the ROP of rac-LA with 1-BPh₄. Polymerization at 70 °C in THF over 3-5 hours gave PLA with number-average molecular weights up to $35\,000$ g mol⁻¹. Consumption of rac-LA followed well-behaved 1st order kinetics and gave linear M_n (GPC) vs. % conversion plots (see the ESI[†]). Fig. 2 (top) shows a plot of M_n vs. equivs rac-LA converted for $[rac-LA]_0$: $[1-BPh_4]_0$ ratios between 50 and 300. The gradient of the best-fit line was 152(3) g mol⁻¹ (equivs converted)⁻¹ ($R^2 = 0.998$) in excellent agreement with that predicted (144.1) for one PLA chain growing per Ca-BH₄ group of 1^+ in a living-type fashion. MALDI-ToF-MS analysis indicated the formation of dihydroxy-terminated HOCH(Me)C(O)-[PLA]-OCH(Me)CH2OH, again consistent with the previously studied coordination-insertion mechanisms with (L)Ln(BH₄) systems.^{6,7} When L-LA was used as a monomer ($[L-LA]_0$: $[1-BPh_4]_0 = 50$) no epimerization occurred according to NMR analysis, and only SSSS (iii) tetrad sequences were detected. While Fig. 2 (top) is consistent with living-type behavior, the M_w/M_n values for the PLAs were ca. 1.4. This is attributed to concomitant intermolecular transesterification processes.

The slow ROP of rac-LA with 1-BPh₄ was alleviated by using 2-BPh₄, the Tpm ligand providing a better-defined coordination environment, and perhaps guarding against binuclear or extensively LA chain chelated resting states. Thus up to 250 equivs rac-LA could be converted at RT within 2 hours with M_w/M_n values between 1.2 and 1.4. The gradient of the best-fit line was 157(11) g mol⁻¹ (equivs $(converted)^{-1}$ in excellent agreement with that predicted (144.1) for one PLA chain (see the ESI[†]), but in general the $M_{\rm n}$ values were a little higher than expected (e.g. 43 200 g mol⁻ (GPC) vs. $32\,800$ g mol⁻¹ (predicted) for [rac-LA]₀: $[2-BPh_4]_0 = 250$). Nonetheless, it is clear that the slow rac-LA ROP rates typically associated with cationic initiators^{4a,8b} can be alleviated with the appropriate supporting ligand, thus offering considerable potential for further development.¹⁴

The PLAs formed with **1–BPh₄** and **2–BPh₄** were atactic. However, it is known that use of bulkier ancillary ligands can induce tacticity through chain-end control. Drawing upon Chisholm's reports on $(Tp'^{Bu})Ca(X)(THF)$ ($X = N(SiMe_3)_2$ or O-2,6-C₆H₃ⁱPr₂)^{3c} we turned to the bulky tris(pyrazolyl)hydroborate complex $(Tp'^{Bu,Me})Ca(BH_4)(THF)$ (**3**, Scheme 1) which is readily prepared at RT directly from Ca(BH₄)₂(THF)₂ and KTp'^{Bu,Me} in 65% recrystallized yield. The IR and NMR data for formally zwitterionic **3** are consistent with the structure proposed in Scheme 1 which is analogous to that of cationic **2**⁺ and Sella and Takats' recently reported $(Tp'^{Bu,Me})Yb(BH_4)(THF).^{15}$



Fig. 2 M_n (as measured by GPC) *vs.* equivs *rac*-LA converted using $[Ca(BH_4)(THF)_5][BPh_4]$ (**1–BPh**_4, top) and $(Tp^{^{f}Bu,Mc})Ca(BH_4)(THF)$ (**3**, bottom). The gradient of the fitted lines ($R^2 = 0.998$ in each case) are 152(3) and 162(4) g mol⁻¹ for **1–BPh**_4 and **3**, respectively (expected 144.1 g mol⁻¹), with an intercept of $M_n = 0$. Conditions for **1–BPh**_4: THF, 70 °C, 3 or 5 h, [*rac*-LA]_0 : [**1–BPh**_4]_0 = 50, 100, 150, 200, 250, 300; for **3**: THF, -20 °C, 5 min, [*rac*-LA]_0 : [**3**]_0 = 40, 100, 120, 160, 200.

A benchmarking experiment of 3 with ε -CL again gave efficient conversion of 200 equivs to α, ω -dihydroxy telechelic PCL within 10 minutes. The molecular weight control achieved with **3** $(M_n \text{ (GPC)} = 17600 \text{ g mol}^{-1}; M_w/M_n = 1.3; M_n$ (calcd) = 22 820 g mol⁻¹) was better than with **1–BPh₄** under analogous conditions (M_n (GPC) = 39200 g mol⁻¹; $M_{\rm w}/M_{\rm n} = 1.3$; $M_{\rm n}$ (calcd) = 22820 g mol⁻¹). Gratifyingly, 3 is also a very efficient initiator for the ROP of rac-LA either at RT or -20 °C. For example, with $[rac-LA]_0$: $[3]_0 =$ 200, >90% conversion was achieved within 5 min at both temperatures. Fig. 2 (bottom) shows a plot of experimental $M_{\rm p}$ vs. equivs rac-LA converted for $[rac-LA]_0$: [3]₀ ratios between 50 and 200. The gradient of the best-fit line is 162(4) g mol⁻¹ (equivs converted)⁻¹ ($R^2 = 0.998$) in very good agreement with that predicted (144.1 g mol^{-1} (equiv. converted)⁻¹) for one PLA chain growing per Ca–BH₄ group of 3 in a living-type fashion. The corresponding plot for ROP at RT was also linear ($R^2 = 0.996$, see the ESI[†]) but the gradient of the best-fit line was 239(7) g mol⁻¹ (equivs converted)⁻¹ indicating less optimal control of the relative rates of initiation and propagation for this very active system. Tetrad analysis of the CH(Me)O region of the selectively homonuclear decoupled ¹H NMR spectra of the PLA samples formed with 3 revealed heterotactically-enriched polymer with high P_r values of 0.88–0.90 at -20 °C (ca. 0.80 at RT).

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