Supplementary Material (ESI) for Chemical Communications

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

Michael G. Cushion and Philip Mountford*

Supporting Information

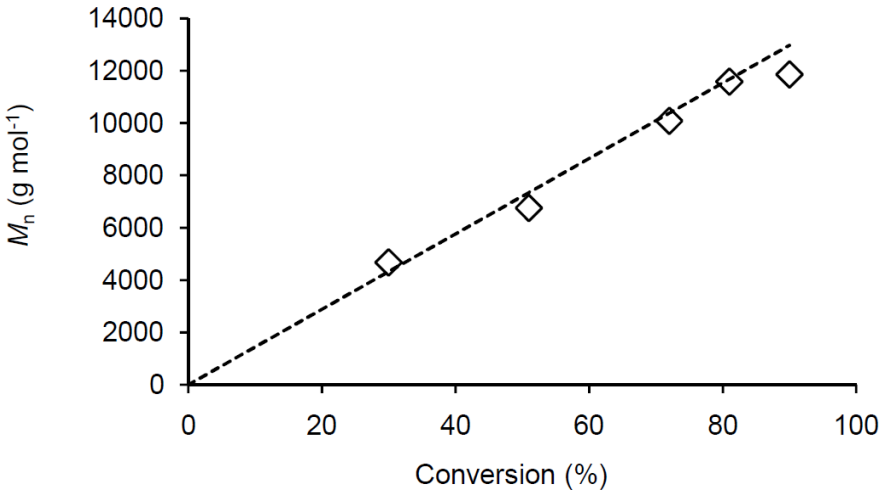

Figure S1. M_n (as measured by GPC) *vs* % *rac*-LA converted using $[Ca(BH_4)(THF)_5][BPh_4]$ (**1-BPh$_4$**). The dotted line is that expected for one PLA chain per BH_4 group. Conditions: THF, 70 ^oC, 4.5 hours, $[rac\text{-LA}]_0$:$[\mathbf{1\text{-}BPh_4}]_0$ = 100. M_w/M_n values are 1.3, 1.2, 1.2, 1.2, 1.3.

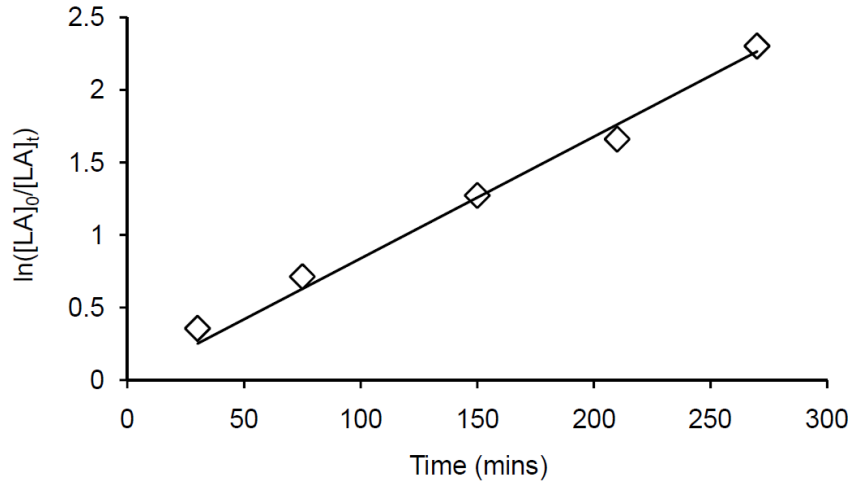

Figure S2. First order plot (linear fit, R^2 = 0.987) for *rac*-LA consumption using $[Ca(BH_4)(THF)_5][BPh_4]$ (**1-BPh$_4$**). Conditions: THF, 70 ^oC, 4.5 hours, $[rac\text{-LA}]_0$:$[\mathbf{1\text{-}BPh_4}]_0$ = 100. Apparent first order propagation rate constant (k_{app}) = 8.4(2) x 10^{-3} min^{-1}.

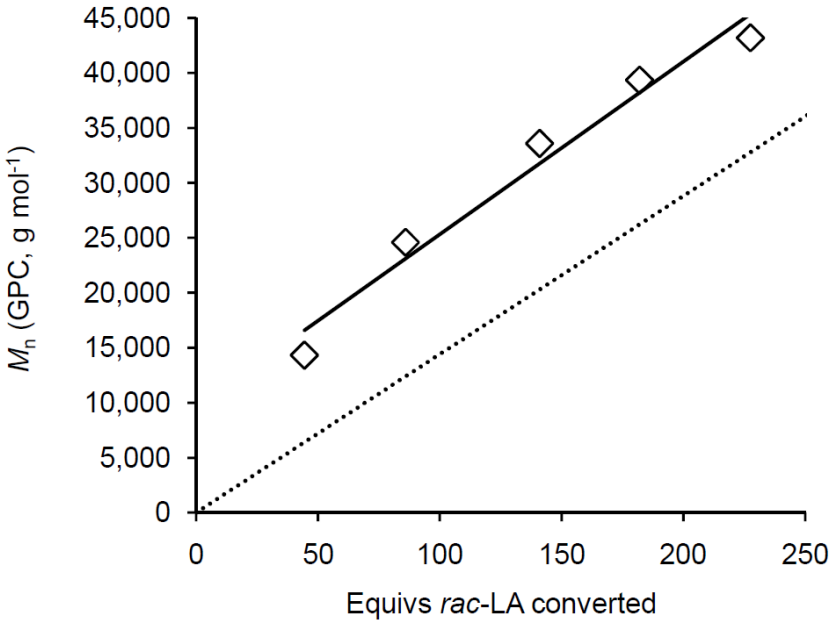

Figure S3. M_n (as measured by GPC) *vs* equivs. *rac*-LA converted using [(Tpm)Ca(BH$_4$)(THF)$_2$][BPh$_4$] (**2-BPh$_4$**). The gradient of the fitted line (R^2 = 0.982) is 157(11) g mol^{-1} (equivs. converted)$^{-1}$ (expected 144.1 g mol^{-1}) with an intercept of M_n = 9580(1890). Conditions: THF, RT, 2 hours, [*rac*-LA]$_0$:[**2-BPh$_4$**]$_0$ = 50, 100, 150, 200, 250. M_w/M_n values are 1.2, 1.3, 1.4, 1.4, 1.4.

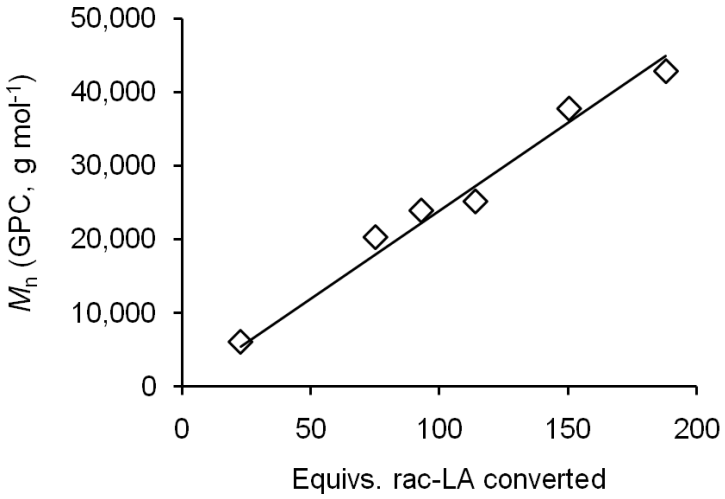

Figure S4. M_n (as measured by GPC) *vs* equivs. *rac*-LA converted using (Tp^{tBu,Me})Ca(BH$_4$)(THF) (**3**). The gradient of the fitted line (R^2 = 0.996) is 239(7) g mol^{-1} (equivs. converted)$^{-1}$ (expected 144.1 g mol^{-1}) with an intercept of M_n = 0. Conditions: THF, RT, 5 mins, [*rac*-LA]$_0$:[**4**]$_0$ = 40, 80, 120, 160, 200. M_w/M_n values are 1.6, 1.7, 1.6, 1.6, 1.7, 1.6.

Experimental Details

General methods and instrumentation. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. Toluene and THF was refluxed over sodium or potassium, respectively, and distilled. Deuterated solvents were dried over potassium (C_6D_6, THF-d_8,) or phosphorous oxide (CD_2Cl_2), distilled under reduced pressure and stored under argon in Teflon valve ampoules.

NMR tube samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H, ^{13}C-^{1}{H} and ^{11}B-{^{1}H} NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers at ambient temperature unless stated otherwise. ^{11}B spectra were referenced externally to $BF_3{\cdot}Et_2O$. Other NMR spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). ^{1}H and ^{13}C assignments were confirmed using two dimensional ^{1}H-^{1}H and ^{13}C-^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Nicolet Magna 560 E.S.P. FTIR spectrometer. Samples were prepared in a dry-box as Nujol mulls or in solution between NaCl plates, and the data are quoted in wavenumbers (cm^{-1}). Elemental analyses were carried out by Elemental Microanalysis Ltd., Okehampton, UK.

MALDI-ToF mass spectra were measured using a Waters MALDI micro equipped with a 337 nm nitrogen laser. An accelerating voltage of 25 kV was applied. The polymer samples were dissolved in THF at a concentration of 1 mg mL^{-1}. The cationization agent used was potassium trifluoroacetate (Fluka, > 99 %) dissolved in THF at a concentration of 5 mg mL^{-1}. The matrix used was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg mL^{-1}. Solutions of matrix, salt and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in the refectron mode. Polymer molecular weights (M_n, M_w) were determined by GPC using a Polymer Laboratories Plgel Mixed-D column (300 mm length, 7.5 mm diameter) and a Polymer Laboratories PL-GPC50 Plus instrument equipped with a refractive index detector. THF (HPLC grade) was used as an eluent at 30 °C with a rate of 1 mL min^{-1}. Linear polystyrenes were used as primary calibration standards, and Mark-Houwink corrections for poly(ε-CL) and poly(*rac*-LA) in THF were applied for the experimental samples.[1-3]

Starting materials. [Et_3NH][BPh_4], $HC(Me_2pz)_3$ (Tpm), 3,5-^{t}BuMepzH and $KTp^{tBu,Me}$ were prepared according to literature methods.[4-7] $HC(Me_2pz)_3$ was further purified by trituration with

pentane. ε-CL was dried over CaH_2 for 5 d at RT and then distilled and stored over 4 Å molecular sieves at 4 °C. *Rac*-LA was recrystallized twice from sodium-dried toluene and subsequently sublimed twice prior to use. $Ca(BH_4)_2(THF)_2$ was purchased from Sigma-Aldrich and used as received.

$[Ca(BH_4)(THF)_5][BPh_4]$ (1-BPh_4). A solution of $[Et_3NH][BPh_4]$ (3.94 g, 9.40 mmol) in THF (20 mL) was added to a solution of $Ca(BH_4)_2(THF)_2$ (2.00 g, 9.40 mmol) in THF (20 mL) at -78 °C. The resulting white suspension was stirred for 30 min at this temperature, then allowed to warm to RT and stirred for a further 2 h (gas evolution was observed). The volatiles were removed under reduced pressure, leaving a white solid. This was extracted into THF (3 x 15 mL), and the solution concentrated and cooled to -30 °C, yielding **1-BPh_4** as a colorless microcrystalline solid. Yield: 3.50 g (51 %). Diffraction-quality crystals were grown from a saturated THF solution at -30 °C. ^{1}H NMR (CD_2Cl_2, 299.9 MHz, 293 K): 7.35 (8 H, m, *o*-$B(C_6H_5)_4$), 7.05 (8 H, t, ^3J = 7.5 Hz, *m*-$B(C_6H_5)_4$), 6.90 (4 H, t, ^3J = 7.5 Hz, *p*-$B(C_6H_5)_4$), 3.83 (20 H, m, $OC\underline{H}_2CH_2$), 1.95 (20 H, m, $OCH_2C\underline{H}_2$), -0.19 (4 H, q, $^1J_{BH}$ = 82 Hz) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, 293 K): 164.4 (*i*-$B(C_6H_5)_4$), 153.3 (136.3 (*o*-$B(C_6H_5)_4$), 125.9 (*m*-$B(C_6H_5)_4$), 122.1 (*p*-$B(C_6H_5)_4$), 69.2 ($O\underline{C}H_2CH_2$), 25.7 ($OCH_2\underline{C}H_2$) ppm. $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 96.2 MHz): δ = -6.6 (BPh_4), -36.1 (BH_4). IR (NaCl plates, Nujol mull, cm^{-1}): 2725 (s), 2670(s), 2336(s), 2261(s), 2217(s), 1261(s), 1150(m), 1092(s), 1023(s), 870(m), 732(s), 705(s). IR (NaCl cell, THF, ν(B-H), cm^{-1}): 2406 (s, B-H_t of BH_4), 2260 and 2208 (s, B-H_b of BH_4; 52 cm^{-1} splitting). Anal. found (calcd. for $C_{44}H_{64}B_2CaO_5$): C, 71.75 (71.93); H, 8.72 (8.78) %. ES^+-MS (THF): *m/z* = 415 ($[\mathbf{1}]^+$).

$[(Tpm)Ca(BH_4)(THF)_2][BPh_4]$ (2-BPh_4). A solution of Tpm (0.300 g, 1.00 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of $[Ca(BH_4)(THF)_5][BPh_4]$ (0.670 g, 1.00 mmol) in CH_2Cl_2 (20 mL) at -78 °C. The resulting pale yellow solution was stirred at this temperature for 2 h, then allowed to warm to RT and stirred for a further h. The volatiles were removed under reduced pressure, leaving a spongy yellow solid. Recrystallisation from CH_2Cl_2:pentane (1:3) at -30 °C, gave **2-BPh_4** as an off-white microcrystalline solid. Yield: 0.61 g (74 %). Diffraction-quality crystals were grown from a hexane-layered THF solution at RT. These were also used for elemental analysis. Both batches contained residual THF according to analysis. ^{1}H NMR (CD_2Cl_2, 299.9 MHz, 293 K): 7.80 (1 H, s, $\underline{H}C(Me_2pz)_3$), 7.33 (8 H, m, *o*-$B(C_6H_5)_4$), 7.00 (8 H, t, ^3J = 7.2 Hz, *m*-$B(C_6H_5)_4$), 6.84 (4 H, t, ^3J = 7.2 Hz, *p*-$B(C_6H_5)_4$), 5.98 (3 H, s, $N_2C_3Me_2\underline{H}$), 3.82 (8 H, m, $OC\underline{H}_2CH_2$), 2.41 (9 H, s, 3-$N_2C_3\underline{Me}_2H$), 2.29 (9 H, s, 5-$N_2C_3\underline{Me}_2H$), 1.94 (8 H, $OCH_2C\underline{H}_2$), 0.15 (4 H, q, $^1J_{BH}$ = 82 Hz) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, 293 K): 164.5 (*i*-$B(C_6H_5)_4$), 153.3 (3-$N_2\underline{C}_3Me_2H$), 141.5 (5-$N_2\underline{C}_3Me_2H$), 136.3 (*o*-$B(C_6H_5)_4$), 125.9 (*m*-$B(C_6H_5)_4$), 122.1 (*p*-$B(C_6H_5)_4$), 69.2 (overlapping $H\underline{C}(Me_2pz)_3$ and $O\underline{C}H_2CH_2$), 25.7 ($OCH_2\underline{C}H_2$), 14.0 (3-$N_2C_3\underline{Me}_2H$), 11.4 (5-

$N_2C_3\underline{Me}_2H$) ppm. $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 96.2 MHz). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 96.2 MHz): δ = -6.9 (BPh_4), -35.6 (BH_4). IR (NaCl plates, Nujol mull, cm^{-1}): 2725 (s), 2670(s), 2336(s), 2269(s), 2214(s), 1377 (s), 1306 (s), 1260(s), 1154(m), 1098(m), 1032(s), 977(s), 858(s). IR (NaCl cell, THF, ν(B-H), cm^{-1}): 2410 (s, B-H_t of BH_4), 2270 and 2220 (s, B-H_b of BH_4; 50 cm^{-1} splitting). Anal. found (calcd. For $C_{52}H_{70}B_2CaN_6O_3$ (**2-BPh$_4$**·THF)): C, 69.98 (70.27); H, 7.93 (7.94); N, 9.43 (9.45) %. ES^+-MS (THF): *m/z* = 426 ([**2**-THF]$^+$), 353 ([**2**-2(THF)]$^+$).

(Tp^{tBu,Me})Ca(BH$_4$)(THF) (3). A suspension of $KTp^{tBu,Me}$ (0.500 g, 1.08 mmol) in THF (30 mL) was added dropwise over 30 mins to a solution of $Ca(BH_4)_2(THF)_2$ (0.230 g, 1.08 mmol) in THF (20 mL) at RT. The resulting suspension was stirred for 3 h. After this time, the suspension was filtered and the volatiles removed under reduced pressure, leaving a white residue. This was extracted into benzene (3 x 10 mL) and the volatiles were removed under reduced pressure to give a spongy white solid. This was recrystallised from THF :pentane (1:3) to give **3** as a colorless microcrystalline solid. Yield: 0.37 g (65 %). ^1H NMR (C_6D_6, 299.9 MHz, 293 K): 5.68 (3 H, s, pz$\underline{H}$), 3.26 (4 H, m, OC$\underline{H}_2$CH$_2$), 2.19 (9 H, s, $N_2C_3{}^t$Bu$\underline{Me}$H), 1.42 (27 H, s, $N_2C_3{}^t\underline{Bu}$MeH), 1.17 (4 H, m, OCH$_2$C$\underline{H}_2$), B-H of $Tp^{tBu,Me}$ and B$\underline{H}_4$ not observed. $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 293 K): 163.4 (3-$N_2\underline{C}_3{}^t$BuMeH), 145.3 (5-$N_2\underline{C}_3{}^t$BuMeH), 103.1 (4-$N_2\underline{C}_3{}^t$BuMeH), 68.6 (O$\underline{C}$H$_2$CH$_2$), 32.2 ($N_2C_3\underline{C}$(Me$_3$)MeH), 31.5 ($N_2C_3C(\underline{Me}_3)$MeH), 25.5 (OCH$_2\underline{C}H_2$), 13.5 ($N_2C_3{}^tBu\underline{Me}$H) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6, 96.2 MHz): δ = -7.9 ($Tp^{tBu,Me}$), -32.1 (BH_4). IR (NaCl plates, Nujol mull, cm^{-1}): 2558 (s), 2396(s), 2255(m), 2214(s), 1541(s), 1334(s), 1240(s), 1199(s), 1178(s), 1068(s), 1027(s), 705(s). IR (NaCl cell, CH_2Cl_2), ν(B-H), cm^{-1}) : 2565 (s, B-H of $Tp^{tBu,Me}$), (2413 (s, B-H_t of BH_4), 2304 and 2247 (s, B-H_b of BH_4; 57 cm^{-1} splitting). Anal. found (calcd. for $C_{28}H_{52}B_2CaN_6O$): C, 60.67 (61.10); H, 9.35 (9.52); N, 14.56 (15.27) %. EI-MS: *m/z* = 478 (80 %, [**3**-THF]$^+$).

Procedure for polymerization of ε-CL. ε-CL (3.31 mmol) was weighed into a Schlenk tube and dissolved in 2 mL of anhydrous THF. A sufficient quantity of catalyst ($[\varepsilon\text{-CL}]_0:[Ca]_0$ = 200) was weighed into a separate Schlenk and dissolved in 1.4 mL anhydrous THF. The ε-CL solution was added in one portion with vigorous stirring. The polymerization was quenched by addition of a few drops of wet THF. An aliquot was taken for NMR analysis (determination of conversion). Poly(ε-CL) was precipitated from ethanol (100 mL), filtered and dried to constant weight *in vacuo*. Low molecular weight samples for MALDI-ToF MS analysis ($[\varepsilon\text{-CL}]_0:[Ca]_0$ = 20) were prepared in an analogous way except that the polymerization mixtures were simply evaporated to dryness.

Procedure for polymerisation of *rac*-LA. *Rac*-lactide (3 mmol) was weighed into a Schlenk tube and dissolved in 3 mL of anhydrous THF. A sufficient amount of catalyst for the required $[rac\text{-LA}]_0:[Ca]_0$ ratio was weighed into a separate Schlenk tube and dissolved in 1.0 mL of anhydrous THF. The *rac*-LA solution was added in one portion with vigourous stirring. After the desired time

interval the polymerisation was quenched by addition of *ca.* 0.5 mL of wet THF. Samples were evaporated to dryness and conversions were determined by ^{1}H NMR integration of the OCHMe resonance relative intensities of the residual *rac*-LA and poly(*rac*-LA). Low molecular weight samples for MALDI-ToF MS analysis ($[\varepsilon\text{-CL}]_0:[\text{Ca}]_0 = 20$) were prepared as above for ε-CL. An analogous method and was used for the -20 ^{o}C polymerisations using **3** in the case of [*rac*-LA]$_0$:[Ca]$_0$ > 100 except that the volume of THF used for the *rac*-LA solution was increased to 5 mL (due to the lower solubility of *rac*-LA at this temperature) and the *rac*-lactide and initiator solutions were cooled to -20 ^{o}C prior to mixing, and maintained at this temperature until quenching.

References

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